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Sincerely,

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MERCURY AND AIR TOXIC ELEMENT IMPACTS OF COAL COMBUSTION BY-PRODUCT DISPOSAL AND UTILIZATION

Final Report

(for the period January 23, 2003 – December 31, 2006)

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MERCURY AND AIR TOXIC ELEMENT IMPACTS OF COAL COMBUSTION BY-PRODUCT DISPOSAL AND UTILIZATION

ABSTRACT

The University of North Dakota Energy & Environmental Research Center (EERC) conducted a multiyear study to evaluate the impact of mercury and other air toxic elements (ATEs) on the management of coal combustion by-products (CCBs). The ATEs evaluated in this project were arsenic, cadmium, chromium, lead, nickel, and selenium. The study included laboratory tasks to develop measurement techniques for mercury and ATE releases, sample characterization, and release experiments. A field task was also performed to measure mercury releases at a field site.

Samples of fly ash and flue gas desulfurization (FGD) materials were collected preferentially from full-scale coal-fired power plants operating both without and with mercury control technologies in place. In some cases, samples from pilot- and bench-scale emission control tests were included in the laboratory studies. Several sets of "paired" baseline and test fly ash and FGD materials collected during full-scale mercury emission control tests were also included in laboratory evaluations. Samples from mercury emission control tests all contained activated carbon (AC) and some also incorporated a sorbent-enhancing agent (EA).

Laboratory release experiments focused on measuring releases of mercury under conditions designed to simulate CCB exposure to water, ambient-temperature air, elevated temperatures, and microbes in both wet and dry conditions.

Results of laboratory evaluations indicated that:

- Mercury and sometimes selenium are collected with AC used for mercury emission control and, therefore, present at higher concentrations than samples collected without mercury emission controls present.

- Mercury is stable on CCBs collected from systems both without and with mercury emission controls present under most conditions tested, with the exception of vapor-phase releases of mercury exposed to elevated temperatures.

- The presence of carbon either from added AC or from unburned coal can result in mercury being sorbed onto the CCB when exposed to ambient-temperature air.

The environmental performance of the mercury captured on AC used as a sorbent for mercury emission control technologies indicated that current CCB management options will continue to be sufficiently protective of the environment, with the potential exception of exposure to elevated temperatures. The environmental performance of the other ATEs investigated indicated that current management options will be appropriate to the CCBs produced using AC in mercury emission controls.

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NOMENCLATURE

AA	atomic absorption
AAS	atomic absorption spectrophotometer
AC	activated carbon
ACI	activated carbon injection
AF	atomic fluorescence
ASTM	American Society for Testing and Materials
ATE	air toxic element
CAA	Clean Air Act
CARRC®	Coal Ash Resources Research Consortium®
CCB	coal combustion by-product
CVAAS	cold-vapor atomic absorption spectrometry
CVAFS	cold-vapor atomic fluorescence spectrometry
DMA	direct mercury analyzer
DOE	U.S. Department of Energy
EA	enhancing agent
EERC	Energy & Environmental Research Center
EPA	U.S. Environmental Protection Agency
ESP	electrostatic precipitator
FGD	flue gas desulfurization
GC	gas chromatography
HDPE	high-density polyethylene
HNO_3	nitric acid
ICP–AES	inductively coupled plasma–atomic emission spectroscopy
ICP–MS	inductively coupled plasma–mass spectroscopy
KCl	potassium chloride
LLQ	lower level of quantitation
LOI	loss-on-ignition
LTL	long-term leaching
MPN	most probable number
MWLP	mine water leaching procedure
NA	not applicable
NETL	National Energy Technology Laboratory
NMLRC	National Mine Land Reclamation Center
NO_x	nitrogen oxides
NQ	not quantitated
NT	not tested
ORD	Office of Research and Development
pc	pulverized coal
PCD	pollution control device
PDW	primary drinking water
PP	pyrophosphate
PRB	Powder River Basin
PTYG	peptone–tryptone–yeast extract–glucose

PYG	peptone–yeast extract–glucose
RCRA	Resource Conservation and Recovery Act
SBLP	serial batch leaching procedure
SCR	selective catalytic reduction
SDA	spray dryer absorber
SGLP	synthetic groundwater leaching procedure
SO_x	sulfur oxides
SO_2	sulfur dioxide
SPME	solid-phase microextraction
TCLP	toxicity characteristic leaching procedure
UND	University of North Dakota
UNR	University of Nevada–Reno
WVWRI	West Virginia Water Research Institute

MERCURY AND AIR TOXIC ELEMENT IMPACTS OF COAL COMBUSTION BY-PRODUCT DISPOSAL AND UTILIZATION

EXECUTIVE SUMMARY

The University of North Dakota Energy & Environmental Research Center (EERC) conducted a laboratory and field investigation designed to evaluate the impact of mercury and other air toxic elements (ATEs) on the management of coal combustion by-products (CCBs). Key objectives were:

- To determine the release potential of mercury and other selected ATEs from CCBs under specific environmental conditions.
- To increase the database of information on mercury and other ATE releases for CCBs.
- To develop comparative laboratory and field data.
- To develop appropriate laboratory and field protocols to measure mercury and ATE releases from CCBs.

The multiyear study comprised several tasks, including laboratory methods development and selection, sample selection, sample characterization, laboratory release experiments, and measurement of mercury releases at a field site.

Laboratory tasks were designed and performed to address fundamental issues critical to determining the release of these constituents over the life cycle of CCBs in a variety of management scenarios. Release mechanisms addressed included:

- Direct leachability of air toxic constituents from CCBs.
- Vapor release of mercury from CCBs at ambient and elevated temperatures.
- Biologically induced leachability and vapor release of mercury and other ATEs from CCBs.

Experimental

The experimental component of this project was important to accomplishing the work in this project since standard experimental protocols were not available at the time the project was initiated. Throughout the duration of the project, the research staff continued efforts to select and develop experimental protocols to simulate mercury and ATE releases under varying conditions and the analytical methods required to quantitate those releases.

Multiple leaching procedures were used to evaluate the potential mobility of mercury and other ATEs from the CCBs obtained for use in the project. Development of laboratory methods

to evaluate vapor-phase mercury releases under ambient and microbiologically mediated conditions continued throughout the project. Methods for quantitation of mercury collected from vapor-phase release experiments and field sampling were developed in parallel with those efforts. Analytical tools were also used to quantitate and speciate organomercury compounds primarily in vapor-phase releases from laboratory experiments.

Using the experimental protocols selected and developed, a large number of samples were evaluated to determine if there was potential for mercury and other ATEs to be released from those samples under conditions to which CCBs would be expected to be exposed in typical management activities.

Results

The results of this project were dependent on the careful selection and collection of samples for inclusion in the laboratory evaluations performed for this task. Identification and basic characterization information was collected and generated for the samples in the final sample set, which included several paired sample sets that were obtained at facilities that were demonstrating mercury emission control technologies. A paired sample set included a baseline sample collected under normal operating conditions and one or more test samples collected during demonstration of mercury control. A summary of the samples included in the study is shown in Table ES-1, and the paired sample sets are listed in Table ES-2.

Total mercury content was determined for nearly all samples in the sample set, and total elemental concentrations of the ATEs evaluated in this project (arsenic, cadmium, chromium, lead, nickel, and selenium) were determined for a large number of samples in the sample set. When mercury emission controls were in place, fly ash samples exhibited consistently higher total mercury concentrations. For some fly ash samples collected from systems with mercury emission controls in place, selenium was also elevated. This was most noteworthy in samples collected from mercury emission control systems where activated carbon (AC) was injected after the primary particulate control device. It was determined that the total concentrations of all elements, except mercury and selenium, were similar for fly ash and for flue gas desulfurization–spray dryer absorber (FGD–SDA) material samples generated with and without mercury emission controls present. While no wet FGD material samples were collected from systems with mercury emission controls in place, the total elemental data for these materials indicated significantly higher levels of most ATEs in wet FGD material + fly ash (fixated wet FGD material).

The moisture content and loss on ignition (LOI) of solid CCBs were determined as part of the fundamental characterization. It has long been known that LOI is not a direct measurement of carbon content of fly ash; however, when AC is being added to fly ash, as with most test samples evaluated in this project, the LOI value typically reflected the amount of carbon present in a fly ash sample. Fly ash samples collected from mercury control technology testing exhibited LOI values ranging from 0.59% to 24.4%. Fly ash without mercury control had LOI ranging from 0.22% to 21.2%. These ranges were similar, and the highest LOI values were atypical of the samples evaluated, although the fly ash samples collected in demonstrations where the AC was

Table ES-1. Summary of Project Samples and Fundamental Characterization Data

Coal Type	Type of SO_2 Control	No. of Samples	Sample Type with Hg Control Description	24-hour pH Range	LOI Range, %	Total Hg Concentration Range, µg/g
Bituminous	No SO_2 control	21	Fly ash	5.52–12.65	0.47–21.2	<0.01–0.685
		6	Fly ash + AC (post-primary PCD[1])	3.99–9.20	12.6–24.4	0.742–120
		2	Fly ash + AC (pre-primary PCD)	NT[2]	NT	NT
	Wet Mg-enhanced lime	2	FGD gypsum	7.75–7.88	1.22–1.92	0.032–0.044
	Wet limestone – forced oxidation	3	FGD gypsum	7.72–7.95	1.60–2.26	0.043–0.103
	Wet limestone – nonoxidized	3	FGD filtercake	7.70–7.88	4.20–6.19	0.162–0.305
		3	Fixated FGD	10.50–12.43	3.11–4.17	0.136–0.249
Subbituminous	No SO_2	3	Fly ash	12.27–12.56	0.32–1.08	0.261–1.22
		4	Fly ash + AC (pre-primary PCD)	10.95–11.90	2.28–4.14	1.09–5.81
	SDA	1	FGD–SDA	12.22	2.07	0.105
Lignite	No SO_2 control	13	Fly ash	10.50–12.74	0.22–7.48	<0.01–0.878
		8	Fly ash + AC (post-primary PCD)	10.52–11.41	0.59–13.2	0.147–64.5
		6	Fly ash + AC (pre-primary PCD)	11.86–12.61	0.96–4.21	0.225–12.7
		3	Fly ash + EA[3] + AC (pre-primary PCD)	12.29–12.77	1.04–2.49	0.287–0.640
		1	Fly ash + EA	11.77	1.70	0.717
	SDA	3	FGD–SDA	12.50	0.95–12.5	<0.01–2.55
	SDA	1	FGD–SDA + EA + AC (pre-SDA)	12.54	1.12	0.332

[1] Pollution control device.
[2] Not tested.
[3] Enhancing agent.

Table ES-2. Paired Samples and Fundamental Characterization Data

ID No.	Sample Type	24-hour pH	LOI, %	Hg, µg/g
02-070	Fly ash	8.50	5.87	0.194
02-069	Fly ash + AC (post-primary PCD)	8.43	12.60	0.742
02-072	Fly ash	8.83	5.29	0.163
02-071	Fly ash + AC (post-primary PCD)	8.63	17.22	0.975
03-061	Fly ash	12.56	1.04	0.578
03-060	Fly ash + AC (pre-primary PCD)	11.90	2.38	1.86
04-035	Fly ash	12.74	2.46	0.159
04-036	Fly ash + EA + AC (pre-primary PCD)	12.77	2.33	0.287
05-001	Fly ash	12.51	0.90	<0.01
05-003	Fly ash + EA + AC (pre-SDA)	12.29	1.04	0.565
05-005	Fly ash	11.57	1.29	0.431
05-017	Fly ash + EA	11.77	1.70	0.717
05-038	Fly ash	11.73	0.22	0.104
05-013	Fly ash + AC (post-primary PCD)	11.33	13.2	39.0
05-023	Fly ash + AC (pre-primary PCD)	12.00	3.84	12.7
05-024	Fly ash + AC (post-primary PCD)	11.41	9.45	35.9
05-025	Fly ash + AC (pre-primary PCD)	11.99	3.19	12.6
05-040	Fly ash + AC (post-primary PCD)	11.36	9.68	44.5
06-001	Fly ash + AC (post-primary PCD)	11.37	11.6	64.5
05-002	Fly ash + FGD–SDA	12.50	0.95	<0.01
05-004	Fly ash + FGD–SDA + EA + AC (pre-SDA)	12.54	1.12	0.332

injected after the primary PCD had the highest LOI values. For that type of ACI (activated carbon injection), a portion of the fly ash produced is collected in the PCD, and a typically small amount of fly ash that passes through the PCD remains in the flue gas stream to the point of ACI, resulting in a higher AC content in the fly ash + AC stream. For FGD–SDA samples, the LOI is likely dependent on the LOI of the fly ash that is incorporated into the FGD–SDA final by-product material.

In an effort to learn more about the impact of carbon forms on mercury capture and potential release, an evaluation of the carbon forms present in several fly ash samples was performed. The three major morphological carbon forms are inertinite, isotropic coke, and anisotropic coke, and each exhibits distinct and predictable physical properties. The reactivity series of these carbon forms is:

anisotropic coke > isotropic coke > inertinite

Fly ash samples with AC present contained more reactive carbon forms, indicating that the presence of high-sorbing carbon forms can be an indicator of elevated mercury in fly ash samples and that AC contains these high-sorbing carbon forms.

The pH of all samples of sufficient quantity was determined, and since the pH of a material can influence the leaching profile and may impact the performance in certain utilization scenarios, including bulk placement in engineered fills, several pH measurements were made to develop the most accurate pH data possible.

On review of pH data by coal type, the following observations were made:

- Eastern bituminous fly ash samples exhibited a wide range of pH values in all tests. This range was greater in the fly ash samples without AC than with AC.

- The South American and western bituminous fly ash sample pH ranges were narrower and more similar to those of subbituminous and lignite fly ash samples than eastern bituminous fly ash samples. All fly ash + AC (pre-primary PCD) pH values for the South American bituminous, subbituminous, and lignite samples in the project were similar.

- For some fly ash samples, the pH changed significantly over time.

The pH development data are interesting because pH is a primary factor in leachability and an indicator of the potential for secondary hydration phases to impact leachability and engineering performance. These data suggested that pH measurements for CCBs should include an equilibration time of at least 24 hours. The pH values reported for all FGD–SDA samples fell within a narrow range regardless of the presence of AC. The pH for these samples is primarily a result of the presence of unreacted sorbent, which is present as calcium hydroxide. Calcium hydroxide has a pH of 12.4, which is very similar to the pH values measured in the FGD–SDA samples. The ranges of pH values of FGD materials and liquids were acidic to near-neutral pH, with the exception of the fixated wet FGD materials.

The release of constituents found in CCBs is most likely to occur through exposure to water or direct leaching. Laboratory leaching was performed using multiple tests (toxicity characteristic leaching procedure [TCLP, U.S. Environmental Protection Agency Method 1311], synthetic groundwater leaching procedure [SGLP], and long-term leaching [LTL] with 30- and 60-day equilibration periods) on a large number of the samples assembled for this project. Mercury and other ATEs were determined on leachates. The fly ash leaching data are included in Table ES-3.

Leaching results indicated that mercury is not readily leachable from fly ash, fly ash + AC and/or EA, FGD–SDA samples, and wet FGD materials. Most samples had leachate mercury concentrations below the 0.01-µg/L analytical method reporting limit. Short-term (18-hour SGLP) leaching results from fly ash samples collected from systems without mercury emission controls in place are shown in Figure ES-1. Figure ES-2 shows the 18-hour SGLP mercury-leaching data for fly ash + AC and/or EA samples plotted against the total mercury content of the sample. Results of short- and long-term leaching for fly ash indicated that total mercury content did not correlate with leachate mercury concentrations. The results plotted in Figure ES-2 indicated that the higher total concentrations of mercury associated with the presence of AC were stable and not readily released through leaching.

Table ES-3. Ranges of Leachate Results for Fly Ash, µg/L

Element	Fly Ash	Fly Ash + AC (pre-primary PCD)	Fly Ash + EA + AC (pre-primary PCD)	Fly Ash + EA	Fly Ash + AC (post-primary PCD)
As	<2–336	<2–16.3	<2–15.2	46.3–95.9	8.1–842
Cd	<0.2–8.30	<0.2–1.49	<0.2–0.39	<0.3–2.68	0.85–2.46
Cr	1.40–277	3.60–560	<2–134	182–211	17.3–680
Pb	<0.001–8.50	<0.001–3.00	<0.001–3.00	<2	<2
Hg	<0.01–0.325	<0.01–0.068	<0.01–0.061	<0.01–0.02	<0.01–0.07
Ni	<2–80.6	<2–23.1	<2–25.2	<2–2.8	<2–23.4
Se	<2–514	<2–147	<2–47.2	<4–97.0	45.2–8620
pH	3.54–12.81	3.80–12.60	12.21–12.61	11.69–12.01	3.79–11.82

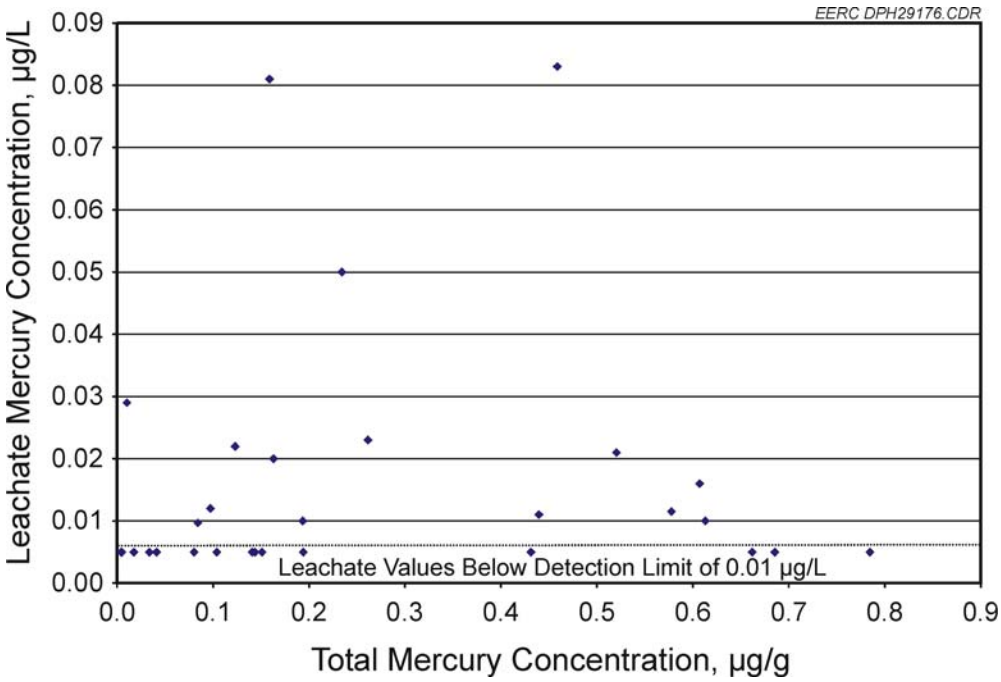

Figure ES-1. Fly ash 18-hour SGLP leachate mercury plotted against total mercury content.

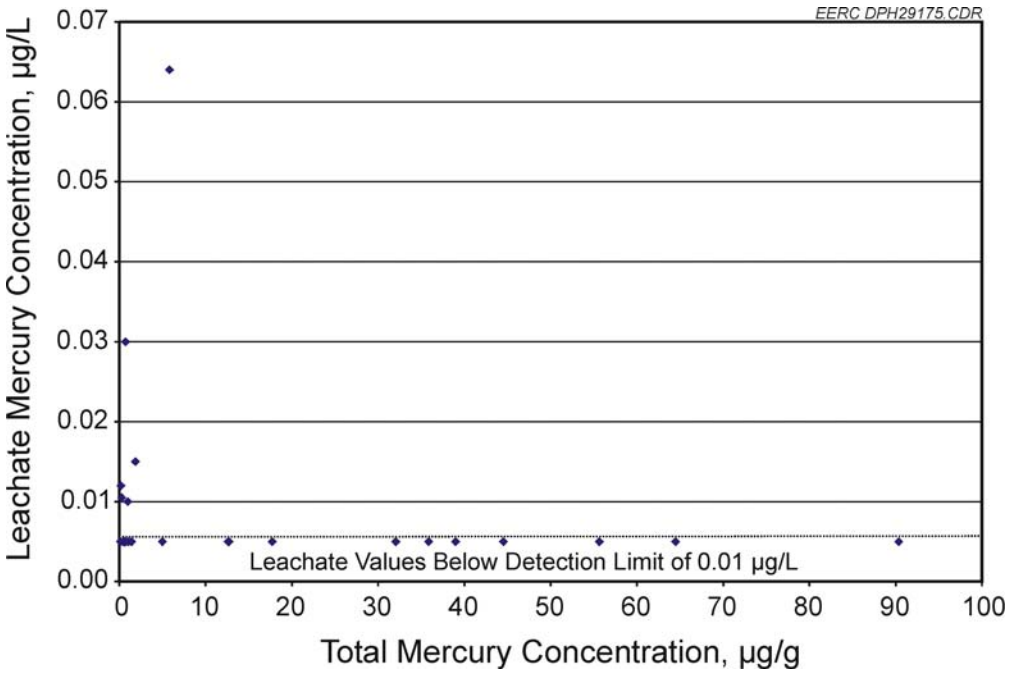

Figure ES-2 Fly ash + AC and/or EA 18-hour SGLP leachate mercury plotted against total mercury content.

In leachate from FGD–SDA samples collected both with and without mercury emission controls in place, mercury was measured either at very low concentrations or was below the analytical reporting limit. As noted for fly ash, no correlation between the total and leachate mercury concentrations was observed.

Mercury leachate concentrations from the FGD materials were also generally low, but the 18-hour SGLP results for the wet FGD filtercake and fixated wet FGD material were higher than the other wet FGD materials, FGD–SDA, and fly ash samples. Leaching of FGD gypsum resulted in the lowest mercury leachate concentrations of all the wet FGD material samples.

The laboratory leaching results all indicated that mercury is expected to be stable on CCBs when exposed to water. The potential for mercury to leach from CCBs is very low and is not expected to impact current fly ash management practices.

Selenium was the only ATE other than mercury identified as having increased total concentration in some fly ash + AC samples. Specifically, fly ash + AC samples where the AC was injected post-primary PCD exhibited an elevated total selenium content compared to the baseline for the single paired sample set of that type. Other fly ash paired samples that had the AC injected before the primary PCD did not exhibit this notable increase in total selenium content. In paired samples, selenium leaching was elevated in the short-term leachates with higher total selenium content; however, leachate selenium concentrations generally decreased in long-term leachates.

Arsenic leachate concentrations of fly ash + AC (pre-primary PCD), fly ash + EA + AC (pre-primary PCD), and fly ash + EA all were measured to be within the range reported for leachates from fly ash only. Total arsenic was not elevated in any samples with AC or EA present. For one paired fly ash and fly ash + AC (post-primary PCD) sample set, increased leachate arsenic concentrations were noted for several of the fly ash + AC test samples even though total arsenic concentrations were similar. Arsenic mobility from all FGD–SDA samples and wet FGD materials evaluated was low.

Leaching results for cadmium, chromium, lead, and nickel generally indicated that these elements had very low leachability in all sample types with and without mercury emission controls in place.

Ambient and elevated-temperature vapor-phase release of mercury was determined in laboratory experiments. Ambient-temperature experiments were performed in batches and were run for up to 200 days with mercury measurements taken at intervals. The data indicated that some samples released mercury and some samples sorbed mercury. An example of results from the ambient-temperature experiments is shown in Figure ES-3.

The sample set shown in Figure ES-3 included fly ash, fly ash + AC (pre-primary PCD), and FGD–SDA samples from eastern bituminous, Powder River Basin (PRB) subbituminous, and lignite coal. One paired sample set with a baseline fly ash (03-060) and a fly ash + AC test

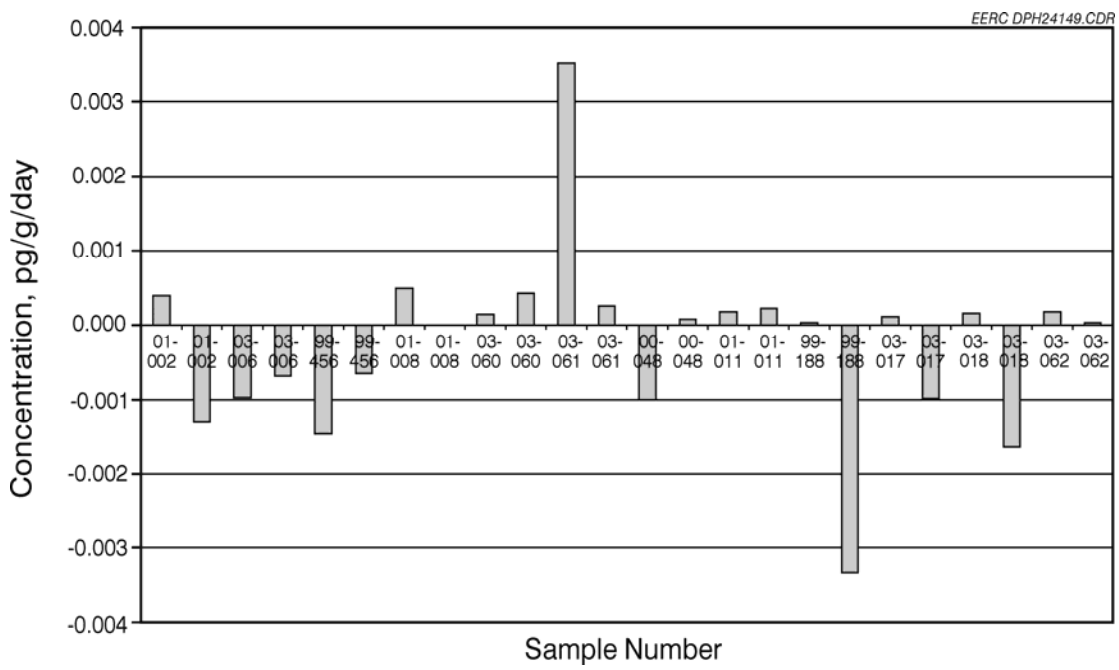

Figure ES-3. Sample Set 1 (194-day) long-term ambient-temperature mercury release or sorption as related to blank values, pg/g/day. Positive values indicate release, and negative values indicate sorption of mercury. Duplicate bottles are represented.

sample (03-061) was evaluated. Additional experiments provided similar results with fly ash samples collected both with and without mercury emission controls in place exhibiting sorption of mercury more commonly than release. Over the duration of the experiments, the rate of mercury typically decreased for all fly ash samples. FGD–SDA and wet FGD materials typically released mercury, and wet FGD materials exhibited a different release profile than fly ash samples, releasing mercury at a higher rate and for a longer duration. Following extensive exposure to ambient air, some of the wet FGD material samples showed sorption of mercury. Release/sorption rates were extremely low for all samples evaluated.

Fly ash samples were evaluated for the real-time elevated-temperature release of mercury. Thermal desorption curves provided a comparative means of evaluating the elevated-temperature release of mercury. Fly ash samples subjected to the elevated-temperature regime typically generated either one or two mercury peaks, with four being the maximum number of peaks identified for fly ash. Mercury was released at temperatures ranging from 256° to 750°C. Some samples, predominantly eastern bituminous fly ash samples with a LOI greater than 3% or fly ash + AC (post-primary PCD), continued to show increasing mercury release at 750°C. As shown in the sample thermal desorption mercury curve (Figure ES-4), the first peak recorded was typically sharp and well defined. Following peaks, where recorded, tended to show slightly less definition and were usually broader, although the absorption could be higher.

Samples with AC were more difficult to evaluate for elevated-temperature mercury releases, but sorbents that contained other compounds, such as halogens or sulfur, also offered analytical challenges. While sample identifications did not always indicate the exact nature of the

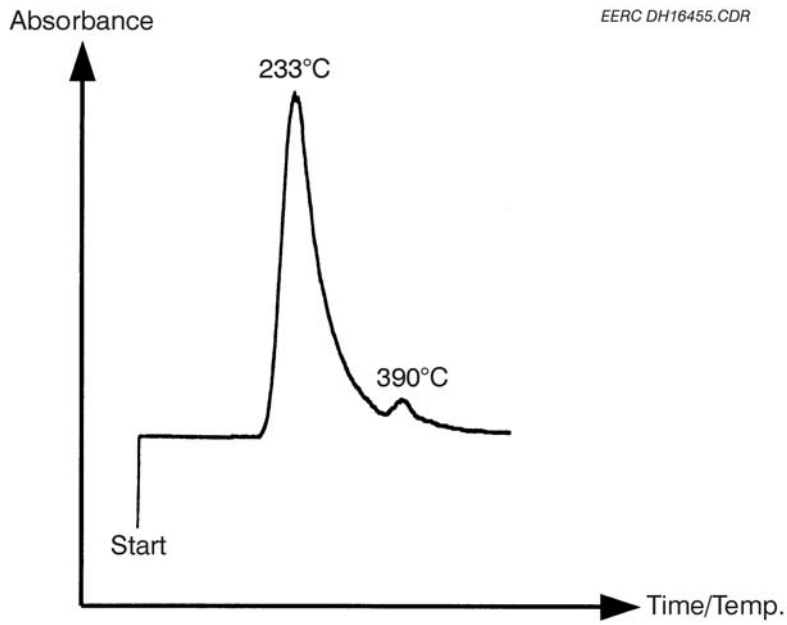

Figure ES-4. Typical two-peak mercury desorption curve for fly ash.

AC used, samples of this type were expected to produce a thermal curve containing multiple peaks. Multiple peaks were noted in a significant number of fly ash samples and were likely because of the presence of multiple mercury compounds in the samples.

Multiple project samples were evaluated for microbiologically mediated mercury leaching and vapor-phase release. These experiments were challenging to carry out because of the requirements to keep the microbes active, the presence of fungi, and analytical interferences. Higher vapor-phase releases of mercury were measured for both elemental and organomercury for all samples evaluated in systems under aerobic conditions compared to those with anaerobic conditions. FGD–SDA and wet FGD filtercake samples exhibited significantly higher vapor-phase mercury release rates than the fly ash samples evaluated, and the FGD–SDA sample evaluated had the highest release rate of vapor-phase mercury. Methylation of mercury did predictably occur in the experimental systems, but the apparent rate and resultant concentrations of methylmercury were extremely small.

A field task was accomplished in two subtasks: 1) Evaluation of Vapor-Phase Mercury at CCB Disposal Sites and 2) Small-Scale Vapor-Phase Mercury Release from Soil–Ash Mixtures.

The first subtask of the field investigation task was performed at CCB management facilities associated with a lignite-fired power plant where materials were collected for laboratory characterization and in situ mercury fluxes were measured by two methods. Even though the substrates measured varied slightly between the two types of measurements, a comparison of the results indicated good agreement for total mercury flux relative to substrate type as noted in Table ES-4.

An evaluation of the impact of the interaction between soil and CCBs on mercury release from CCBs was also performed on mixtures of 20% CCB addition to a soil–peat moss sample. Elemental mercury and organomercury release measurements were obtained on several samples and compared to a soil sample. The CCB–soil mixtures generally exhibited low levels of elemental mercury release, while the soil–peat moss sample (only one data point) sorbed elemental mercury. CCB–soil mixtures containing samples that had AC present released lower percentages of elemental mercury than those without AC present. On average, the samples with

Table ES-4. Total Mercury Field Flux Results Comparisons

EERC Measurements	University of Nevada, Reno (UNR) Measurements
Wet FGD Material + Mill Rejects	Wet FGD Material + Mill Rejects
> Stabilized Wet FGD Material (with fly ash)	> Stabilized Wet FGD Material (with fly ash)
> Fly Ash	> Fly Ash
> Wet FGD Material	> Agricultural Land (sample not evaluated by the EERC)
> Natural Grasslands (background soil)	= Wet FGD Material
> Vegetated Fly Ash with Soil Cover	> Vegetated Fly Ash with Soil Cover
> Bottom Ash/Mill Rejects + Wet FGD Material (sample not evaluated by UNR)	> Natural Grasslands (background soil)

AC present released mercury an order of magnitude lower percentage than the sample from a similar coal source without AC. However, the measured elemental mercury release rate (pg mercury/g mixture/day) was higher for the fly ash + AC (post-primary PCD) samples. The results indicated that more organomercury was released from four of 13 replicate CCB–soil mixture bottles than from the bottle containing only the soil–peat moss sample. All organomercury releases were low. Again, the samples with AC generally exhibited a lower-percentage release of organomercury than those without AC present, although the difference was not as consistent as that observed for elemental mercury releases.

CONCLUSIONS

Conclusions drawn for the extensive laboratory and field work performed under this project can be summarized as follows:

- Results for baseline fly ash or FGD–SDA and test samples with AC indicated that total mercury content was higher in the test samples.

- The total selenium content was higher for the fly ash samples + AC (post-primary PCD) test samples than the baseline fly ash.

- Total concentrations of arsenic, cadmium, chromium, lead, and nickel were similar for all fly ash samples and for FGD–SDA samples collected from systems with or without mercury emission controls in place.

- Direct leaching tests indicated that mercury was not readily leached from fly ash or FGD materials. Leachate mercury concentrations were below the 0.01-µg/L analytical reporting limit for most samples evaluated.

- Mercury leachate concentrations did not correlate to total mercury concentrations.

- When exposed to ambient-temperature air in laboratory experiments, fly ash samples either released or sorbed small amounts of mercury. Samples containing unburned or AC tended to sorb mercury in ambient-temperature vapor-phase experiments.

- Laboratory data indicated that the potential for ambient-temperature vapor-phase mercury releases from CCBs are unlikely to impact atmospheric mercury loading.

- Mercury was not released to the vapor phase at temperatures below 250°C in elevated-temperature experiments, but for most samples, 100% of the mercury on the CCB was released by 750°C.

- Under microbiologically mediated conditions, only very low levels of elemental and organomercury were released in the vapor phase and leachate, although more elemental mercury was released.

- Field experiments at a lignite CCB disposal site indicated low-level vapor-phase releases of mercury, as was generally noted in laboratory experiments for lignite fly ash samples. Releases from FGD materials were noted both in laboratory and field measurements.

- Laboratory methods were developed to evaluate the potential for mercury releases under several release mechanisms.

MERCURY AND AIR TOXIC ELEMENT IMPACTS OF COAL COMBUSTION BY-PRODUCT DISPOSAL AND UTILIZATION

1.0 INTRODUCTION

Research has been under way for many years at the Univeristy of North Dakota (UND) Energy & Environmental Research Center (EERC) and elsewhere to evaluate the environmental performance of coal combustion by-products (CCBs) from coal-based combustion systems (ADA-ES, Inc., 2003; Carey et al., 1999; Energy & Environmental Research Center, 2005; Gustin and Ladwig, 2004; Hassett, 1994; Hassett and Heebink, 2002, 2007; Hassett et al., 2002, 2003, 2004, 2005; Heebink and Hassett, 2002; Heebink et al., 2004, 2006; Hower et al., 2004; Keating and Chaisson, 1999; Laudal et al., 2000, 2001; Pavlish, 1999; Pflughoeft-Hassett et al., 1996, 2004; Sanchez et al., 2006; Schwalb and Withum, 2003; Xin et al., 2006). A majority of this work has focused on the mobility of trace constituents from CCBs into the environment when these materials are beneficially used, especially when they are used in soil stabilization, engineered fill, or mine reclamation applications. Much of this work has been driven by the 1970 Clean Air Act (CAA), which brought significant changes to the federal air quality program requiring the U.S. Environmental Protection Agency (EPA) to establish national air quality standards as well as national standards for significant new pollution sources and for all facilities emitting hazardous substances. The regulation of CCBs has been closely tied to environmental regulation of coal-fired power plants in the United States. Particulate control, flue gas desulfurization (FGD), and strategies to reduce nitrogen oxide emissions have all influenced the type and characteristics of CCBs being produced. The characteristics and performance of CCBs were evaluated under a mandate from EPA, and as a result, a final regulatory determination was made by EPA for fly ash, bottom ash, boiler slag, and FGD material, which became effective September 2, 1993. The rule stated that regulation of CCBs generated by coal-fired electric utilities and independent power producers as hazardous waste is unwarranted and that the materials will remain exempt from regulation as a hazardous waste under the Resource Conservation and Recovery Act (RCRA). This determination was upheld in a second EPA report in 1999, which focused on the management of fluidized-bed combustion wastes, low-volume wastes, pyrites, and comanaged wastes for which EPA determined that these materials would continue to be exempted from regulation under Subtitle C for hazardous wastes.

Significant work was performed and data reviewed for the 1993 and 1999 EPA determinations on CCBs. Review of those data indicated that the information on mercury in CCBs and its potential to be released into the environment was limited because the standard analytical methods used were generally not sensitive enough to measure mercury in CCBs or CCB leachates. This lack of quantitative data on the mercury content of and release from CCBs coupled with the understanding that coal-based power plant mercury emissions would likely be regulated in the future and that mercury emission control strategies would likely impact the character and behavior of the CCBs provide the motivation for the work undertaken in this project.

The scope of work was developed to provide data on the environmental acceptability of CCBs produced in systems with conventional and advanced emission controls by evaluating the

release of air toxic elements (ATEs) from CCB samples under controlled laboratory conditions and in select utilization and disposal field settings.

It was the goal of the project to compare the mercury and ATE release data generated from CCBs as currently produced and produced with advanced emission controls in place. The comparative data would provide a better understanding of the environmental performance of CCBs potentially to be generated with mercury emission controls in place. The project included work to:

- Provide comparative information on CCBs from systems with various emission controls, which will aid utilities in selecting emission control technologies consistent with existing CCB management plans.

- Develop scientifically sound experimental protocols for determining air toxic releases from CCBs based on CCB properties and management scenarios.

- Provide information to the state and federal agencies that regulate disposal and utilization options.

Laboratory tasks addressed three areas: 1) direct leachability of air toxic constituents from CCBs, 2) vapor release of mercury from CCBs at ambient and elevated temperatures, and 3) microbiologically induced leachability and vapor release of Hg and other ATEs from CCBs. A field task addressed mercury release at CCB management sites. The laboratory tasks were accomplished in conjunction with development of reliable methods to determine the release of ATEs from CCBs. While laboratory leaching has long been used to evaluate the mobility of various constituents from CCBs, the evaluation of vapor-phase transport and microbiologically mediated releases of ATEs required continued method development throughout most of the project. Development and use of appropriate methods to develop a project data set on currently produced CCBs and CCBs produced under experimental/simulated conditions provided an opportunity for the CCB industry to become aware of the potential impacts of mercury emission technologies on the CCBs produced, the expected environmental performance, and impacts to current CCB management strategies.

On initiation of this project, it was hypothesized that if CCBs as currently produced and from systems with proposed mercury emission control systems in place were found to exhibit comparable environmental performance, standard management scenarios could continue to be employed and CCB utilization could be expected to increase even after implementation of mercury emission controls. It was not the focus of this project to evaluate the impact of specific sorbents on the engineering performance of CCBs; however, over the course of this project, the EERC and others (Heebink et al., 2006; Lockert et al., 2005; ADA-ES, Inc., 2003; Gasiorowski et al., 2003) did find that the presence of activated carbon (AC) in fly ash is expected to impact the use of fly ash in concrete because of the reactivity of the AC and interaction with chemical admixtures used in concrete.

The presence of Hg and other ATEs in CCBs has raised concern by state regulatory agencies (Federal Register, 2000) and citizen groups about the potential environmental stability

of these elements under disposal and utilization conditions. This project has addressed the technical aspects of that concern, and it is important that the results of this study be communicated with the CCB industry, the regulatory community, and other stakeholders. The project results are expected to allow CCB managers and marketers to better evaluate management options for CCBs that may be produced after implementation of mercury emission controls. The data can also serve to aid in the selection of mercury emission controls for those CCB producers that manage their CCBs primarily through marketing.

2.0 BACKGROUND

Recent projections from the Energy Information Administration indicate that U.S. demand for energy will increase from 97.3 quadrillion to 130.1 quadrillion Btu between 2001 and 2020, reflecting an annual growth rate of 1.5%. By 2025, total energy consumption is projected to reach 139.1 quadrillion Btu (Energy Information Administration, 2004). Fossil fuel combustion, including the burning of coal, natural gas, or oil, provides about 85% of the present energy production in the United States. Of this amount, over 50% is provided by coal-fired utilities (Energy Information Administration, 2004). As a result of energy production from coal, CCBs are generated, and CCBs, as produced in the United States, are primarily a result of emission control technologies installed to meet emission regulations.

Emission regulations first mandated reduction of particulate matter released to the atmosphere by utilities, which required utilities to install collection devices for generated fly ash. Later emission regulations significant to CCB production mandated limits on sulfur oxide (SO_x) emissions. As a result, utilities using high-sulfur coal could change coal sources, resulting in a different by-product character or scrub the flue gas using sorbents to remove the SO_x gases. The result of FGD was high volumes of spent FGD sorbent material. There is a wide range of FGD technologies, so FGD materials have broadly varied characteristics but generally contain high concentrations of calcium and sulfur. Currently, utilities are responding to regulations placing limits on nitrogen oxide (NO_x) emissions, which also impacts the character of CCBs, including potentially increasing the amount of unburned carbon in fly ash or adding ammonia to the fly ash. Issues related to ATEs, including mercury, are currently under technical and regulatory scrutiny.

Figure 2-1 includes an excerpt from an EPA Fact Sheet entitled "EPA Proposes Options for Significantly Reducing Mercury Emissions from Electric Utilities," in which some of the concerns about mercury are summarized. On December 14, 2000, EPA announced that it would regulate mercury emissions from coal- and oil-fired electric utility steam-generating power plants (Federal Register, 2000); propose regulations by December 15, 2003; and finalize regulations by December 15, 2004. On December 15, 2003, EPA signed the Utility Mercury Reductions proposal, which seeks comments on two approaches for reducing mercury by up to nearly 70%. On March 15, 2005, EPA issued the first federal rule to permanently cap and reduce mercury emissions from coal-fired power plants (a power plant is defined as an electrical

EERC DPH29177.CDR

Mercury Emissions – Both Naturally Occurring and Man-made Sources

- Mercury is a toxic, persistent pollutant that accumulates in the food chain. Fossil fuel-fired utilities are the largest source of human-generated mercury emissions in the United States.
- Concentrations of mercury in the air are usually low and of little direct concern. However, atmospheric mercury falls to Earth through rain or snow and enters lakes, rivers, and estuaries. Once there, it can transform to its most toxic form, methylmercury, and accumulate in fish and animal tissues.
- Americans are exposed to mercury primarily by eating contaminated fish. Because the developing fetus is the most sensitive to the toxic effects of mercury, women of child-bearing age are regarded as the population of greatest concern. Children who are exposed to low concentrations of methylmercury prenatally are at increased risk of poor performance on neurobehavioral tasks, such as those measuring attention, fine motor function, language skills, visual-spatial abilities, and verbal memory.

EXCERPTED FROM EPA FACT SHEET:
EPA Proposes Options for Significantly Reducing Mercury Emissions from Electric Utilities
December 15, 2003

Figure 2-1. EPA information on mercury emissions (U.S. Environmental Protection Agency, 2003).

generating facility that provides >25 MW_e). The rule is a market-based cap-and-trade program (CAA Section 111) and is similar to the program in place for sulfur dioxide (SO_2). The rule is to be administered in two phases. The first phase places a cap of 38 tons per year of mercury beginning in 2010. The second phase sets a final cap of 15 tons by 2018. Coal-fired power plants currently emit about 48 tons per year; therefore, the reduction in mercury emissions will be 21% and 69%, respectively.

The reduction of emissions at coal-fired power plants has historically impacted the quantity and character of resulting CCBs, and with changing quantities and characteristics, the management and associated costs have also been impacted. One of the most noteworthy industrywide changes occurred when FGD systems were installed in the 1980s and large volumes of FGD materials were produced and required management. The removal or reduction of mercury emissions at coal-fired power plants also has high potential to impact CCB management because several proposed mercury emission control technologies involve the use of solid sorbents that will likely be introduced in the flue gas and collected with the fly ash. Other candidate emission control technologies focus on increasing the mercury sorbed on FGD materials. These mercury emission control technologies will impact the mercury content of CCBs. The question that this project was designed to answer is, Will the changes in CCBs associated with mercury emission controls change the management options for those CCBs as they relate to the potential release of mercury? The U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) (2007) evaluated the cost of activated carbon injection (ACI) mercury control and reported that the incremental costs increased by a fraction of 1.5–3 when including impacts to CCBs in addition to implementation costs. DOE NETL reported costs for seven different power plant case studies, and when costs of impacts to CCBs were

included in the economic evaluation, four case studies had costs exceeding DOE's cost target of $45,000/lb Hg removed.

Since the large volumes of CCBs produced annually in the United States are managed either by disposal or utilization, the design of various tasks in this project focused on simulating potential behavior of CCBs in environments where they are typically managed. Examples of utilization scenarios include:

- The use of fly ash in concrete, soil stabilization, or fills that could be exposed to natural waters or to microbial action.
- The use of FGD gypsum in wallboard, where it may be exposed to high temperatures in production or to natural water under disposal.
- The use of fly ash in cement clinker production, where it would be exposed to extremely high temperatures.
- The use of FGD gypsum or fly ash as an agricultural soil amendment or mine fill, where it would be exposed to natural water and, potentially, microbial action.

In order to adequately address the potential for release of mercury from CCBs, sorbents, and combinations, release mechanisms that must be evaluated include leaching, elevated- and ambient-temperature vapor-phase releases, and microbiologically mediated releases. The EERC initiated research on the potential release of mercury from CCBs in 1999 and found that methods for evaluating the release of mercury from CCBs using these mechanisms were not documented in the scientific literature, with the exception of leaching. As a result, the EERC initiated a program under EPA's Center for Air Toxic Metals® and the Coal Ash Resources Research Consortium® (CARRC®) to develop laboratory methods that would provide information on the potential for CCBs to release mercury and other ATEs under conditions associated with the proposed release mechanisms of direct leaching, direct ambient- and elevated-temperature vapor-phase release, and microbiologically mediated leaching and vapor-phase release.

3.0 OBJECTIVES

The goal of the proposed effort was to evaluate the impact of mercury and other ATEs on the management of CCBs. Supporting objectives are to 1) determine the release potential of selected ATEs, including mercury and arsenic, from CCBs under specific environmental conditions; 2) increase the database of information on mercury and other ATE releases for CCBs; 3) develop comparative laboratory and field data; and 4) develop appropriate laboratory and field protocols.

The specific mechanisms of ATE releases evaluated were leaching releases, vapor releases to the atmosphere, and biologically induced leaching and vapor releases.

4.0 EXPERIMENTAL

4.1 Literature Search

The literature search task was designed originally to allow the preparation of an annotated bibliography that included literature on the following topic areas:

- Mercury and other ATE content of CCBs
- The mobility/stability of those elements from/on CCBs
- Emerging mercury control technologies, especially as they would potentially impact the characteristics or composition of CCBs

In the first project year, it was agreed by project sponsors and researchers that the use of an online database to store and retrieve the assembled documents would have greater value to the project, so the approach was modified to enable the development of an online database for the literature collected, allowing project sponsors access to all information gathered.

Throughout the duration of the project, the project team collected and reviewed various documents that pertained to mercury and other ATEs. The documents were gleaned from journals, symposium and conference proceedings, news articles, and several other sources. Both national and international documents were collected.

4.2 Analytical Methods Selection

To evaluate the potential for release of mercury and other ATEs from CCBs, appropriate methods were required, including both experimental methods and analytical methods. This task focused on the selection and continued development of experimental protocols to simulate Hg and ATE releases under varying conditions and the analytical methods required to quantitate those releases.

4.3 Sample Identification and Selection

Sample identification and selection ranked high in importance in conjunction with other critical components of the project because the results of laboratory tests and experiments are sample-specific. In order for laboratory results to be valid and relate to real-world applications, CCBs evaluated must be representative of those expected to be generated at full-scale coal-fired power plants.

The objective of this task was to identify, select, and obtain CCB samples of appropriate type, quality, and quantity for use in the laboratory evaluation of the stability of mercury and other ATEs.

4.3.1 Sample Prioritization

A sample prioritization was developed based on the behavior of mercury. As shown in Figure 4-1, mercury is a highly volatile element that, along with fluorine and chlorine, is expected to be essentially 100% associated with the flue gas and carried out of the stack. For this reason, mercury that may be associated with CCBs has the greatest likelihood of being associated with the fly ash or FGD materials. The temperatures at which bottom ash and boiler slag leave the combustion system are too high for mercury to associate with these materials, so researchers made the recommendation to project sponsors that these materials be excluded from the sample set, and the recommendation was accepted.

Sample identification and selection activities resulted in the preparation of a target list of samples expected to provide data from which conclusions and generalizations can be drawn over the duration of the project. Sample collection was a major and ongoing task.

Samples of fly ash and FGD material from systems with conventional combustion and emission control technologies were relatively simple to access through the EERC's CCB research program and contacts. These samples generally were collected and submitted as samples for typical utilization applications. Most of these samples were collected as composites or from locations within the plant where "as-managed" samples could be accessed. These samples were most likely to represent the materials that are utilized or sent for disposal and provided the most reliable results for real-world comparisons.

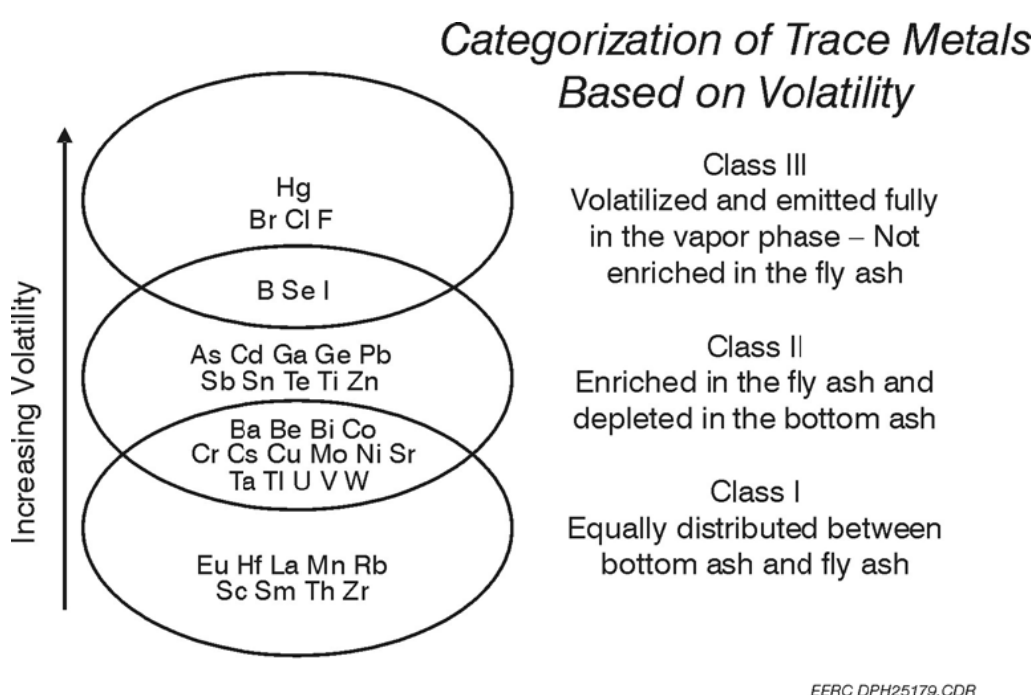

Figure 4-1. Categorization of trace elements associated with coal ash based on volatility.

As-managed samples were generally not available from demonstrations of mercury emission controls. Some of the mercury emission control demonstrations were performed on pilot-scale equipment and some were performed on slipstreams at full-scale power plants. Samples from these types of systems had the disadvantage of not being collected with typical pollution control devices (PCDs). In cases where mercury emission control was demonstrated at full-scale power plants and collected with existing full-scale PCDs, the samples were generally collected from specific fields within the electrostatic precipitator (ESP).

At the Year 1 Project Review Meeting, project sponsors and researchers discussed the advantages and disadvantages of using samples from mercury emission control demonstrations in this effort. In cases where the baseline and mercury control samples were collected at the same location, the samples provided comparative data. However, these data cannot be directly compared to data generated on as-managed samples. Hower et al. (2004) presented information on total mercury content in samples of fly ash collected at different locations at one power plant, as noted in Figure 4-2. The data indicate that samples from a single location in a full-scale power plant are unlikely to represent the mercury content in the associated as-managed sample. Similar variations may be expected for other ATEs.

4.3.2 Sampling and Storage Procedures

The issue of obtaining and maintaining a high-quality sample for laboratory investigations is common across numerous scientific disciplines. In the area of CCB research and testing, some sampling and sample storage issues are critical to performing laboratory work that provides information that can be translated to the real-world management of CCBs whether that is utilization or disposal. These issues can be more or less important based on the type of CCB under consideration. Fly ash and FGD materials, have different sampling and storage requirements. A description of each of these materials follows:

- ***Fly ash*** is homogeneous on the macroscale yet heterogeneous on the microscale. Further, fly ash can vary with changes in the operation of the plant over the course of hours, days, weeks, or months. For this reason, composite samples are generally recommended when fly ash is sampled. For most laboratory evaluations, fly ash is collected from a storage facility, a disposal site, or a truck or train car at the point of delivery. These samples, referred to as "as-managed," are generally representative of the sample to be used or disposed of. Fly ash samples collected from specific locations in the PCD are not considered representations of the bulk material that is used or disposed of.

- ***FGD material*** is generally a high-sulfur material but can have varying physical and chemical characteristics based on the type of FGD system and material-handling protocols. Physically, FGD material can range from a very wet material to nearly dry. Generally, FGD materials to be characterized are usually collected after a dewatering step. This is especially true for FGD materials that are being evaluated for utilization

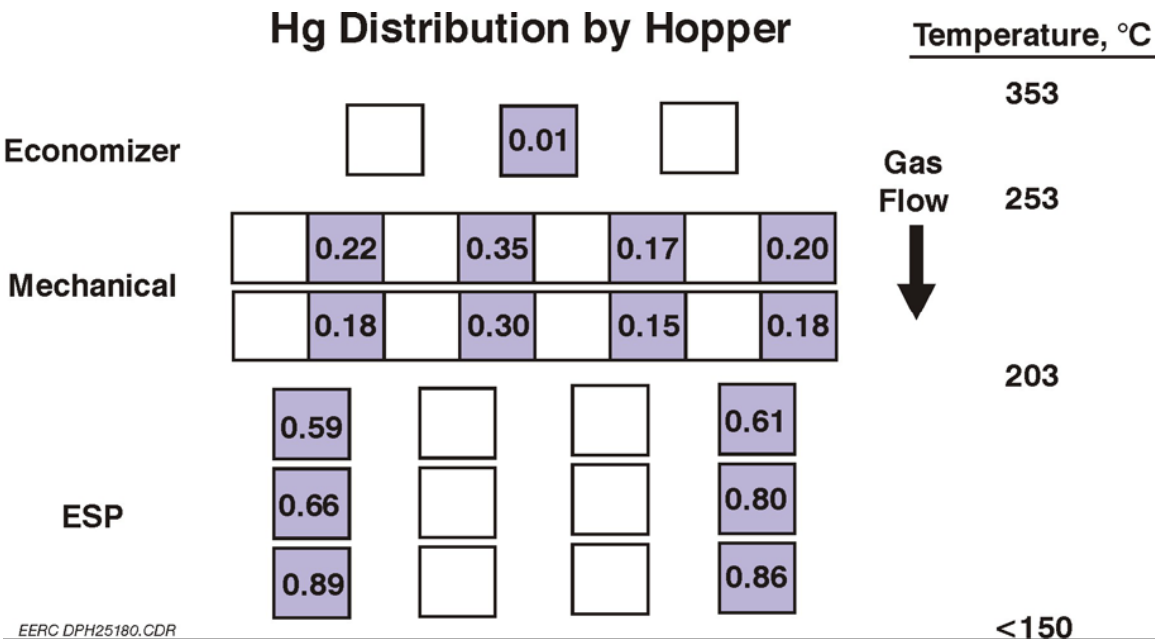

Figure 4-2. Mercury distribution in a power plant (Hower et al., 2004).

applications such as FGD gypsum for use in wallboard. The method of dewatering and collection can impact the chemical composition of the FGD material. FGD material that is destined for disposal may be collected either from a location referred to as the "blowdown" for the wet FGD systems or it may be collected at the point where it exits the transport system to the disposal site. In some instances, wet FGD material may be stabilized by the addition of fly ash or other reagents such as lime prior to use or disposal. In these cases, the added reagent may impact the chemical composition and behavior of the FGD material. FGD material from a spray dry absorber (SDA) system may have fly ash incorporated into the FGD material as part of the system. In selecting and collecting FGD material samples for laboratory evaluations, the sample should represent the material as-managed, and the laboratory personnel must be aware of special handling and reagents that may have been added.

Under ideal conditions, sample collection procedures followed ASTM (American Society for Testing and Materials) International C311 procedures. The standard defines grab samples as samples taken at prescribed intervals over a period of time and having a mass of at least 4 lb. Grab samples can be combined to make a composite sample having a mass of at least 8 lb. According to ASTM C311, samples taken from bulk storage, railcars, or trucks may be taken by siphon tube during loading or by sampling tube from each railcar or truck. If the load is sampled at the point of discharge into a railcar or truck, the top 8 in. must be removed.

Dry material samples (fly ash–sorbent, spent sorbent, and FGD solids) of greater than 1 gal were homogenized to create a representative 2- to 4-L sample that is transferred into a glass jar with Teflon-lined cap to ensure sample integrity was maintained over the duration of the project. Liquid FGD samples were mixed thoroughly, and a 2- to 4-L aliquot was transferred to a glass

jar with a Teflon-lined cap. Liquid sample aliquots were stored under refrigeration (<4°C) until the testing was completed. Homogenized subsamples were stored in the laboratory for use throughout the project. Original containers were stored in a secure area.

Proper storage was important for maintaining the composition and integrity of the samples because the properties of the samples can change with time depending on the material characteristics.

4.3.3 Sample Collection

4.3.3.1 Sample Identification Form

In order to best categorize and interpret project results, information on the sample type, coal used, and system was needed. A sample identification form was developed that allowed each sample submitter to easily identify system and sample information. All sample submitters were given the sample identification form. The sample identification form was extremely useful in this effort because the same identification information is available for most project samples, facilitating data interpretation. A copy of the sample identification form is included in Appendix A.

4.3.3.2 Confidentiality

Confidentiality of sample identity was discussed with sample submitters, and when requested, confidentiality agreements were signed. Each sample was assigned a project number, which was the primary identifier for all samples. Other identifying information has been provided by most sample submitters through the sample submission form. That information included submitter name, location and name of power plant or pilot- or bench-scale system, fuel type, plant configuration, and some operating information. All of these identifiers were kept confidential for this report.

4.4 Chemical and Physical Characterization

The objective of this task was to characterize selected samples in order to understand the physical, engineering, and environmental performance of the materials and ensure that a cross section of fly ash and FGD materials was represented in the investigation. The chemical characterization included determination of bulk chemical composition (major, minor, and trace element constituents) with a focus on the mercury and identified ATEs. In addition to mercury, the ATEs included in the characterization and the overall study were arsenic, cadmium, chromium, lead, nickel, and selenium. Physical characterization included loss on ignition (LOI), moisture content, pH, and carbon forms measurements. Eh was measured in leachate samples from the microbiologically mediated release experiment where a liquid medium was used to promote microbial growth. Data developed in this characterization task were used to aid in interpretation of the results from release experiments.

4.4.1 Analytical Methods for Characterization and Release Experiments

Standard methods were selected and used for sample preparation and analyses where those were available and appropriate for the sample types, volumes, and matrices. Sample preparation and analysis methods were modified or developed as needed where standard methods did not suit the needs of the project.

4.4.1.1 Total Mercury and Air Toxic Elements

The total mercury content of the majority of solid samples was determined using a direct mercury analyzer (DMA-80). Additionally, digestion followed by cold-vapor atomic absorption spectrometry (CVAAS) (EPA Method 7471) (U.S. Environmental Protection Agency, 2005a) was utilized.

The total concentrations of the other ATEs of arsenic, cadmium, chromium, lead, nickel, and selenium were determined using standard methods. Acid digestion was used on the CCB followed by detection using inductively coupled plasma–atomic emission spectroscopy (ICP–AES) (EPA Method 6010B) (U.S. Environmental Protection Agency, 2005b) or ICP–mass spectroscopy (ICP–MS) (EPA Method 6020) (U.S. Environmental Protection Agency, 2005c).

4.4.1.2 Total Bulk Chemical Composition

The major bulk composition, reported as percent oxides, was determined using x-ray fluorescence spectrometry. ASTM D4326-04 Standard Test Method for Major and Minor Elements in Coal and Coke Ash by X-Ray Fluorescence was used (ASTM International, 2004a).

4.4.1.3 LOI and Moisture Content

Standard characterization techniques were used to measure LOI and moisture content. ASTM C311-04 Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete was used (ASTM International, 2004b).

4.4.1.4 pH

The pH of samples was determined using distilled water and/or 1 M KCl. The method employing 1 M KCl was required for many types of solid samples that exhibit a double electric layer that affects the determination of pH. For this task, 25 mL of 1 M KCl solution was mixed with 10 g of CCB, and the resulting pH was measured and recorded. As previously noted, the pH was also determined in slurry of distilled, deionized water. Where both methods were employed in this effort, it was noted that the pH values were similar. A comparison of these data for a relatively broad range of CCB types led researchers to conclude that it is not necessary to use 1 M KCl in determining the pH of CCBs; therefore, remaining samples were evaluated using distilled, deionized water slurries. It is likely that the high concentration of total dissolved solids generated in the pH determination eliminated the double electric layer effect that requires the use of KCl solution in the determination of pH in other types of solid samples. It was found that for

some samples especially those containing added carbon, up to 24 hours of equilibration was required in order to obtain a stable and accurate pH reading.

4.4.1.5 Carbon Forms

Dominant carbon forms were identified in a select group of project samples. The samples on which carbon forms were determined were prepared by mounting in epoxy resin. The sample was dispersed in the bottom of a 1-in.-diameter rubber cup mold. The epoxy was stained using Sudan black, which results in a high contrast between the particles of interest and the mounting medium. The surfaces to be analyzed were polished with incrementally smaller grits, with ¼ µm being the final polishing grit used. The samples were then examined using a reflected-light microscope.

4.4.1.6 Eh

Eh was determined using a platinum electrode with a standard reference electrode.

4.4.1.7 Methods of Measurement Specific to Release Experiments

4.4.1.7.1 Gold-Coated Quartz Traps

Gold-coated quartz mercury collection traps used to collect Hg from various release experiments were desorbed for analysis by heating to approximately 500°C, and the mass of mercury released was determined using double-gold amalgamation with atomic fluorescence (AF) detection. A Brooks Rand Model III cold-vapor atomic fluorescence spectrophotometer (CVAFS) was utilized for mercury concentration determination. Mercury peaks were recorded to allow quantitation using an integrator.

4.4.1.7.2 Measurements of Mercury on Carbotraps

Supelco Carbotrap™ collection traps were also used in several release experiments and were analyzed for total mercury by heating to approximately 300°C, passing the released organomercury through a tube held at about 800°C, and collecting the mercury on a gold-coated quartz trap, which was analyzed as described above.

4.5 Laboratory Evaluation of ATE Releases

Assembled samples were used in laboratory experiments focusing on specific release mechanisms of mercury and other ATEs. Primary release mechanisms are leaching, vaporization, and biologically stimulated leaching and vaporization. ATEs were evaluated including arsenic, cadmium, chromium, lead, mercury, nickel, and selenium for release through leaching. Vapor-release experiments focused on mercury.

4.5.1 Direct Leaching

Methods for leachability were broadly available, but a review of leaching methods was required in order to ensure that reliable results would be generated. The appropriateness of individual leaching procedures is frequently debated, and selection of leaching procedures for this effort was a key activity under this task. The EPA Office of Research and Development (ORD) developed a standard leaching protocol for research related to mercury release from CCBs, and the EERC participated in discussions coordinated by EPA ORD in the development of that protocol.

Leaching is the most likely mechanism of transport of constituents from disposed or utilized CCBs contacted by water. Leaching is typically performed on CCBs to characterize them for management purposes. The leaching tests performed on the samples in this project were the toxicity characteristic leaching procedure (TCLP) (EPA Method 1311) (U.S. Environmental Protection Agency, 1992), the synthetic groundwater leaching procedure (SGLP), and long-term leaching (LTL) with 30- and 60-day equilibration periods (Hassett, 1998). TCLP was included because some regulatory groups continue to use TCLP results to determine whether a "waste" is hazardous. The SGLP–LTL was used because previous EERC work has shown it to yield scientifically valid results on CCBs including reactive CCBs (Hassett, 1994; Hassett et al., 2005).

TCLP is a leaching procedure designed for the evaluation of leaching of wastes when codisposed in a sanitary landfill. Leaching with TCLP utilizes a 20:1 liquid-to-solid ratio, end-over-end agitation at approximately 30 rpm, an 18-h equilibration time, and one of two extraction fluids. The extraction fluid used is dictated by the pH of the material being leached. Extraction Fluid 1, used when the pH is below 5, is prepared by adding glacial acetic acid and sodium hydroxide to reagent water, and has a fluid pH of 4.93 ± 0.05. Extraction Fluid 2, used when the pH of the material is above 5, is prepared by adding glacial acetic acid to reagent water, resulting in a fluid pH of 2.88 ± 0.05.

The SGLP batch-leaching procedure is a relatively simple test that follows many of the conditions of TCLP. The test utilizes a 20:1 liquid-to-solid ratio, end-over-end agitation at approximately 30 rpm, an 18-h equilibration time, and usually employs a leaching solution consisting of water from the site, water that has been prepared in the lab similarly to water likely to contact the CCB, or distilled, deionized water. When distilled water is used as the leaching solution for SGLP, the method is equivalent to the ASTM D3987 Standard Test Method for Shake Extraction of Solid Waste with Water (ASTM International, 2006). Distilled, deionized water was used in this effort. For the long-term component of this procedure, multiple bottles were set up and analyzed at different time intervals. A typical SGLP–LTL test might consist of 18-h, 30-day, and 60-day equilibration times. Although 60 days is often not adequate to achieve complete equilibrium, it is generally long enough to determine the concentration evolution of individual parameters. The most important factor when performing LTL is to have at least three equilibration times to determine a true trend. A draft of the SGLP–LTL method prepared for consideration by ASTM is in Appendix B.

For all leaching procedures, the solids were filtered from the leaching solution through a 0.45-µm filter, the pH of the resulting leachate was measured, and the leachate was preserved with hydrochloric acid (HCl) for mercury determination and with nitric acid (HNO_3) for determination of other trace elements.

Mercury leachate concentrations were determined using CVAAS and CVAFS. Other trace elements were determined using ICP–MS or graphite furnace atomic absorption spectroscopy.

The SGLP method was used preferentially for the project samples, and where TCLP was applied, SGLP was applied for comparative purposes. The SGLP short-term leaching procedure was applied to all samples, but for samples with a pH >10, the LTL option was also used. LTL provides the most valuable information when at least two long-term tests are run (30-day and 60-day LTL or longer as recommended) and reported in conjunction with SGLP results. CCBs exhibiting a high pH have the potential to undergo hydration reactions that can change the leaching profile with time. The EERC documented the impact of ettringite formation on leachate concentrations of several elements that are frequently present in CCBs, such as arsenic, selenium, and boron. The elements that are most likely to be incorporated into the ettringite structure and exhibit a change in leaching profile with time are those that are present as oxyanions at high pH. Examples of leaching profiles of high-pH CCBs for some trace constituents commonly found in CCBs are shown in Figures 4-3 and 4-4.

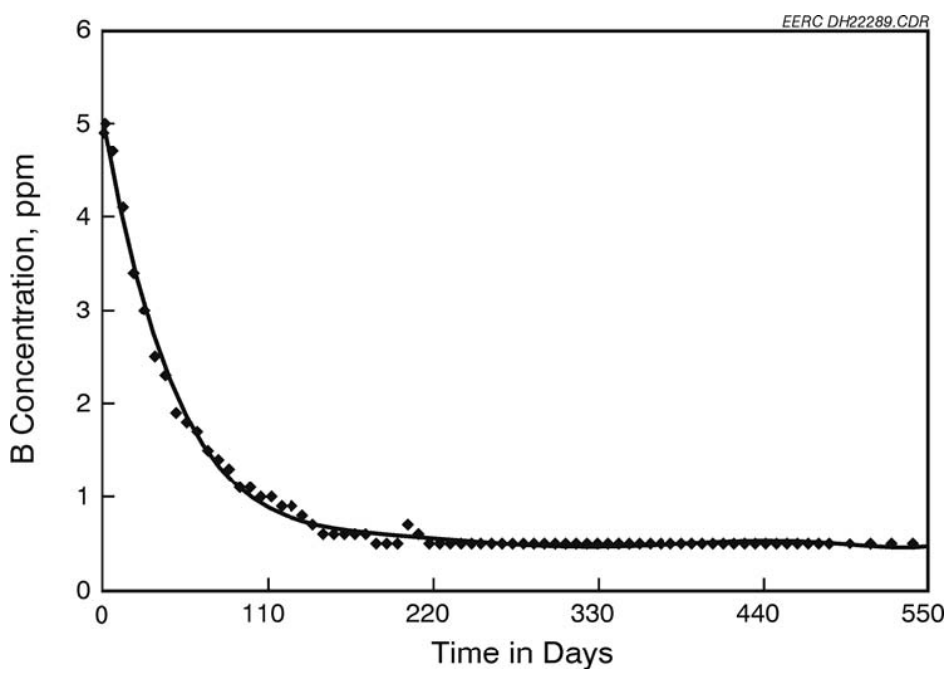

Figure 4-3. Example LTL results for boron.

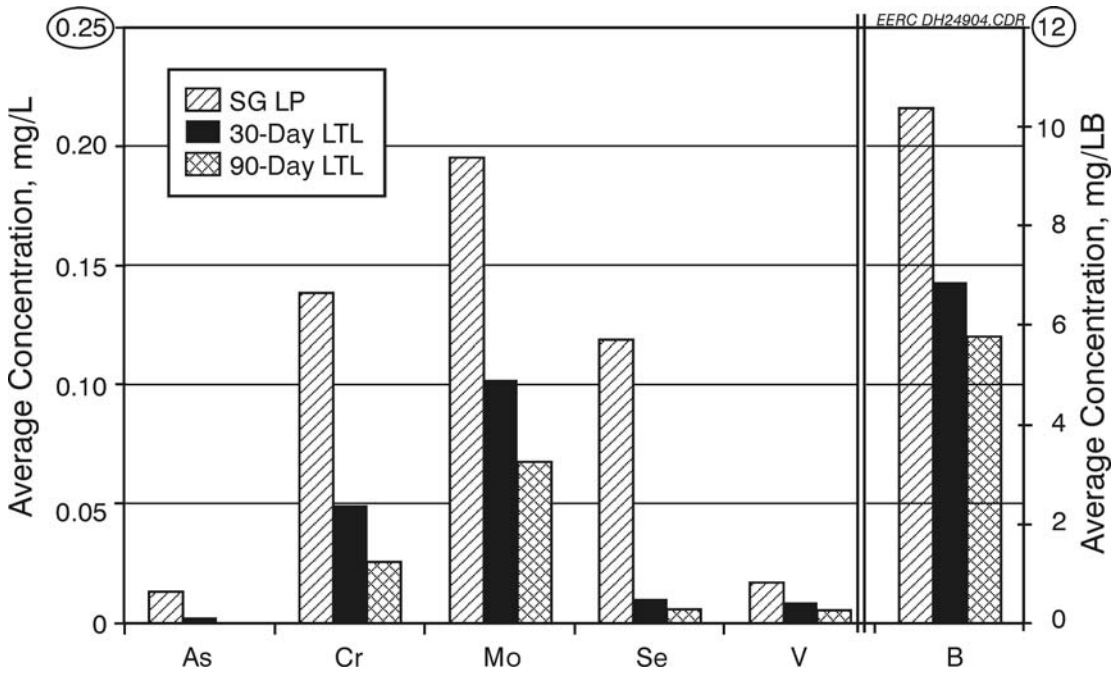

Figure 4-4. Indirect evidence of ettringite formation using SGLP and LTL (note: boron is on a secondary axis).

In Year 2, the task was expanded to include participation in a DOE NETL informal interlaboratory round-robin experiment aimed at providing the industry with appropriate leaching procedures for CCBs. NETL sent a sample to all participating laboratories for evaluation. Samples were requested by the EERC from various utilities burning subbituminous or lignite coal to provide an additional fly ash sample for evaluation. Samples received were evaluated, and one reactive sample was selected for the experiments and sent to participants. Four leaching procedures including the 3-tier leaching protocol (Kosson et al., 2002), the serial batch leaching protocol (SBLP) developed by NETL, the SGLP and LTL with 30- and 60-day equilibration periods (Hassett, 1998), and the mine water leaching protocol (MWLP) proposed by the West Virginia Water Research Institute (WVWRI) National Mine Land Reclamation Center (NMLRC) (Ziemkiewicz, 2005) were part of the informal round-robin experiment. The SBLP and SGLP–LTL tests were performed on the two ash samples at the EERC. A 90-day equilibration period was included at the EERC for this study.

4.5.2 Vapor-Phase Mercury Transport

4.5.2.1 Long-Term Ambient-Temperature Release

In order to develop a method to evaluate the potential for release of mercury from CCBs at ambient temperatures, several preliminary decisions were made based on the practicality of performing this type of evaluation in the laboratory:

- Since most CCBs contain low concentrations of mercury, samples with relatively high concentrations of mercury would be used in experimental development and for initial measurements.

- To facilitate evaluation of multiple samples over long duration, gold-coated quartz mercury collection traps would be used to collect mercury vapor over predetermined time periods, allowing for determination of total mercury released and rate of release. A dedicated mercury analyzer was not available for long-term real-time mercury release measurements.

- In order to evaluate multiple samples with available equipment and instrumentation, released mercury was collected on analytical gold-coated quartz traps.

- Low release of mercury was anticipated, so it was decided to expose a column of CCBs to low-mercury air rather than expose only the surface of a CCB to the ambient-temperature low-mercury air.

Using preliminary premises based on previous EERC work, 250-mL wide-mouth glass test containers with bonded Teflon liner caps were used. Two holes were drilled in the caps to accommodate a silicone tube for gas inlet and a Teflon outlet bulkhead fitting. The gas inlet tube extended only slightly into the container, while the outlet tube extended nearly to the bottom of the container. A shorter outlet tube situated above the sample was used for wet FGD material samples because air could not flow through the sample to the outlet below the sample surface.

Using these test containers, 75–200-g aliquots of CCB provided a column of material through which the low-mercury air could be transported. Breathing-quality air from a cylinder was passed through several sets of gold-coated quartz traps for mercury removal and admitted to each of the bottles through a gas distribution manifold that routed the gas through 0.25-mm-i.d. gas chromatography (GC) capillary tubing to each of the individual bottles. The pressure drop across the GC capillary tubing allowed for the regulation of airflow through each bottle by simply adjusting the length of tubing to each bottle. The length of tubing was a nominal 65 cm. This length of tubing, when pressurized to between 1 and 2 psig through a gas distribution manifold, provided a convenient means of regulating gas flow to approximately 2 cm^3/min. Because of the variability of particle sizes between different CCB samples, the sample with the initial highest gas flow was left with a 65-cm length of GC tubing, and other samples had their tubing lengths shortened until all samples had approximately the same flow rate. The air exiting the GC tubing was given a final scrubbing to remove mercury vapor using a gold-coated quartz trap just prior to entering the bottle containing the CCB. After entering the bottle, the air passed through the CCB and exited to a mercury collection tube containing two separate gold-coated quartz traps. The trap nearest the exit bulkhead fitting, or analytical trap, collected mercury released from the CCB and bottle. The second outlet, or top trap, was used to prevent mercury contamination from atmospheric mercury. This setup is illustrated in Figure 4-5.

The gold-coated quartz analytical trap nearest the exit bulkhead fitting was analyzed multiple times, with the most typical sampling scheme being one 7-day mercury vapor collection

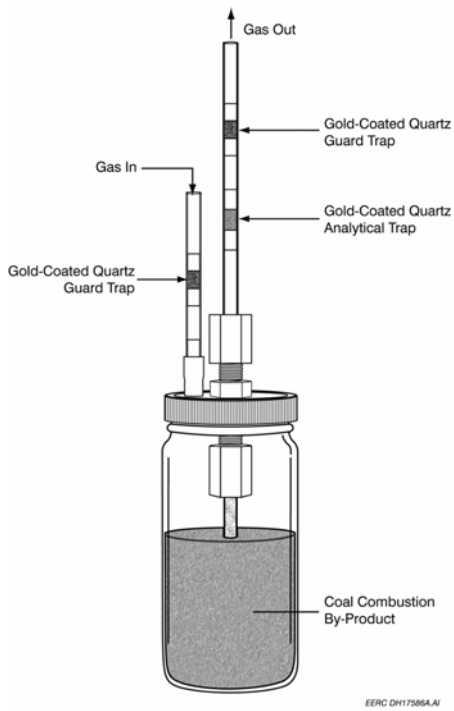

Figure 4-5. Ambient-temperature mercury vapor release collection apparatus.

period followed by two consecutive 90-day mercury vapor collection periods. The gold-coated quartz analytical traps were evaluated according to the method described in the analytical method section. In order to determine the total mercury released over the duration of the experiment, the mercury results from all experimental time segments were combined, and the container blank was subtracted. The container blank was determined on the empty bottles used to hold the samples.

4.5.2.2 Thermal Desorption at Elevated Temperature

Since mercury and mercury compounds are highly volatile, mercury release from CCBs was expected when they were exposed to elevated temperatures. Even mercury that is sorbed onto fly ash, FGD material, or sorbents developed to remove mercury in flue gas was expected to have high potential to be released if exposed to high enough temperatures. Instrumental and equipment constraints existed for the physical testing of elevated-temperature release of mercury from CCBs. These constraints included the following:

- Furnaces available for the experimental apparatus could only achieve maximum temperatures of 750°C.

- Fittings and connecting tubing needed to be heated in order to minimize the loss of mercury in the system.

- Gas flow to remove the mercury from the heated sample cell to the analytical cell needed to be constant.

- Temperature ramping needed to be controlled and consistent between sample runs.

- Detection limit of atomic absorption (AA)-determined sample size.

An apparatus was constructed as shown in Figure 4-6. The CCB sample was weighed into a quartz tube, with quartz wool used to keep the sample in place in the tube. Sample size varied from approximately 300 to 900 mg. The sample tube was placed into a small tube furnace capable of achieving a maximum of 750°C. A programmed temperature controller ramped the furnace from ambient to maximum temperature at 25°C per minute. In preliminary experiments, the maximum temperature achievable was 700°C, but an improved furnace was incorporated into the apparatus to increase the maximum to 750°C. A nitrogen gas flow of 5 cm^3/min was introduced into the tube furnace. As the mercury and mercury compounds desorbed from the CCB in the sample tube, the nitrogen flow carried them through the system to the electrically heated quartz analytical cell. The quartz analytical cell was operated at 800°C, allowing the detection of mercury compounds by thermally decomposing compounds to form elemental mercury, which can be detected by AA. The analytical cell at the top of the diagram was placed in the center-focused beam path of an AA spectrophotometer (AAS). A mercury hollow-cathode lamp was used as the light source, and the AAS detector was set to the 253.7-nm line for mercury. A Hewlett Packard 3395 integrator was used for data collection. Examples of thermal desorption curves generated with this method are shown in Figures 4-7 and 4-8. The integrator used standard algorithms to identify peaks and indicated the time of peak maximum, which is noted in Figures 4-7 and 4-8.

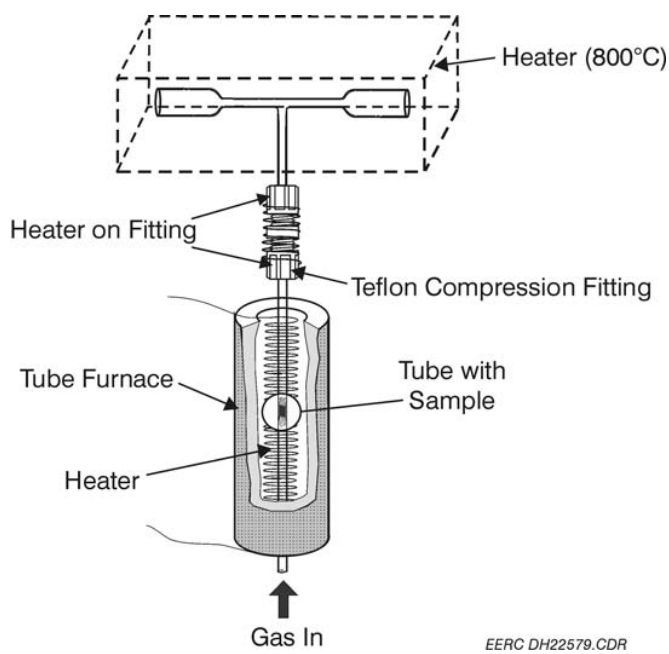

Figure 4-6. Mercury thermal desorption apparatus.

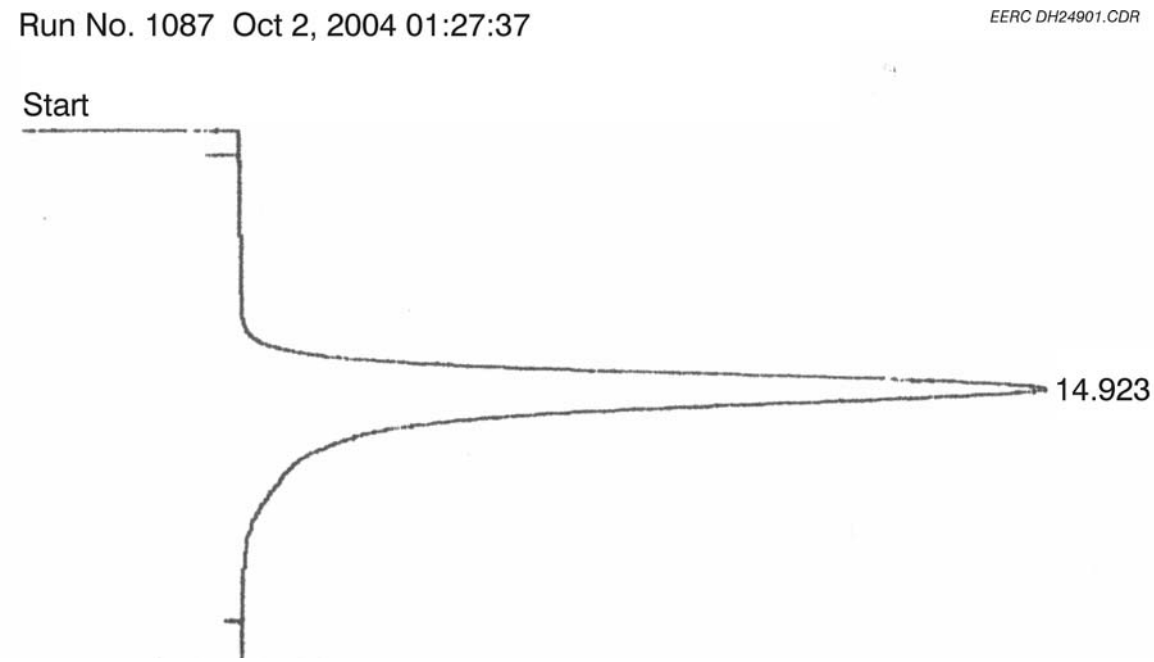

Figure 4-7. Typical thermal desorption curve for fly ash (peak time is noted in minutes for each peak recognized by the electronic integrator used for data collection).

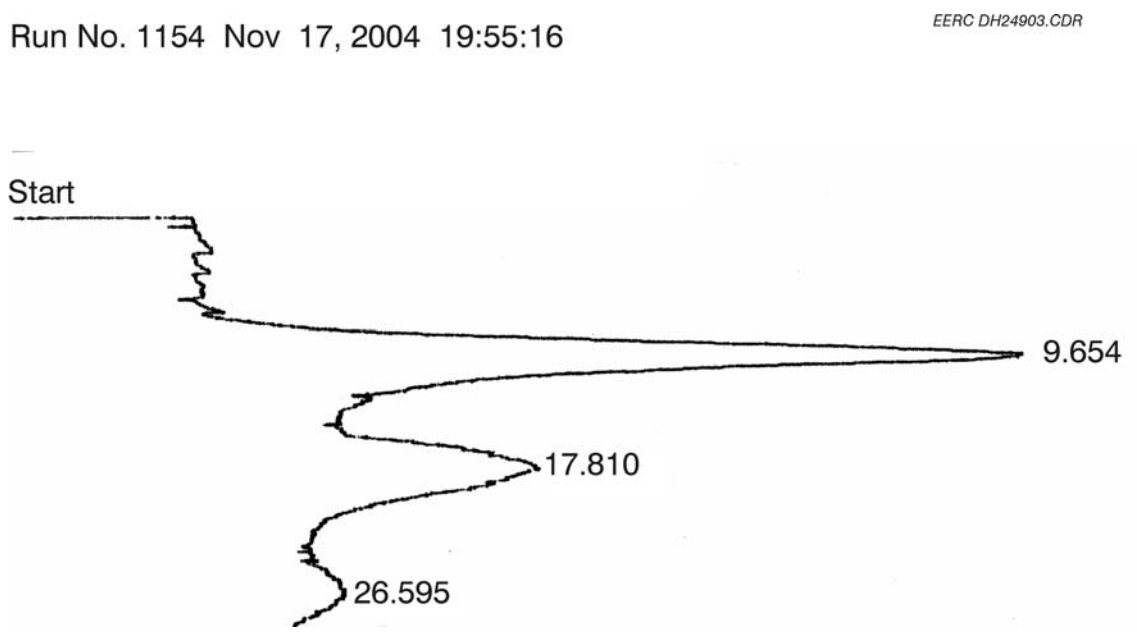

Figure 4-8. Example of thermal desorption curve for an FGD material (peak time is noted in minutes for each peak recognized by the electronic integrator used for data collection).

4.5.2.3 Mercury Speciation Method

It has been hypothesized that the mercury species associated with fly ash, FGD material, or carbon might be identified using thermal desorption techniques. EERC researchers performed numerous experiments to confirm or refute this hypothesis. The experimental design focused on the use of analytical spikes using mercuric chloride and elemental mercury. CCB samples, quartz sand, and quartz powder were all used as a base sample for these evaluations. Mercuric chloride was dissolved in ether and then added to the base samples. Elemental mercury was added in a gaseous form to CCB samples. The spiked samples were then desorbed using the same apparatus and protocol for the elevated-temperature vapor-phase mercury release experiments described above.

4.5.3 Microbiologically Mediated Leaching and Vapor-Phase Transport

4.5.3.1 Description of Initial Apparatus and Method

The first apparatus assembled to conduct microbiologically mediated vapor-phase mercury release used a 250-mL Erlenmeyer flask fitted with an impinger inlet/outlet tube, with the inlet center shortened to 6 cm below the standard taper. Cylinder gas was passed through several sets of gold-coated quartz traps for mercury removal and admitted to each of the flasks through a gas distribution manifold that routed the gas through 0.25-mm GC capillary tubing to each of the individual flasks. A GC capillary length of approximately 60 cm, when pressurized to between 1 and 2 psig through a gas distribution manifold, provided a convenient means of regulating gas flow to approximately 2 cm^3/min. The gas carried mercury vapor from the headspace of the flasks to a mercury vapor collection system at the outlet of the flasks, consisting of two traps. A Supelco Carbotrap™ (for collection of organomercury compounds) and a gold-coated quartz trap (for collection of elemental mercury) were used to collect mercury released in the vapor phase from the flasks.

The flasks were placed on a 16-flask wrist action shaker. The experimental matrix consisted of eight flasks under anaerobic conditions (using argon) and eight flasks under aerobic conditions (using breathing-quality air). In each set of eight flasks, two contained only buffer, three contained the CCB with buffer (starved), and three contained the CCB with buffer and glucose (fed). A 50-g aliquot of CCB was placed in the flasks, and ~100 mL of a phosphate buffer (with or without glucose, as appropriate) was added to create a neutral pH. The CCB-containing flasks also had 100 μL of mixed bacterial culture added. The source of bacteria was a mixed bacterial innoculum from a brackish wetland. This setup is illustrated in Figure 4-9.

4.5.3.2 Modifications of the Apparatus and Experimental Design

The apparatus as described underwent several iterations as difficulties were identified and solutions developed. The wrist-action shaker was abandoned, as it was inadequate to suspend the sample during the experiments. Instead of the wrist action shaker, samples were placed in Erlenmeyer flasks on a 9-place stir plate. This was operated for about 20 min every 3 h to maintain sample agitation over the duration of the experiment. Additionally, the sample size was

Figure 4-9. Early microbiologically mediated mercury vapor-phase collection apparatus utilizing a wrist action shaker to facilitate mixing.

reduced to 20 g and the buffer increased to 135–150 mL to provide adequate sample volume for additional trace element analyses. The buffer composition was also altered. It was found that phosphate and nitrate interfered with a derivitization step in the determination of organomercury compounds in the solid-phase microextraction (SPME) process using gas chromatographic separation followed by detection of the mercury compounds by AF. This technique is described in Section 4.5.3.6. The original buffer utilized nominal concentrations of phosphate and nitrate salts. The improved buffer used only 100 ppm of phosphate and substituted potassium glutamate as the nitrogen source. This simple change appeared to remove the interferences. Additionally, later experiments did not involve the use of starved control samples. In current experiments, all samples are fed with glucose. Table 4-1 summarizes the modifications and indicates the experimental difficulties that the modifications were employed to correct or improve. The final experimental apparatus used for the majority of the project microbiological experiments is illustrated in Figure 4-10.

4.5.3.3 CCB Preparation Methods

Some CCBs, especially fly ash, can be alkaline in nature. CCB alkalinity can be attributed to the dissolution of alkaline metal oxides that react with water to generate net alkalinity. Water-soluble calcium content contributes most of a CCB's net alkalinity. This trend can be seen in the classification of fly ashes; Class C fly ash is enriched in Ca and Mg and subsequently generates pH values considerably higher than Class F fly ash (e.g., pH >10).

Table 4-1. Microbiological Rerelease Apparatus Modifications

Original Experiment or Apparatus Component	Difficulty or Unmet Need	Modified Experiment or Apparatus Component
Wrist Action Shaker, Continuous Shaking	Inadequate suspension of sample.	Magnetic stir plate, intermittent stirring.
50–80-gram Sample Size + ~100-mL Buffer	Inadequate volume of liquid to recover for leachate analysis.	~20-gram sample + 135–150 mL buffer.
Phosphate Nitrate Buffer Solution	Interference with the determination of the organomercury compounds in leachate.	Lower concentration of phosphate with potassium glutamate as nitrogen source.
Glucose-Fed and Starved Experiments	Starved experiments did not promote microbial growth so were deemed unnecessary.	All experiments fed with glucose.
Gold-Coated Quartz Trap Followed by Carbotrap at Gas Exit (only in Experiment 1)	Organomercury was trapped on the gold-coated quartz so organomercury could not be measured separately.	Carbotrap was followed by gold-coated quartz trap at gas exit.

Figure 4-10. Microbiologically mediated mercury vapor-phase collection apparatus utilizing a stir plate to facilitate mixing.

In order for a CCB, or any material, to support biological activity, it must be near-neutral pH. A pH range of 6.5 to 8.5 was used for optimal microbiological activity, requiring substantial neutralization of some CCBs. Prior to initiation of experiments, the buffer for that experiment was added to individual samples, pH of the ash–buffer mixture was measured, and an appropriate volume of acid was added over a period of time to achieve a neutral pH.

4.5.3.4 Microbiological Innoculum Growth Conditions and Media

Since the microbes that promote the release of mercury are ubiquitous, freshly collected sediment from a local brackish wetland was used as the innoculum. This innoculum contained a variety of microbes including both aerobic and anaerobic bacteria and, therefore, was identified as an appropriate innoculum. The source of the innoculum was the same for all experiments.

The innoculum was prepared by using 1 g of sediment taken approximately 2 mm from the surface of the sample so that is was more likely that a high concentration of anaerobic organisms would be present. This sample was added to 10 mL of 0.9% NaCl and vortexed. This suspension was then used to inoculate the CCB slurry samples.

4.5.3.5 Experimental Incubation Conditions

Samples were allowed to incubate in sealed flasks at room temperature for 4 weeks. Experiments were all performed in triplicate. Table 4-2 provides information on the incubation conditions for microbiological rerelease experiments performed under this project.

4.5.3.6 Mercury Analyses

The mercury collected in the traps designed to collect mercury released in the vapor phase was quantitated at the conclusion of each experiment. Hg analytical traps were analyzed as noted in 4.4.1.7 above.

The leachate was separated from the sample in order to determine the concentrations of mercury in solution. Total mercury concentrations of the leachate were determined using CVAFS or CVAAS.

In order to determine organomercury species of the mercury present in the leachates, SPME was used. SPME is a sample collection technique utilizing a fiber coated with polydimethylsiloxane. Samples containing organomercury compounds are first derivatized to increase the volatility of organomercury halides such as methylmercuric chloride. The derivitization reagents used were sodium tetraethyl borate, sodium tetrapropyl borate, and sodium tetraphenyl borate. Sodium tetraethyl borate was most commonly used. In the derivitization procedure, derivatizing agent, acetate buffer, an internal standard (usually propyl mercuric chloride), and sample were mixed in a septum-capped vial. In a relatively fast reaction, the halide is replaced with the appropriate alkyl or aryl group, depending on which derivatizing agent is chosen. Five mL of the liquid plus an aliquot of ethylmercuric chloride as an internal standard was placed into a 15-mL septum-capped nonactinic vial containing a Teflon-coated stir bar. 500 µL of a pH 4.5 acetate buffer was added followed by 200 µL of a 1% solution of sodium tetrapropylborate. SPME sampling was accomplished using a 100-µm polydimethylsiloxane-coated fiber and sampler from Supelco (Bellefonte, Pennsylvania). An SPME fiber was inserted through the septum cap, and the sample was stirred using a Teflon-coated stir bar for 20 min. After this equilibration time, the SPME fiber was introduced into the heated inlet zone of a GC. Sample separation can be accomplished using a 0.53-mm capillary column 15 or 30 m in length.

Table 4-2. Microbiological Experimental Incubation Conditions

Experiment No.	Number of Samples Run in Triplicate	Apparatus Used	Acid Addition	Buffer	Ash-to-Buffer Ratio	Incubation Conditions
1	1	Original apparatus	None	Phosphate/nitrate buffer	50 g to 94 mL	Anaerobic and aerobic both with glucose-fed and starved conditions
2	1	Original apparatus	None	Phosphate/nitrate buffer	50 g to 100 mL	Anaerobic and aerobic both with glucose-fed and starved conditions
3	1	Original apparatus	Phosphoric acid added to neutralize solution pH to allow microbial growth	Phosphate/nitrate buffer	80 g to 100 mL	Anaerobic and aerobic both with glucose-fed and starved conditions
4	3	Modified apparatus	Sulfuric acid added to neutralize solution pH to allow microbial growth	Phosphate/glutamic acid buffer	20 g to 150 mL	Anaerobic and aerobic with glucose-fed conditions
5	3	Modified apparatus	Sulfuric acid added to neutralize solution pH to allow microbial growth for fly ash samples	Phosphate/glutamic acid buffer	20 g to 150 mL	Anaerobic and aerobic with glucose-fed conditions; no bacterial innoculum for FGD sample
6	4	Modified apparatus	Sulfuric acid added to neutralize solution pH to allow microbial growth	Phosphate/glutamic acid buffer	18 g to 135 mL	Anaerobic and aerobic with glucose-fed conditions

The exit end of the column was connected to a heated quartz tube (800°C), and makeup helium gas was added to increase the total flow to between 25 and 30 mL per minute. The gas was then routed to an AF detector for determination of the separated mercury compounds.

4.5.3.7 Microbiological Analysis

Bacterial counts were performed upon completion of the experiments to determine if there were adequate active microbes present at the completion of the experiment to account for any mercury releases found. A 1-mL aliquot of solution was taken from each flask. Prior to processing, the ash sample was stored in a flask at 4°C. When processing, 100 µL was removed and added to 9.9 mL sodium pyrophosphate (PP) buffer (0.1% w/v) pH 7.0 with three glass beads in each test tube. This was vortexed for 30 s then serially diluted into PP buffer (up to 1/1000 dilution). These dilutions were used to inoculate a 3-tube most probable number (MPN) assay with 1% peptone–tryptone–yeast extract–glucose (PTYG) buffer. Four mL of PTYG was placed in each 13 × 100-mm tube along with innoculum and incubated at room temperature. Tubes and plates (peptone–yeast extract–glucose [PYG] agar) inoculated with samples from the anaerobic ash suspension were incubated under anaerobic conditions (anaerobic hood), and aerobic ash suspension samples were exposed to atmospheric oxygen. At week intervals, they were scored based on turbidity.

4.6 Field Investigations

The objective of this task was to develop information to facilitate an understanding of how laboratory results can be used effectively to determine potential releases of ATEs from CCBs in real-world management settings. Phase one of this task included a field sampling event at a lignite-based power plant disposal facility. Following assembly of the phase one results, project sponsors and researchers agreed that additional field measurements would not be expected to yield adequate data to allow the development of a method that directly correlated laboratory data with field data, so an alternate laboratory evaluation for measuring microbiologically mediated Hg releases was designed as phase two of the task.

4.6.1 Field Task 1

Phase one of the field investigation was performed at CCB management facilities associated with a lignite-fired power plant. The field task consisted of three key activities: 1) collection of near-surface solid samples and water samples where available, 2) mercury flux measurements taken at near-surface locations, and 3) collection of mercury samples from CCB and fill air at near-surface locations. The EERC contracted with the University of Nevada–Reno (UNR) to perform the mercury flux measurements.

The EERC methodology for determining CCB landfill air mercury levels was performed at several locations at the CCB management facility including a fly ash disposal site, a site where wet FGD material and mill rejects were codisposed, a reclaimed fly ash landfill site, near a disposal pond containing wet FGD material and bottom ash, and near a disposal pond containing wet FGD material stabilized with fly ash. The mercury-sampling sites are outlined in Table 4-3.

Table 4-3. Mercury Measurement Site Descriptions

Substrate Type	Site Description
Fly Ash	Uncovered, fly ash landfill
Vegetated Fly Ash with Soil Cover	Closed, reclaimed (vegetated) fly ash landfill with 2-ft clay cap and 3-ft soil cover
Wet FGD Material + Mill Rejects	Uncovered disposal of material from ash Pond 91 during 2003
Wet FGD Material (wet disposal)	Wet disposal in the middle of the pond (unstabilized)
Bottom Ash/Mill Rejects + Wet FGD material (wet disposal)	Wet disposal in the middle of the pond (unstabilized) surrounded by a bottom ash embankment
Stabilized Wet FGD Material (with fly ash)	Uncovered HDPE[1]-lined facility (stabilized)
Natural Grasslands (background soil)	Natural grassland
Agricultural land	Agricultural land actively farmed

[1] High-density polyethylene.

CCB landfill air was drawn through gold-coated quartz traps and tubes containing Supelco Carbotrap™. The combination of collection on these two types of analytical traps allowed assessment of inorganic mercury (gold trap) and organomercury species (Supelco Carbotrap™). Traps were analyzed as noted in the laboratory methods section of this report (4.4.1.7).

Solid samples and water samples were obtained for laboratory testing. Solid composite samples were taken of the substrate on which the mercury air sampling was conducted. Composite samples are described in Table 4-3. Liquid samples were collected at disposal ponds where possible. A map showing sampling locations is shown in Figure 4-11.

In situ mercury flux was measured by UNR research staff using two field flux chambers linked to a total mercury analyzer (Tekran 2537A) systems. Mercury fluxes for the field chamber measurements were calculated using the Hg flux rate, outlet and inlet air Hg concentrations, airflow rate, and soil surface area covered by the chamber. Chamber blanks were also obtained. This method has been successfully applied before at other fly ash sites (Gustin and Ladwig, 2004). Micrometeorological parameters were also measured during the same time frame as the flux measurements. These included air and substrate temperatures, relative humidity, and incident light. Several solid samples were collected at each field sampling location for determination of total mercury. For each material, fluxes were measured from at least three locations (Xin et al., 2006)

4.6.2 Alternate Field Task

The phase two field investigation (alternate field task) was designed to evaluate the impact of interaction between soil and fly ash on mercury release from fly ash. The interaction of greatest interest was that caused by inherent microbiological organisms typically found in soils. The CCB–soil laboratory experimental apparatus was designed to evaluate microbiologically

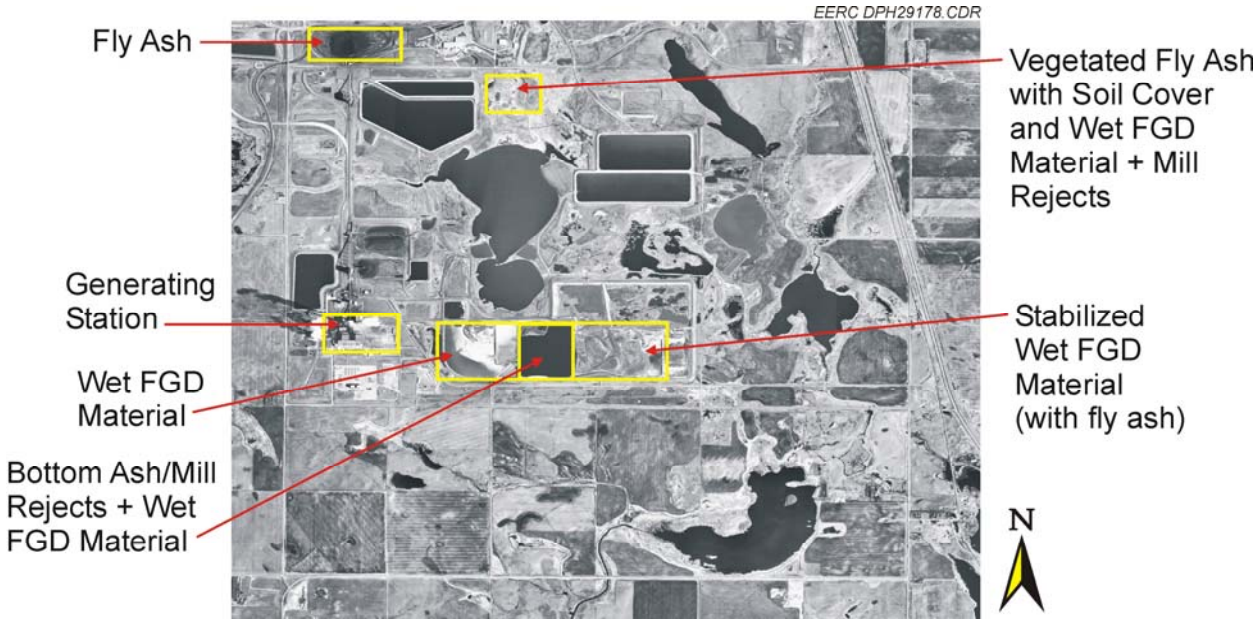

Figure 4-11. Field sampling site map.

mediated mercury release from CCB–soil mixtures, analogous to utilization management practices in the field. The experimental protocol was similar to the long-term ambient-temperature experiment and used a similar apparatus. A schematic of the apparatus is shown in Figure 4-12. Note that an inverted funnel was placed over the soil–ash bed to facilitate collection of released mercury.

A 20% addition of CCBs was combined with the soil and mixed thoroughly. The soil consisted of a mixture of topsoil, potting soil, and peat moss, which had moisture added to increase existing microbial activity. Approximately 200 grams of this mixture was placed in sample containers. Mercury-free air entered the sample container, swept over the sample, and exited through an inverted glass funnel. Organomercury compounds were captured on a collection trap containing Supelco Carbotrap™, and elemental mercury was captured on gold-coated quartz. Six fly ash–soil mixtures, one FGD material–soil mixture, and soil alone were set up in duplicate.

After a period of mercury collection, the Supelco Carbotrap™ and gold-coated quartz analytical traps were analyzed for captured mercury as noted previously. All sample containers were subjected to a blanking process to account for elemental mercury present in the empty container and the scrubbed air entering the system.

4.7 Data Reduction and Interpretation

The quality objectives of this effort support continued environmentally responsible management of CCBs and appropriate federal regulation of CCBs. The quality objective was to

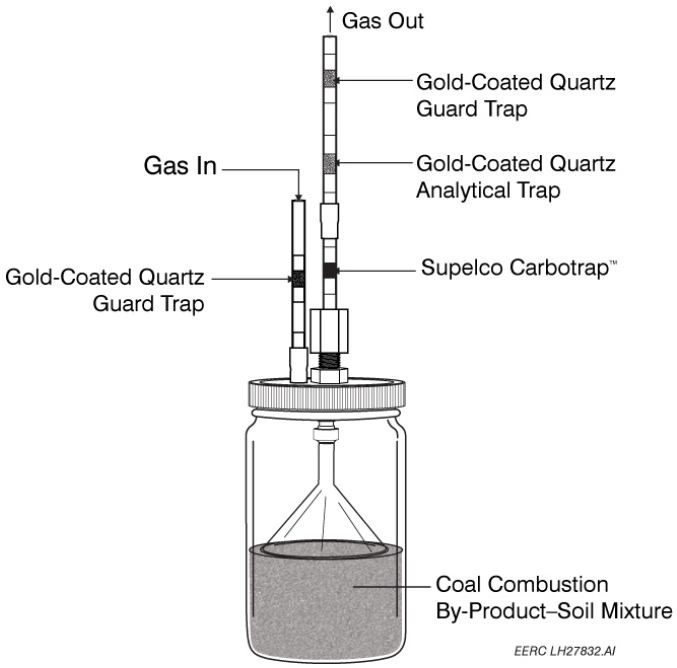

Figure 4-12. CCB–soil mercury vapor release collection apparatus.

select and/or modify experimental methods that would be most appropriate for the material types.

Because this was a laboratory project to evaluate mercury stability in CCBs, most of the analyses of the samples were done using standard EPA-approved laboratory methods. Other laboratory techniques that did not have specific EPA-approved methods were performed in accordance with standard EERC laboratory practice.

5.0 RESULTS AND DISCUSSION

5.1 Literature Search

The online database of literature gathered over the project duration, modeled after the EERC's FIRST SEARCH database, is located on the Coal Ash Resource Center Web site at www.undeerc.org/carrc/mercury. A user name and password are required, which allows only project sponsors and researchers to access the database. The database can be quickly searched using the "Quick Search" tool or the "Advanced Search" tool; it can be searched for a specific title, author, source/publisher, or abstract text. Users may also browse all publications in alphabetical order by title. The majority of publications contain abstract text, and a method is provided to acquire the full text. In several instances, full text is provided free of charge by following the full text instructions. The database contained 526 documents. In addition to these documents being made available to project researchers and sponsors, many of these documents

were used in preparation of research status reports under a separate effort for the Canadian Electric Association, and those reports are included in Appendix C.

The literature assembled indicated the following:

- Most work in the area of mercury stability/release from CCBs has been published after 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, including the EERC's reports from this project, reported low mobility of mercury from fly ash due to leaching.

- The mechanisms of vapor-phase rerelease and microbiologically mediated leaching and vapor-phase rerelease were investigated since 2004 but the data reported in the literature were limited.

- Field-generated data were consistent with laboratory data even though only limited field investigations were reported in the literature.

5.2 Analytical Methods Selection

The methods selected for use in this project are listed and described in the experimental section. For the most part, methods used were standard methods. Both ASTM and EPA methods were used when available. Where required, exceptions to the use of standard methods were also described in the experimental section and in a report prepared earlier in the project to summarize the analytical and release methods selected. That report is included in Appendix D.

The leaching method selected, SGLP–LTL, was selected based on EERC experience and familiarity with a large number of leaching procedures used to characterize CCBs and the appropriate application of those tests. SGLP–LTL meets the criteria that EERC researchers have identified for leaching procedures to provide scientifically valid information. These criteria are as follows:

- Reactivity or other properties of the material being leached that may influence the leaching profile.

- The setting where the material is to be placed and the water that will most likely contact that material in that setting.

- The leaching time required to allow adequate time for hydration reactions to occur in reactive materials, such as high-calcium coal fly ash.

The elevated-temperature vapor-phase release method, developed at the EERC in 1998 (Pavlish, 1999) underwent minor modifications early in the project as described in the experimental section of this report, but has been shown to provide reproducible data. The

remaining technical challenge with the method as employed for this project is the limitations associated with the maximum achievable temperature to be applied to the CCB under investigation, and this cannot be addressed under this project. The method also has limitations for samples with high sulfur content because sulfur compounds are released as a gas on sample exposure to elevated temperatures and are an interference to the determination of mercury.

The ambient-temperature vapor-phase release method developed for this work also presents technical challenges, but these are related to the quantitation limitations for mercury. The extremely low levels of mercury released at ambient temperatures are frequently near the levels of detection for the analytical system being used. The physical nature of the CCB samples also results in variable data and the need to modify the method. As an example, using the apparatus to evaluate the potential for release of mercury from a wet FGD material required modification of the apparatus to shorten the gas inlet tube to above the level of the sample because gas could not be forced through the material when the inlet was near the bottom of the sample container.

The EERC method developed to evaluate the microbiologically mediated release of mercury underwent significant modifications during the project. For samples of low to moderate pH and low sulfur content, the apparatus noted in Figure 4-10 was appropriate and allowed collection and analysis of mercury released in the vapor phase and by leaching. For alkaline samples and those with high sulfur content, including FGD materials, the apparatus shown in Figure 4-12 was developed and used for determining the microbiologically mediated releases of mercury from CCBs by mixing the CCB sample with soil and introducing a low-mercury airstream. Analytical traps were used to capture organomercury and total mercury released as a vapor. This apparatus was used to complete the microbiological experiments, and because soil was used in the sample setup, these experiments also served to complete the work for the field task, which had been modified as noted in the experimental section.

5.3 Sample Identification and Selection

Sample selection was initiated by identifying samples that would potentially be available through government, industry, and marketing contacts. CCBs were selected from systems with conventional emission control technologies and advanced emission control technologies. Samples included 1) currently produced fly ash from a variety of coal sources and system configurations; 2) wet and dry FGD materials, focusing on processes with a higher probability for future installation; and 3) CCBs from pilot-scale or experimental emission control technologies with a high potential to be implemented under existing or expected regulations. For activities related to experimental protocol and analytical methods development, high-mercury fly ash samples were used in order to allow measurements of mercury above the lower level of quantitation (LLQ). These samples were selected from systems producing fly ash with higher-than-average carbon content or, in some cases, those from fabric filter collection systems. The best choices for samples were those collected from full-scale combustion and FGD systems; however, these were not always available, especially for mercury control technologies and early in the project before large-scale DOE mercury emission control tests were initiated. Throughout the project, samples from systems with advanced emission controls were collected from system technologies in the research, development, and demonstration phases under DOE and other

programs focused on emission control. Some samples were collected from bench- or pilot-scale studies because those samples were the only ones available at the time.

5.3.1 Sample Prioritization

A sample prioritization was performed as part of the project kickoff meeting, and the results of that effort (included in Appendix E) provided a target list of sample types to include in the project sample set. The highest-priority samples were identified to be those generated using the following:

- Bituminous, subbituminous, and lignite in pulverized coal (pc)-fired units and fuel oil
- Fabric filter or ESP cold side
- No FGD system or wet calcium-based FGD process or SDA.
- No ammonia-based system or ammonia injection or selective catalytic reduction (SCR).

High priority was also given to samples that could be collected from full-, pilot-, or bench-scale systems for mercury emission control as follows:

- Carbon injection
- Noncarbon sorbent injection
- Modified FGD
- Fine particulate control
- Fly ash from carbon removal technologies

It was also noted that, where possible, samples representing a "baseline" and "test" sample pair should be obtained. The project sample set included primarily samples identified as high priority. Samples generated from pc-fired systems using 100% bituminous, subbituminous, and lignite constituted the majority of the samples collected for the effort. The majority of fly ash samples that were collected from demonstrations of mercury emission control systems had AC used as a sorbent. Only one paired set of fly ash samples was obtained from a fine particulate control system being tested for mercury capture. While no noncarbon-based sorbent samples were collected, one sample where a chemical "enhancing agent" was added was obtained and evaluated.

A summary of samples finally selected for use in this project is included in Tables 5-1–5-3. A complete listing of samples and the identification information are included in Appendix F. Based on the sample quantity, quality, and relevance to the project, mercury and ATE release experiments were performed using these samples; however, not all samples were subjected to all types of release experiments, and some samples collected or submitted for the project were not included in the final sample selection. Reasons for excluding samples from the selected sample set were the following:

- Insufficient sample to perform characterization analyses and release experiments
- Insufficient sample identification information
- Sample not representative of typical coal-based systems
- Sample poorly taken or stored prior to receipt so integrity was in question

Table 5-1. Summary of Fly Ash Samples and Fundamental Characterization Data

Coal Type	No. of Fly Ash Samples	No. of Fly Ash Samples from Hg Control	24-hour pH Range	LOI Range, %	Total Hg Concentration Range, µg/g
Eastern Bituminous	17		5.52–12.44	0.47–6.27	<0.01–0.685
		6 with AC (post-primary PCD)	3.99–9.20	12.6–24.4	0.742–120
South American Bituminous	2		9.13	12.7–21.2	0.151–0.607
		2 with AC (pre-primary PCD)	NT[1]	NT	NT
Western Bituminous	2		10.38–12.65	1.42–2.56	0.144–0.521
Subbituminous	3		12.27–12.56	0.32–1.08	0.261–1.22
		4 with AC (pre-primary PCD)	10.95–11.90	2.28–4.14	1.09–5.81
Lignite	13		10.50–12.74	0.22–7.48	<0.01–0.878
		4 with AC (pre-primary PCD)	11.86–12.61	0.96–4.21	0.225–2.22
		3 with EA[2] + AC (pre-primary PCD)	12.29–12.77	1.04–2.49	0.287–0.640
		1 with EA	11.77	1.70	0.717
		10 with AC (post-primary PCD)	10.52–12.00	0.59–13.2	0.147–64.5

[1] Not tested.
[2] Enhancing agent.

As noted, the sponsor sample prioritization process indicated that an effort should be made to collect "paired" samples from full-scale demonstrations of mercury emission control technologies. These sample pairs included a baseline sample (collected when the system was running with standard conditions and no mercury emission control was imposed) and a test sample (collected during a mercury emission test). These samples were collected from the same location at a single site; however, the sample collection point and protocol varied between sites because of differences in the type of emission control and availability of sampling locations. Table 5-4 lists the paired sample sets, a brief description of the mercury control technology used, and fundamental characteristics of the samples. A total of eight paired sample sets were collected and evaluated in various release experiments in the project.

Table 5-2. Summary of FGD–SDA Samples and Fundamental Characterization Data

Coal Type	No. of FGD–SDA Samples	No. of FGD–SDA Samples from Hg Control	24-hour pH Range	LOI Range, %	Total Hg Concentration Range, µg/g
Lignite	3		12.50	0.95–12.5	<0.01–2.55
		1 with EA + ACI (pre-SDA)	12.54	1.12	0.332
Subbituminous	1		12.22	2.07	0.105

Table 5-3. Summary of Eastern Bituminous Wet FGD Material Samples and Fundamental Characterization Data

SO_2 Control	No. of FGD Samples by Sample Type	24-hour pH Range	LOI Range, %	Total Hg Concentration Range, µg/g
Wet Mg-Enhanced Lime	2 FGD gypsum	7.75–7.88	1.22–1.92	0.032–0.044
Wet Limestone – Forced Oxidation	3 FGD gypsum	7.72–7.95	1.60–2.26	0.043–0.103
Wet Limestone – Nonoxidized	3 FGD filtercake	7.70–7.88	4.20–6.19	0.162–0.305
Wet Limestone – Nonoxidized	3 Fixated FGD	10.50–12.43	3.11–4.17	0.136–0.249

5.3.2 Sample Handling

Fly ash as produced from full-scale coal-based systems is generally considered to be homogeneous on the macroscale and heterogeneous on the microscale. This means that a sample of fly ash collected using appropriate compositing techniques will usually provide a high-quality, representative sample on which the bulk characteristics can be determined with good accuracy. On the microscale, however, the individual particles will not necessarily reflect the bulk characteristics of the material because of the manner in which the individual particles are formed during the combustion process. FGD materials are generally considered homogeneous on both the macro- and microscale.

For this project, the fly ash samples frequently were visually nonhomogeneous because of the presence of AC. Research staff frequently noted the presence of carbon as discreet particles within the fly ash sample matrix and also noted that the particle sizes of carbon present could be easily distinguished visually. On agitation of the glass sample containers, the segregation of fly ash and carbon was also frequently noted. This obvious nonhomogeneity required increased care in obtaining analytical subsets of the bulk samples. Several approaches were used to ensure representative samples were used. Bulk samples were gently agitated, and the sample was

Table 5-4. Paired Samples and Fundamental Characterization Data

ID Nos.	Sample Type	24-hour pH	LOI, %	Hg, µg/g
02-070	Fly ash	8.50	5.87	0.194
02-069	Fly ash + AC (post-primary PCD)	8.43	12.60	0.742
02-072	Fly ash	8.83	5.29	0.163
02-071	Fly ash + AC (post-primary PCD)	8.63	17.22	0.975
03-061	Fly ash	12.56	1.04	0.578
03-060	Fly ash + AC (pre-primary PCD)	11.90	2.38	1.86
04-035	Fly ash	12.74	2.46	0.159
04-036	Fly ash + EA + AC (pre-primary PCD)	12.77	2.33	0.287
05-001	Fly ash	12.51	0.90	<0.01
05-003	Fly ash + EA + ACI (pre-SDA)	12.29	1.04	0.565
05-005	Fly ash	11.57	1.29	0.431
05-017	Fly ash + EA	11.77	1.70	0.717
05-038	Fly ash	11.73	0.22	0.104
05-013	Fly ash + AC (post-primary PCD)	11.33	13.2	39.0
05-023	Fly ash + AC (pre-primary PCD)	12.00	3.84	12.7
05-024	Fly ash + AC (post-primary PCD)	11.41	9.45	35.9
05-025	Fly ash + AC (pre-primary PCD)	11.99	3.19	12.6
05-040	Fly ash + AC (post-primary PCD)	11.36	9.68	44.5
06-001	Fly ash + AC (post-primary PCD)	11.37	11.6	64.5
05-002	Fly ash + FGD–SDA	12.50	0.95	<0.01
05-004	Fly ash + FGD–SDA + EA + AC (pre-SDA)	12.54	1.12	0.332

observed to get the carbon distributed representatively through the bulk sample container. For the total mercury and ATE analyses, duplicate samples were used, and in some cases where the carbon content was especially problematic or the mercury content very low or very high, up to eight replicates were run. For the elevated-temperature release experiments, where only very small samples could be introduced into the experimental apparatus, samples with large carbon particles present were ground to produce a more homogeneous sample.

FGD material samples with water standing were dewatered for use in release experiments. This was done by pouring of the majority of water and filtering through a Büchner funnel or pressing the solid, depending on the experiment the sample was to be used in.

5.3.3 Sample Descriptions

The samples selected for evaluation in this project were obtained from samples collected from bench-, pilot-, and full-scale combustion systems and from demonstration of multiple mercury emission control systems and types. In order to adequately describe the samples for the purpose of the discussion of the data and to draw conclusions while maintaining confidentiality of sample identity, the following sample descriptors were developed and are used throughout this report.

Fly ash – Fly ash sample that was generated under operating conditions that were not influenced by a mercury control technology. These samples may be generated in systems with NO_x, SO_x, or other emission controls, and the specific system type is noted in Appendix F.

Fly ash + AC (pre-primary PCD) – Fly ash that has AC present as a result of ACI for mercury emission control. The AC was injected before the primary PCD.

Fly ash + EA (EA on coal) + AC (pre-primary PCD) – Fly ash that has AC present as a result of ACI for mercury emission control and has another chemical that was also introduced to enhance mercury uptake by the fly ash + AC. The EA was added to the coal. The AC was injected before the primary PCD.

Fly ash + EA (EA on coal) – Fly ash that has a chemical that was introduced to enhance mercury uptake by the fly ash or to change the oxidation state of the mercury present to enhance mercury uptake in an existing FGD system. The EA was added to the coal.

Fly ash + AC (post-primary PCD) – Fly ash that has AC present as a result of ACI for mercury emission control. The AC was injected after the primary PCD and the fly ash + AC were collected in a secondary PCD. This type of sample would include samples produced in a TOXECON™ system. In this type of system, a portion of the fly ash would have already been removed by the primary PCD, so only a fraction of the total fly ash generated would be mixed with AC.

FGD–SDA – An FGD material from a SDA configuration. FGD–SDA uses a calcium-based sorbent (lime or hydrated lime) to remove SO_2 from the flue gas. Calcium sulfite and calcium sulfate are the primary products of the reaction of the sorbent and the SO_2. In the United States (and in all project samples), fly ash is usually incorporated into the SDA system, so the solid by-product contains a mixture of the calcium sulfite and sulfate and fly ash.

FGD–SDA + EA (EA on coal) + AC (pre-primary PCD) – An FGD material from a SDA configuration where EA was added to the coal and AC was injected ahead of the SDA.

Wet FGD material – Any material producted from wet flue gas scrubbing utilizing a calcium-based sorbent.

FGD gypsum – FGD material from a wet system employing forced oxidation, producing gypsum (ca $SO_4 \cdot 2H_2O$). The sorbent may be limestone or magnesium-enhanced lime, also called dolomitic lime.

Wet FGD slurry – Material produced in a wet FGD system that uses inhibited oxidation or natural oxidation. It is typically a wet, thixotropic material containing both calcium sulfite and calcium sulfate. It may also be referred to as “nonoxidized” FGD material.

FGD filtercake – The resulting material after filtration of wet FGD slurry.

Fixated wet FGD material – Wet FGD material that has a stabilizing agent (typically fly ash) added to it to facilitate handling.

5.4 Chemical and Physical Characterization

The bulk chemical and physical characterization task focused on determining trace element composition, moisture content, LOI, pH, and carbon forms. Total major and minor constituents were also determined on a limited number of samples.

5.4.1 Total Mercury and ATEs

In order to adequately determine the release of mercury and other ATEs from fly ash and FGD materials, the total concentrations of these elements needed to be determined. The total trace element results for all samples evaluated are included in Appendix G. The ranges for all samples (fly ash with and without mercury control and all FGD materials) evaluated are as follows:

- <1–492 µg/g arsenic
- <1–8.59 µg/g cadmium
- 2.90–160 µg/g chromium
- <3–272 µg/g lead
- <0.01–120 µg/g mercury
- <1–277 µg/g nickel
- <2–457 µg/g selenium

A more detailed summary of the ranges of total trace elemental concentrations in the fly ash, FGD–SDA samples, and wet FGD material samples selected for this project are shown in Tables 5-5, 5-6, and 5-7, respectively.

Table 5-5. Range of Total Trace Elements in Fly Ash Samples, µg/g

Element	Fly Ash	Fly Ash + AC (pre-primary PCD)	Fly Ash + EA + AC (pre-primary PCD)	Fly Ash + EA	Fly Ash + AC (post-primary PCD)
As	5.90–492	19.4–73.9	26.8–46.3	NT[a]	35.3–444
Cd	<1–8.59	<1–1.97	<1–0.942	NT	<1–3.38
Cr	43.4–160	39.1–111	44.8–49.1	NT	35.5–115
Pb	17.4–272	30.3–87.1	18.3–25.9	NT	49.0–85.3
Hg	<0.01–1.22	0.225–12.7	0.287–0.640	0.717	0.147–120
Ni	17.2–277	18.6–67.6	23.1–41.5	NT	15.4–94.5
Se	3.97–44.7	13.4–69.4	9.86–18.3	NT	19.6–457

[a] Not tested.

Table 5-6. Range of Total Trace Elements in FGD–SDA Samples, µg/g

Element	FGD–SDA	FGD–SDA + EA + AC (pre-primary PCD)
As	14.7–22.6	21.8
Cd	<1	<1
Cr	26.3–42.8	37.3
Pb	18.6–37.0	20.9
Hg	<0.01–2.55	0.332
Ni	12.9–29.7	25.3
Se	9.15–9.92	9.79

Table 5-7. Range of Total Trace Elements in Wet FGD Material Samples, µg/g

Element	FGD Gypsum	Wet FGD Slurry	Wet FGD Filtercake	Fixated Wet FGD Material
As	<1–1.65	<1	<1	53.4–53.8
Cd	<1–1.89	<1	<1	1.08–1.24
Cr	2.90–4.13	6.61	10.2–10.4	51.6–53.6
Pb	<3	<3	<3–4.40	80.3–86.7
Hg	0.032–0.103	<0.1–0.196	0.162–0.305	0.136–0.249
Ni	<1–6.83	2.87	3.50–3.98	87.2–98.7
Se	<2–2.68	3.01	<2–2.64	3.71–4.46

For all elements except mercury and selenium, the fly ash samples from mercury control tests were within the ranges of fly ash samples without mercury control (Table 5-5). The concentrations of arsenic, cadmium, chromium, lead, and nickel measured in fly ash (without mercury control) selected for this project are also consistent with the concentrations of these elements measured in fly ash samples from previous EERC projects (Hassett and Heebink, 2002; Pflughoeft-Hassett et al., 2004, 1996).

Total mercury concentrations in the fly ash-based samples ranged as follows:

- Fly ash (without mercury control) – <0.01–0.878 µg/g
- Fly ash + AC (pre-primary PCD collection) – 0.225–12.7 µg/g
- Fly ash + AC (post-primary PCD collection) – 0.147–120 µg/g

In all cases where ACI was used, the total mercury concentration range was higher than that noted for fly ash samples, providing an indication of increased mercury capture on the fly ash + AC samples. The highest individual mercury concentrations were noted for the fly ash + AC (post-primary PCD) category of fly ash samples.

Total selenium concentrations in the fly ash-based samples ranged as follows:

- Fly ash (without mercury control) – 3.97–44.7 µg/g
- Fly ash + AC (pre-primary PCD collection) – 9.86–69.4 µg/g
- Fly ash + AC (post-primary PCD collection) – 19.6–457 µg/g

Similar to the mercury data, the total selenium concentration range was higher for the fly ash + AC samples than the fly ash. Again, the highest individual selenium concentrations were noted for the fly ash + AC (post-primary PCD) category of fly ash samples.

Total concentrations of ATEs were determined in the FGD–SDA samples using the same analytical techniques as those used for the fly ash samples. Only a limited number of FGD–SDA samples were obtained for use in this project. The data in Table 5-6 represent two samples of FGD–SDA and one sample of FGD–SDA + EA + AC. The FGD–SDA + EA + AC had total trace elemental concentrations that fell within the range noted for the FGD–SDA samples evaluated.

The total mercury concentration in FGD material samples was determined by DMA or EPA Method 7471. Total concentrations of ATEs were determined in the FGD material samples using the same analytical techniques as those used for the fly ash samples. A limited number of FGD materials from wet systems were collected for evaluation in this project. None of the wet FGD materials were collected from systems with mercury emission controls in use. Total mercury and ATE content ranges for each wet FGD material type are noted in Table 5-7. The ATE concentrations are generally similar for the wet FGD filtercake, slurry, and gypsum; however, several of the ATE concentrations are elevated in the fixated wet FGD material, most notably the arsenic, chromium, lead, and nickel. It was hypothesized that the fly ash added to the wet FGD material as a stabilizer resulted in these elevated ATE concentrations. No associated fly ash sample was available to confirm or refute this hypothesis.

One FGD gypsum sample set was collected from a single plant with an SCR. One sample was collected when the SCR was on, and the second sample was collected when the SCR was off. However, these samples were not considered "paired" as the collection dates were 3 months apart, and it could not be ascertained if the coal source and other operating conditions were consistent between sample dates. The information for these samples is noted in Table 5-8.

Liquid from FGD samples was also analyzed for total trace elemental concentrations. These included FGD gypsum filtrate and lab-dewatered FGD liquor samples from FGD filtercake and FGD slurry. The ranges of total trace elemental concentrations are given in Table 5-9. All results are in Appendix H.

Table 5-8. Total Trace Elements in FGD Gypsum Samples Comparing SCR On and SCR Off, µg/g

Element	FGD Gypsum SCR On	FGD Gypsum SCR Off
As	1.65	<2
Cd	<1	<1
Cr	3.39	3.95
Pb	<3	<3
Hg	0.043	0.103
Ni	6.83	6.81
Se	2.56	2.68

Table 5-9. Range of Total Trace Elements in FGD Liquor Samples, µg/L

Element	FGD Gypsum Filtrate	Wet FGD Slurry Liquor	Wet FGD Filtercake Liquor
As	82.8	114	33.1–121
Cd	4.79	0.790	2.09–4.34
Cr	9.90	10.1	2.90–5.70
Pb	<2	<2	<2
Hg	<0.01	<0.15	<0.15
Ni	338	258	88.8–333
Se	684	1140	154–759
pH	5.20	6.75	5.92–7.56

The total ATE concentrations were determined in these liquid samples in order to better understand the distribution of ATEs in FGD systems. Mercury was undetected in all FGD liquid samples as expected based on previous work (Hassett and Moe, 1997). Arsenic, nickel, and selenium were present in the liquid samples in relatively high concentrations. Since no mercury emission controls were in use while these samples were collected, it was not possible to determine if the ATE concentrations for FGD liquids will be impacted by mercury emission controls.

5.4.1.1 Paired Samples

Several sets of "paired" fly ash samples and one set of FGD–SDA samples were collected and evaluated in this effort; the sample pairs and total mercury content are presented in Table 5-4. Total ATE content is noted for these paired fly ash samples in Table 5-10.

5.4.1.2 Total Mercury and ATE Discussion

Fly ash selected for this project generally contained low concentrations of mercury (see Table 5-5), and total mercury concentrations were consistent with those reported elsewhere (Energy & Environmental Research Center, 2004; Energy & Environmental Research Center, 2005; Sanchez et al., 2006). Total mercury content of fly ash + AC, regardless of ACI point, had higher ranges of mercury. Paired fly ash samples (Tables 5-4 and 5-10) clearly indicated that injection of AC does capture mercury, which results in elevated total mercury contents in the fly ash + AC samples as compared to the baseline fly ash samples. Other ATEs measured in all fly ash samples were generally present at similar concentrations regardless of whether the samples were collected with or without mercury emission controls in place.

For all FGD–SDA samples, the total concentrations of individual ATEs, including mercury, were similar for those with and without mercury emission controls in place.

The wet FGD material samples generally had lower total ATE concentrations than the fly ash and FGD–SDA samples, with the exception of the fixated wet FGD material. The concentrations of most ATEs were higher in those samples than the other wet FGD materials, likely because of added fly ash that was used for the fixation process.

Table 5-10. Paired Samples and Total ATE Content, µg/g

ID Nos.	Sample Type	As	Cd	Cr	Pb	Hg	Ni	Se
03-061	Fly ash	43.5	1.72	67.6	59.5	0.578	93.9	44.5
03-060	Fly ash + AC (pre-primary PCD)	19.4	1.87	76.7	82.2	1.86	67.6	34.2
04-035	Fly ash	36.0	<1	55.4	21.9	0.159	17.2	9.78
04-036	Fly ash + EA + AC (pre-primary PCD)	44.9	<1	48.8	18.7	0.287	23.5	10.4
05-001	Fly ash	24.4	<1	45.1	17.4	<0.01	30.3	8.84
05-003	Fly ash + EA + AC (pre-SDA)	28.6	<1	45.5	21.2	0.565	25.7	11.5
05-038	Fly ash	43.4	<1	43.4	90.1	0.104	21.1	23.4
05-013	Fly ash + AC (post-primary PCD)	38.6	<1	36.5	73.2	39.0	15.4	60.3
05-023	Fly ash + AC (post-primary PCD: high fly ash)	48.3	<1	42.6	87.1	12.7	18.6	22.5
05-024	Fly ash + AC (post-primary PCD)	42.5	<1	35.5	82.2	35.9	17.6	87.3
05-025	Fly ash + AC (post-primary PCD: high fly ash)	46.8	<1	39.1	84.7	12.6	20.4	30.1
05-040	Fly ash + AC (post-primary PCD)	38.4	<1	42.2	74.5	44.5	22.0	42.2
06-001	Fly ash + AC (post-primary PCD)	35.5	<1	39.8	72.0	64.5	20.6	38.9
05-002	Fly ash + FGD–SDA	22.6	<1	42.8	18.6	<0.01	29.7	9.15
05-004	Fly ash + FGD–SDA + EA + AC (pre-SDA)	21.8	<1	37.3	20.9	0.332	25.3	9.79

Review of the total ATE concentrations for the paired samples indicated that most ATE concentrations remained consistent between paired samples. Mercury was the only ATE that was consistently elevated in the test samples as compared to the baseline sample. A significant increase was noted in the total selenium concentration in fly ash + AC (post-primary PCD) over the baseline and fly ash + AC (pre-primary PCD) in one sample set.

5.4.2 Total Bulk Chemical Composition

A limited number of samples were analyzed for total bulk chemical composition early in the project. The major and minor elements determined were silicon, aluminum, iron, calcium, magnesium, sodium, potassium, barium, manganese, titanium, phosphorus, strontium, and sulfur. The results of these analyses, reported as oxides as is convention with fly ash, are included in Appendix I. The data are summarized in Table 5-11, which also includes the ASTM C618 specification for fly ash for use as a mineral admixture in concrete.

Table 5-11. Summary of Total Bulk Chemical Composition Compared to ASTM C618 Specifications, %

Parameter	Fly Ash	Fly Ash + AC (pre-primary PCD)	FGD–SDA	FGD Gypsum	ASTM C618 Class F Fly Ash Specifications	ASTM C618 Class C Fly Ash Specifications
SiO_2 + Al_2O_3 + Fe_2O_3	46.76–92.25	53.57–63.29	52.02	0.47	70 min.	50 min.
SO_3	0.06–4.73	1.43–5.89	13.60	51.14	5.0 max.	5.0 max.
Moisture Content	0.01–0.14	0.05–0.23	1.01	17.37	3.0 max.	3.0 max.
LOI	0.32–4.25	0.91–4.22	1.49	12.68	6.0 max.	6.0 max.

The sample set included five samples of bituminous fly ash, one sample of lignite fly ash, four samples of lignite fly ash + AC (pre-primary PCD), one subbituminous fly ash, and one subbituminous fly ash +AC (pre-primary PCD). The sample set also included one sample of FGD gypsum and one sample of FGD–SDA. Initially, it was proposed that these analyses would be valuable in data interpretation because they would provide information on the potential utilization options (mineral admixture for concrete, raw feed for cement kiln, cementitious applications, etc.) for the samples collected. The fly ash data shown in Table 5-11 indicated that the limited samples evaluated were typical of samples used as mineral admixtures for concrete, and even the samples with added AC met the specification for LOI in ASTM C618. It was determined that the LOI and chemistry of fly ash samples were not adequate to provide an indication of utilization performance, so this task was not providing the type of information anticipated. Further, it became apparent that many of the samples selected for release experiments in this project were not collected from locations typical of "as managed" samples that are usually evaluated for utilization potential. A decision was made with agreement from project sponsors to discontinue this subtask for those reasons.

5.4.3 LOI and Moisture Content

The moisture content and LOI of solid CCBs were determined. Ranges of moisture content and LOI are presented in Tables 5-12 through 5-14. Moisture content and LOI results for all samples evaluated are included in Appendix J. As noted in Table 5-12, fly ash from mercury control technology testing had LOI values ranging from 0.59% to 24.4%. Fly ash without mercury control had LOI ranging from 0.22% to 21.2%.

Table 5-12. Range of Moisture Content and LOI in Fly Ash Samples, %

Parameter	Fly Ash	Fly Ash + AC (pre-primary PCD)	Fly Ash + EA + AC (pre-primary PCD)	Fly Ash + EA	Fly Ash + AC (post-primary PCD)
Moisture Content	0.02–1.00	0.00–1.07	0.05–0.85	0.05	0.10–5.56
LOI	0.22–21.2	0.96–4.21	1.04–2.49	1.70	0.59–24.4

Table 5-13. Range of Moisture Content and LOI in FGD–SDA Samples, %

Parameter	FGD–SDA	FGD–SDA + EA + AC (pre-primary PCD)
Moisture Content	1.08–3.00	0.75
LOI	0.95–12.5	1.12

Table 5-14. Range of Moisture Content and LOI in FGD Material Solid Samples, %

FGD Material Type	Moisture Content	LOI
FGD Gypsum	21.6–26.7	1.22–2.26
Wet FGD Slurry	56.8–65.7	4.37–6.38
Wet FGD Filtercake	28.6–43.3	4.20–6.19
Fixated Wet FGD	26.6–31.9	3.11–4.17

Moisture content and LOI for the paired fly ash and FGD–SDA samples selected for this project are shown in Table 5-15. LOI increased for all but one sample pair with the injection of AC. The largest increases in moisture content and LOI from the fly ash to the paired samples were noted in the fly ash + ACI (post-primary PCD) samples. The fly ash + ACI (post-primary PCD: high ash) samples in the largest paired sample set showed increased LOI values over the fly ash but were minimal compared to the other fly ash + ACI (post-primary PCD) samples within the sample set. The fly ash and FGD–SDA samples containing an enhancing agent on the coal in the mercury control technology testing generally showed the least change in moisture content and LOI.

Moisture content and LOI data for FGD–SDA samples selected for this project are noted in Table 5-13. For FGD–SDA samples, the LOI is likely dependent on the LOI of the fly ash that is incorporated into the FGD–SDA final by-product material. Most frequently, fly ash incorporated into FGD–SDA material is alkaline and provides some sorptive capacity for SO_2 capture. It is also generally true that alkaline fly ash tends to have lower LOI than nonalkaline fly ash; however, as noted in the data in Table 5-13, a relatively high LOI value of 12.5% was measured in one FGD–SDA sample. Since no paired fly ash sample was available for testing, it is not known if this high LOI value is due to carbon present in the incorporated fly ash or is due to dehydration of hydrated phases present in FGD–SDA. FGD–SDA usually comprises relatively high percentages of calcium sulfite hemihydrate ($CaSO_3 \cdot ½H_2O$, or hannebachite), which will lose water of hydration as well as SO_2 at temperatures above 600°C. Since LOI determinations are carried out at 750°C, the values reported will be indicative of these losses as well as any carbon that may be in the sample.

Table 5-14 shows the data on moisture content and LOI for a variety of wet FGD materials selected for use in this project. The moisture content values reflect the water typically present in wet FGD materials. With the exception of FGD gypsum, the types of wet FGD materials noted in Table 5-14 comprise calcium sulfite and sulfate phases and, prior to filtering or fixation, are a thixotropic material with high water content and problematic handling properties. Even after

Table 5-15. Paired Samples Moisture Content and LOI, %

ID Nos.	Sample Type	Moisture Content	LOI
02-070	Fly ash	0.20	5.87
02-069	Fly ash + AC (post-primary PCD)	0.78	12.6
02-072	Fly ash	0.17	5.29
02-071	Fly ash + AC (post-primary PCD)	1.18	17.2
03-061	Fly ash	0.17	1.04
03-060	Fly ash + AC (pre-primary PCD)	0.17	2.38
04-035	Fly ash	0.14	2.46
04-036	Fly ash + EA + AC (pre-primary PCD)	0.06	2.33
05-001	Fly ash	1.00	0.90
05-003	Fly ash + EA + AC (pre-SDA)	0.85	1.04
05-005	Fly ash	0.02	1.29
05-017	Fly ash + EA	0.05	1.70
05-038	Fly ash	0.04	0.22
05-013	Fly ash + AC (post-primary PCD)	0.29	13.2
05-023	Fly ash + AC (post-primary PCD: high ash)	0.13	3.84
05-024	Fly ash + AC (post-primary PCD)	0.23	9.45
05-025	Fly ash + AC (post-primary PCD: high ash)	0.07	3.19
05-040	Fly ash + AC (post-primary PCD)	0.10	9.68
06-001	Fly ash + AC (post-primary PCD)	0.39	11.6
05-002	FGD–SDA	1.08	0.95
05-004	FGD–SDA + EA + AC (pre-SDA)	0.75	1.12

filtering or fixation, a significant level of moisture is maintained. The LOI is likely a result of loss of water of hydration or, in the case of the fixated FGD material, unburned carbon in the fly ash used as the fixation agent may contribute to the LOI.

FGD gypsum (calcium sulfate·$2H_2O$), generally 95+% pure, exhibits lower moisture content because it is more readily separated from the water phase because of its crystalline form. The LOI for FGD gypsum is likely due to loss of water.

5.4.3.1 pH

The pH of all samples of sufficient quantity was determined in distilled water with a 10–15-minute equilibration time. Previous experience with fly ash and pH measurement raised questions about the most appropriate method to determine pH of CCBs. Since the pH of a material can influence the leaching profile and may impact the performance in certain utilization scenarios, including bulk placement in engineered fills, it is important to determine the pH as accurately as possible, even though the pH may change with time. It was decided to perform additional pH measurements including 24-hour (distilled water) pH and 10–15-minute pH using

1 M KCl (potassium chloride). All pH data collected on project samples are included in Appendix K.

Table 5-16 separates the pH values for all fly ash samples by coal type and pH test. Eastern bituminous fly ash samples exhibited a wide range of pH values in all tests. This range was greater in the fly ash samples without AC than with AC. The South American and western bituminous fly ash sample pH ranges were narrower and were closer to those of subbituminous and lignite fly ash samples than eastern bituminous fly ash samples. All fly ash + ACI (pre-primary PCD) pH values, for the South American bituminous, subbituminous, and lignite samples in the project, were similar. The pH of all types of lignite fly ash samples were similar; however, the fly ash + AC (post-primary PCD) samples had pH values below 10 reported. The high-ash samples in the lignite fly ash + AC (post-primary PCD) exhibited the highest 24-hour pH values in that sample set. Overall, the difference between the 10–15-min and 24-hour pH tests is not significant but can be seen on a per-sample basis.

Some samples exhibited a near-neutral 10–15-minute pH, but after 24 hours of stirring, the pH increased to an alkaline value. During this equilibration time, the samples were stirred at 350 rpm. As stated above, numerous samples exhibited pH values that changed substantially after 24 hours. Table 5-17 shows the sample information for these samples and the associated LOI.

Table 5-16. Range of pH in Fly Ash Samples

Coal Type	pH Test	Fly Ash	Fly Ash + AC (pre-primary PCD)	Fly Ash + EA + AC (pre-primary PCD)	Fly Ash + EA	Fly Ash + AC (post-primary PCD)
Eastern Bituminous	10–15-min	3.76–12.56	NA	NA	NA	3.47–9.59
	24-hour	5.52–12.44	NA	NA	NA	3.99–9.20
	1 M KCl	4.42–12.72	NA	NA	NA	3.51–9.43
South American Bituminous	10–15-min	9.93–11.72	10.34–11.79	NA	NA	NA
	24-hour	9.13	NT	NA	NA	NA
	1 M KCl	10.66	NT	NA	NA	NA
Western Bituminous	10–15-min	11.52–13.00	NA	NA	NA	NA
	24-hour	10.38–12.65	NA	NA	NA	NA
	1 M KCl	11.40–12.83	NA	NA	NA	NA
Subbituminous	10–15-min	11.89–12.56	10.65–11.47	NA	NA	NA
	24-hour	12.27–12.56	10.95–11.90	NA	NA	NA
	1 M KCl	11.96–12.62	10.48–11.16	NA	NA	NA
Lignite	10–15-min	11.20–12.84	11.74–12.69	12.39–12.85	12.04–12.19	6.69–11.67
	24-hour	10.50–12.74	11.86–12.61	12.29–12.77	11.77	10.52–12.00
	1 M KCl	11.05–12.84	12.38–12.84	12.82	NT	9.42–11.73

Table 5-17. Fly Ash Samples Exhibiting a Greater-than-One-pH-Unit Change over a 24-hour Period

ID No.	Sample Type	Coal Type	10–15-min pH	24-hr pH	pH Change	LOI, %
05-040	Fly ash + AC (post-primary PCD)	Lignite	7.03	11.36	4.33	9.68
03-083	Fly ash	Eastern bituminous	4.75	9.00	4.25	1.20
06-001	Fly ash + AC (post-primary PCD)	Lignite	7.20	11.37	4.17	11.62
05-024	Fly ash + AC (post-primary PCD)	Lignite	7.43	11.41	3.98	9.45
03-004	Fly ash	Eastern bituminous	4.54	7.08	2.54	3.34
05-013	Fly ash + AC (post-primary PCD)	Lignite	9.00	11.33	2.33	13.24
03-006	Fly ash	Eastern bituminous	4.82	6.78	1.96	5.24
03-005	Fly ash	Eastern bituminous	4.45	5.88	1.43	3.60
03-007	Fly ash	Eastern bituminous	4.38	5.52	1.14	4.48
05-018	Fly ash	Eastern bituminous	7.42	8.49	1.07	3.01
04-006	Fly ash	Western bituminous	11.56	10.38	−1.18	1.42
02-076	Fly ash	South American bituminous	10.38	9.13	−1.25	21.06
02-072	Fly ash	Eastern bituminous	10.09	8.83	−1.26	5.29
02-070	Fly ash	Eastern bituminous	9.98	8.50	−1.48	5.87

The fly ash samples that exhibited an increase in pH from the 10–15-minute measurement to the 24-hour measurement were either bituminous or lignite samples, but the lignite samples all contained AC from injection after the primary PCD and an associated relatively high LOI. The 10–15-minute pH for the lignite fly ash + AC samples was 7 or higher, and the increase in pH at 24 hours ranged from 2.3 to 4.3 units. The bituminous fly ash samples had 10–15-minute pH values of ~4.4–7.4 and had LOI values of 1.2%–5.2%. Most of these samples exhibited a pH increase of ~1–2 units; however, the sample with the lowest LOI (1.2%) had an increase of over 4 units. For the lignite fly ash + AC samples, the reason for the increases noted was not evident but may be associated with the AC present, hydration reactions, or solubility of surface coatings or specific phases in the sample.

Four bituminous fly ash samples exhibited a decrease in pH from the 10–15-minute measurement to the 24-hour measurement. Solubility of specific phases or coatings or hydration reactions may also have an impact on these samples and cause changes to the pH. This decrease could also be due to uptake of CO_2 from the atmosphere.

These pH development data are interesting because pH is a primary factor in leachability. It has been shown that at pH values over 10.5, ettringite can and will form in fly ash samples. This is important because of the fact that ettringite can incorporate numerous oxyanions such as borate, chromate, and selenate into its structure, thus rendering them insoluble. It is important, especially with alkaline ash types, to know the true equilibrium pH in order to decide if LTL is necessary. LTL is always suggested at 18-hour and 30- and 60-day equilibration times in ash samples with equilibrium pH values above 10.5. The only exception to this is if mercury is the only analyte. Mercury does not appear to be affected by ettringite formation. These data suggest that pH measurements for CCBs should include an equilibration time of at least 24 hours.

The pH values reported for all FGD–SDA samples (Table 5-18) fell within a narrow range regardless of the presence of AC. The pH for these samples is primarily a result of the presence of unreacted sorbent, which is present as calcium hydroxide. Calcium hydroxide has a pH of 12.4, which is very similar to the pH values measured in the FGD–SDA samples. The presence of alkaline fly ash may also influence the pH of FGD–SDA samples, but the lack of a separate fly ash sample from these systems does not allow a discussion of the impact of the fly ash on pH. The pH of the FGD–SDA +EA + AC samples is slightly elevated from the FGD–SDA samples. It was hypothesized that the increased pH, while minimal, could be associated with the presence of AC or the EA, which was unidentified.

The ranges of pH values of FGD materials and liquids are shown in Tables 5-19 and 5-20 and Appendices H and K. With the exception of the fixated wet FGD materials, the wet FGD materials and liquids all exhibited acidic to near-neutral pH. This is due to either complete reaction of the alkaline scrubbing material or coating of the alkaline phase with neutral calcium sulfate. The fixated wet FGD material likely exhibits an alkaline pH because of the presence of fly ash used to fixate the material.

Table 5-18. Range of pH in FGD–SDA Samples

Coal Type	pH Test	FGD–SDA	FGD–SDA + EA + AC
Subbituminous	10–15-min	12.34–12.41	NA
	24-hour	12.22	NA
	1 M KCl	12.53	NA
Lignite	10–15-min	12.18–12.85	12.51–13.06
	24-hour	12.50	12.54
	1 M KCl	NT	NT

Table 5-19. Ranges of pH in Wet FGD Material Sample

	FGD Gypsum	Wet FGD Slurry	Wet FGD Filtercake	Fixated Wet FGD
10–15-min pH	8.07–8.83	7.84–8.95	7.47–8.18	10.87–12.75
24-hour pH	7.72–7.95	8.75	7.70–7.88	10.50–12.43
1 M KCl pH	NT	NT	NT	11.75–12.30

Table 5-20. Ranges of pH in Liquid from Wet FGD Material Samples

	FGD Gypsum Filtrate	FGD Slurry Liquor	FGD Filtercake Liquor	FGD Filtrate
10–15-min pH	5.40–5.49	6.73–6.78	6.53–7.36	7.20–7.26
24-hour pH	5.20–5.25	7.38	5.92–7.56	8.13–8.17

5.4.4 Carbon Forms

It is well known that unburned carbon associated with coal fly ash takes on many different morphological forms, three major forms of which are generally recognized. These morphologically different carbon forms are inertinite, isotropic coke, and anisotropic coke. Each of these forms has distinct and predictable physical properties. Isotropic and anisotropic coke have gone through the combustion process and undergone considerable changes including melting and reaction with oxygen, while inertinite appears to be relatively unaffected by the combustion process. Isotropic cokes represent extensively reacted, nongraphitizable carbon particles, and anisotropic cokes represent extensively reacted, more highly aligned carbon particles (Maroto-Valer et al., 1999a). In a study of carbon forms associated with Class F fly ash, it was found that inertinites exhibit the lowest surface area (15–25 m^2/g), isotropic coke particles presented intermediate surface areas (25–35 m^2/g), and anisotropic coke exhibited the highest surface areas (35–60 m^2/g) (Maroto-Valer et al., 1999b). Therefore, inertinites represent low-density, low-surface-area particles; isotropic cokes represent intermediate-density, intermediate-surface-area particles; and anisotropic cokes represent high-density, high-surface-area particles. Studies on Class C fly ashes, generally derived from subbituminous and lignite coals, have shown much higher surface areas (200–400 m^2/g) (Maroto-Valer et al., 1999b), indicating that the properties of fly ashes are not only dependent on petrographic composition, but also on the rank of coal from which they are derived (Maroto-Valer et al., 1999b). Probably, in part, due to the differences in surface area, the adsorption of mercury has shown the same series with anisotropic coke > isotropic coke > inertinite.

A limited number of fly ash samples were analyzed to determine carbon forms present (Appendix L). A summary of the data collected is shown in Table 5-21, including the types of fly ash samples evaluated, the identified dominant carbon forms, and the mercury content of the samples.

As indicated by the data in Table 5-21, fly ash samples without any AC present had a broad range of LOI, which generally reflects the amount of unburned carbon present. While other chemical changes can contribute to LOI, these are usually small contributions. The results

Table 5-21. Number of Samples per Carbon Form with Total Hg and LOI Ranges

	Fly Ash			Fly Ash + AC (Pre-Primary PCD)			Fly Ash + AC (Post-Primary PCD)		
Dominant Carbon Form	No. Samples	Hg Range, µg/g	LOI Range, %	No. Samples	Hg Range, µg/g	LOI range, %	No. Samples	Hg Range, µg/g	LOI Range, %
Anisotropic Coke	2	0.607–0.785	2.54–21.2	2	0.289–1.86	0.97–2.47	2	55.6–120	22.2–24.4
Isotropic Coke	2	0.440–0.578	1.00–7.48	1	1.09	2.84	0	NA	NA
Inertinite	1	0.097	3.20–3.48	2	0.225–2.22	0.96–4.21	0	NA	NA
Vitrinite	4	<0.01–0.662	0.24–4.54	0	NA	NA	0	NA	NA
Unburned Carbon	5	0.017–0.197	1.20–12.7	1	0.490	1.26–1.29	0	NA	NA

indicated that unburned carbon was the dominant carbon form in most of these samples, with the second most prominent form of carbon present being vitrinite, another relatively low-sorbing carbon form. The fly ash samples from systems without AC addition also contained the lowest concentrations of mercury, and those with unburned carbon, vitrinite, and inertinite as the dominant carbon form generally had the lowest mercury content within that sample's set.

Very limited samples of fly ash with AC (fly ash + AC [pre-primary PCD]) and fly ash + AC [post-primary PCD]) were available for analyses; however, the data indicate that these samples contain more reactive carbon forms. The two samples of fly ash + AC (post-primary PCD) evaluated both had anisotropic coke as the dominant carbon form. The LOI of these samples was very high as was the mercury content, which is consistent with the presence of a high-sorbing carbon form. For the fly ash + AC (pre-primary PCD) samples, three of six samples evaluated had either anisotropic or isotropic coke as the dominant carbon form. The LOI and mercury contents of these samples were similar to the four samples of fly ash without mercury control that had anisotropic and isotropic carbon as the dominant carbon forms.

The carbon form data verify that the presence of high-sorbing carbon forms can be an indicator of elevated mercury in fly ash samples and that AC contains these high-sorbing carbon forms.

5.5 Laboratory Evaluation of ATE Releases

5.5.1 Direct Leaching

Leaching was performed using multiple tests. As already noted, the methods were TCLP (EPA Method 1311, 1992), SGLP, and LTL with 30- and 60-day equilibration periods. Mercury and other ATEs were determined on leachates as the sample quantity allowed. Complete leachate data are reported in Appendix M. Summaries of leachate data are shown by sample type in Tables 5-22 through 5-24.

Table 5-22. Ranges of Leachate Results for Fly Ash, µg/L

Element	Fly Ash	Fly Ash + AC (pre-primary PCD)	Fly Ash + EA + AC (pre-primary PCD)	Fly Ash + EA	Fly Ash + AC (post-primary PCD)
As	<2–336	<2–16.3	<2–15.2	46.3–95.9	8.1–842
Cd	<0.2–8.30	<0.2–1.49	<0.2–0.39	<0.3–2.68	0.85–2.46
Cr	1.40–277	3.60–560	<2–134	182–211	17.3–680
Pb	<0.001–8.50	<0.001–3.00	<0.001–3.00	<2	<2
Hg	<0.01–0.325	<0.01–0.068	<0.01–0.061	<0.01–0.02	<0.01–0.07
Ni	<2–80.6	<2–23.1	<2–25.2	<2–2.8	<2–23.4
Se	<2–514	<2–147	<2–47.2	<4–97.0	45.2–8620
pH	3.54–12.81	3.80–12.60	12.21–12.61	11.69–12.01	3.79–11.82

Table 5-23. Ranges Leachate Results for FGD–SDA, µg/L

Element	FGD–SDA	FGD–SDA + EA + AC (pre-primary PCD)
As	2.1–3.5	3.6–4.3
Cd	<0.2–0.59	<0.2–0.2
Cr	34.6–223	21.8–87.7
Pb	<2	<2
Hg	<0.01–0.095	<0.01–0.012
Ni	<2–39.1	<2–29.3
Se	11.3–65.8	12.0–24.3
pH	11.41–12.47	12.41–12.60

Table 5-24. Ranges of Leachate Results for Wet FGD Material, µg/L

Element	FGD Gypsum	Wet FGD Slurry	Wet FGD Filtercake	Fixated Wet FGD
As	<4	<4	<2–3.7	<2–24.0
Cd	<0.2–0.46	<0.3	<0.2–0.830	0.30–0.66
Cr	<2	<1	<2	2.2–4.7
Pb	<2	<0.001	<2	<2–14.3
Hg	<0.01	0.047	<0.01–0.476	<0.01–0.289
Ni	<2–28.4	15.0	6.10–32.1	<2–4.00
Se	2.70–18.7	65.0	41.0–71.2	<2–3.40
pH	7.42–8.17	8.02	7.57–8.39	11.31–12.34

A leaching topical report was published in August 2005 and can be found in Appendix N. Leaching experiments continued after the leaching topical report was published, but the added data were consistent with those presented in the topical report and supported the observations made. The results for each element included in the study are presented and discussed in detail in the following sections.

5.5.1.1 Mercury

Mercury leachate results for fly ash, FGD–SDA, and FGD material samples are reported on separately. Total mercury concentrations discussed throughout the section are included in Appendix G.

The ranges of mercury leachate results for fly ash are reported by leaching test in Table 5-25. Table 5-26 shows that data separated by coal type. Figure 5-1 shows the 18-hour SGLP mercury leaching data for fly ash samples plotted against the total mercury content of the sample. Figure 5-2 shows the 18-hour SGLP mercury leaching data for fly ash + AC and/or EA samples plotted against the total mercury content of the sample.

For fly ash and fly ash + AC and/or EA, mercury is not readily leachable. Most samples have a leachate concentration below the 0.01 µg/L analytical method reporting limit. All fly ash sample leachates had mercury concentrations below the 2.0-µg/L primary drinking water (PDW) limit. The graphical representations of the mercury leachate data for fly ash and fly ash + AC and/or EA samples, as shown in Figures 5-1 and 5-2, also indicated that total mercury content does not correlate with leachable mercury. This is true for all leaching methods used in this project. The leachability of mercury from fly ash is not expected to impact current fly ash management practices.

Review of the total mercury content and leachate concentrations for the paired fly ash samples indicated that the total mercury concentration increased with the introduction of AC (with or without an EA) regardless of the location where the AC was injected (see Tables 5-27–5-29). The total mercury concentrations of fly ash + AC collected from post-primary PCD locations showed the greatest increase over the concentrations measured in the baseline fly ash samples. The mercury leachate concentrations reported for the paired fly ash samples do not reflect the increased total mercury content, and the mercury leachate concentrations are similar for all fly ash samples within the paired sample set for all leaching procedures, time frames, and final leachate pH. Most fly ash samples, both the paired sample set and the overall project sample set, had mercury leachate results of <0.01, the analytical reporting limit of the method used. The total mercury content does not correlate with the mercury leachate concentrations.

Table 5-25. Ranges of Fly Ash Mercury Leachate Results by Leaching Test, µg/L

Test	Fly Ash	Fly Ash + AC (pre-primary PCD)	Fly Ash + EA + AC (pre-primary PCD)	Fly Ash + EA	Fly Ash + AC (post-primary PCD)
18-hour SGLP	<0.01–0.083	<0.01–0.064	<0.01–0.016	<0.01	<0.01–0.03
30-day LTL	<0.01–0.113	<0.01	<0.01–0.061	<0.01	<0.01
60-day LTL	<0.01–0.325	<0.01–0.068	<0.01–0.016	<0.01–0.02	<0.01–0.028
TCLP	<0.01–0.034	<0.01	NT	NT	<0.01–0.070

Table 5-26. Ranges of Fly Ash Mercury Leachate and Leachate pH Results by Coal Type and Leaching Test

Coal Type	Sample Type	TCLP Hg Leachate and pH	18-hour SGLP Hg Leachate and pH	30-day LTL Hg Leachate and pH	60-day LTL Hg Leachate and pH
Eastern Bituminous	Fly ash	<0.01–0.03 µg/L 3.54–4.97	<0.01–0.05 µg/L 4.71–12.67	<0.01–0.104 µg/L 9.38–11.49	<0.01–0.239 µg/L 5.55–11.36
Eastern Bituminous	Fly ash + AC (post-primary PCD)	<0.01–0.07 µg/L 3.79–4.76	<0.01–0.03 µg/L 4.00–9.89	NT	NT
South American Bituminous	Fly ash	<0.01–0.034 µg/L 3.89–4.11	<0.01–0.016 µg/L 11.18–11.68	NT	NT
South American Bituminous	Fly ash + AC (pre-primary PCD)	<0.01 µg/L 3.80–4.20	<0.01 µg/L 10.71–11.71	NT	NT
Western Bituminous	Fly ash	NT	<0.01–0.021 µg/L 11.59–12.81	0.035–0.076 µg/L 11.37–12.54	<0.01–0.087 µg/L 11.31–12.52
Sub-bituminous	Fly ash	NT	<0.01–0.023 µg/L 12.09–12.49	<0.01 µg/L 12.36–12.63	<0.01–0.325 µg/L 12.45–12.58
Sub-bituminous	Fly ash + AC (pre-primary PCD)	<0.01 µg/L 5.51–6.56	<0.01–0.064 µg/L 11.08–12.21	<0.01 µg/L 11.84–12.46	<0.01–0.068 µg/L 11.85–12.38
Lignite	Fly ash	NT	<0.01–0.083 µg/L 10.95–12.60	<0.01–0.113 µg/L 11.34–12.65	<0.01–0.124 µg/L 11.25–12.54
Lignite	Fly ash + AC (pre-primary PCD)	NT	<0.01 µg/L 12.60	<0.01 µg/L 12.34	<0.01 µg/L 12.40
Lignite	Fly ash + EA + AC (pre-primary PCD)	NT	<0.01–0.016 µg/L 12.34–12.57	<0.01–0.061 µg/L 12.21–12.61	<0.01–0.016 µg/L 12.48–12.59
Lignite	Fly ash + EA	NT	<0.01 µg/L 11.94	<0.01 µg/L 11.79	0.011 µg/L 12.00
Lignite	Fly ash + AC (post-primary PCD)	NT	<0.01–0.012 µg/L 11.00–11.88	<0.01 µg/L 11.52–12.05	<0.01–0.028 µg/L 11.43–12.09

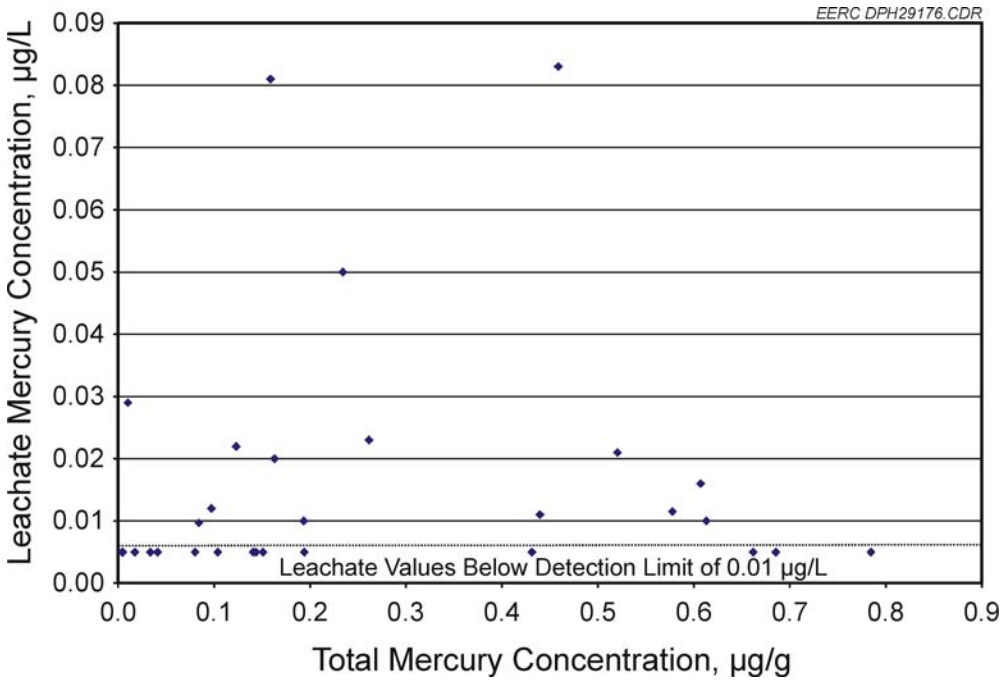

Figure 5-1. Fly ash 18-hour SGLP leachate mercury plotted against total mercury content.

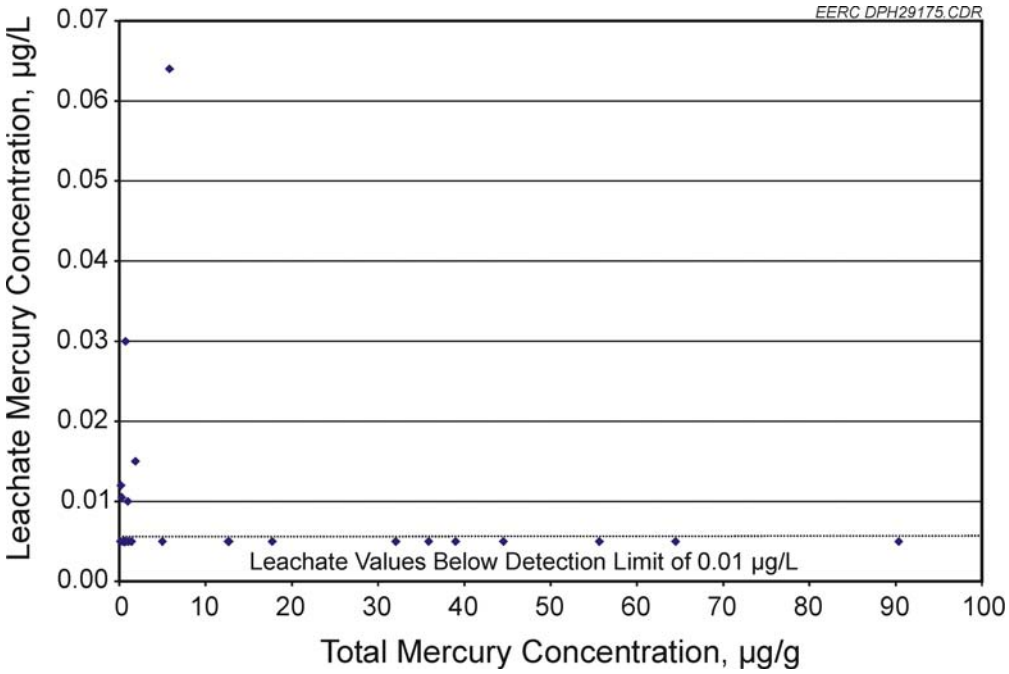

Figure 5-2. Fly ash + AC and/or EA 18-hour SGLP leachate mercury plotted against total mercury content.

Table 5-27. Paired Samples Mercury 18-hour SGLP and TCLP Leachates and Fundamental Characterization Data

ID Nos.	Sample Type	Total Hg, µg/g	18-hour SGLP Hg Leachate and pH	TCLP Hg Leachate and pH
02-070	Fly ash	0.194	0.01 µg/L 10.55	0.03 µg/L 3.56
02-069	Fly ash + ACI (post-primary PCD)	0.742	0.03 µg/L 9.48	0.07 µg/L 3.79
02-072	Fly ash	0.163	0.02 µg/L 10.81	0.02 µg/L 3.54
02-071	Fly ash + ACI (post-primary PCD)	0.975	0.01 µg/L 9.89	<0.01 µg/L 4.06
02-076	Fly ash	0.607	0.016 µg/L 11.18	<0.01 µg/L 3.89
03-009	Fly ash + ACI (pre-primary PCD)	NT	<0.01 µg/L 11.71	<0.01 µg/L 4.20
03-010	Fly ash + ACI (pre-primary PCD)	NT	<0.01 µg/L 10.71	<0.01 µg/L 3.80

Table 5-28. Paired Mercury Leachates and Fundamental Characterization Data of Fly Ash Samples with Enhancing Agent and ACI

ID Nos.	Sample Type	Total Hg, µg/g	18-hour SGLP Hg Leachate and pH	30-day LTL Hg Leachate and pH	60-day LTL Hg Leachate and pH
04-035	Fly ash	0.159	0.081 µg/L 12.60	0.02 µg/L 12.65	<0.01 µg/L 12.54
04-036	Fly ash + EA + ACI (pre-primary PCD)	0.287	0.011 µg/L 12.56	<0.01 µg/L 12.61	<0.01 µg/L 12.59
05-001	Fly ash	<0.01	<0.01 µg/L 12.42	0.011 µg/L 12.32	0.011 µg/L 12.39
05-003	Fly ash + EA + ACI (pre-SDA)	0.565	<0.01 µg/L 12.34	0.043 µg/L 12.30	0.015 µg/L 12.49
05-005	Fly ash	0.431	<0.01 µg/L 11.69	<0.01 µg/L 11.74	<0.01 µg/L 11.83
05-017	Fly ash + EA	0.717	<0.01 µg/L 11.94	<0.01 µg/L 11.79	0.011 µg/L 12.00

In leachate from FGD–SDA samples (Table 5-30), mercury was measured either at very low concentrations or was below the analytical reporting limit. Samples collected with and without mercury emission controls in place had similar mercury leachate concentrations. These data indicated that current management practices can continue to be used for these samples. The paired sample data (as seen in Table 5-31) showed a definite increase in the total mercury content of the test sample over the baseline samples; however, no significant difference was noted in the mercury leachate concentrations for the FGD–SDA paired samples. No correlation between the total and leachate mercury concentrations was observed.

Table 5-29. Paired Mercury Leachates and Fundamental Characterization Data of Fly Ash Samples with AC

ID Nos.	Sample Type	Total Hg, µg/g	18-hour SGLP Hg Leachate and pH	30-day LTL Hg Leachate and pH	60-day LTL Hg Leachate and pH
03-061	Fly ash	0.578	0.012 µg/L 12.45	<0.01 µg/L 12.63	0.325 µg/L 12.58
03-060	Fly ash + AC (pre-primary PCD)	1.86	0.015 µg/L 12.18	<0.01 µg/L 12.46	0.037 µg/L 12.38
05-038	Fly ash	0.104	<0.01 µg/L 11.85	<0.01 µg/L 12.00	<0.01 µg/L 12.09
05-013	Fly ash + AC (post-primary PCD)	39.0	<0.01 µg/L 11.45	<0.01 µg/L 11.66	<0.01 µg/L 11.61
05-023	Fly ash + AC (post-primary PCD: high ash)	12.7	<0.01 µg/L 11.85	<0.01 µg/L 12.05	<0.01 µg/L 12.09
05-024	Fly ash + AC (post-primary PCD)	35.9	<0.01 µg/L 11.51	<0.01 µg/L 11.67	<0.01 µg/L 11.68
05-025	Fly ash + AC (post-primary PCD: high ash)	12.6	<0.01 µg/L 11.88	<0.01 µg/L 12.04	<0.01 µg/L 12.07
05-040	Fly ash + AC (post-primary PCD)	44.5	<0.01 µg/L 11.47	<0.01 µg/L 11.55	<0.01 µg/L 11.54
06-001	Fly ash + AC (post-primary PCD)	64.5	<0.01 µg/L 11.39	<0.01 µg/L 11.52	<0.01 µg/L 11.47

Table 5-30. Ranges of FGD–SDA Mercury Leachate Results by Leaching Test, µg/L

Test	FGD–SDA	FGD–SDA + EA + AC (pre-primary PCD)
18-hour SGLP	<0.01	<0.01
30-day LTL	<0.01–0.050	<0.02
60-day LTL	0.013–0.043	0.012

Table 5-31. Paired FGD–SDA Mercury Leachates and Fundamental Characterization Data

ID Nos.	Sample Type	Total Hg, µg/g	18-hour SGLP Hg Leachate and pH	30-day LTL Hg Leachate and pH	60-day LTL Hg Leachate and pH
05-002	FGD–SDA	<0.01	<0.01 µg/L 12.40	0.050 µg/L 12.32	0.013 µg/L 12.47
05-004	FGD–SDA + EA + AC (pre-SDA)	0.332	<0.01 µg/L 12.43	<0.02 µg/L 12.48	0.012 µg/L 12.60

Mercury leachate concentrations from the FGD materials noted in Table 5-32 were also generally low, but the 18-hour SGLP results for the wet FGD filtercake and fixated wet FGD material were higher than the other wet FGD materials, FGD–SDA, and fly ash samples. Leachate data indicated that short-term mercury leachate concentrations from sulfite-rich wet FGD samples were somewhat elevated over the long-term mercury leachate concentrations, as also noted in Table 5-32. Leaching of FGD gypsum resulted in the lowest mercury leachate concentrations of all the wet FGD material samples. The total mercury concentrations for all wet FGD material samples were very similar, but the data were insufficient to determine if there is a correlation between total and leachate mercury concentrations. Further evaluation of a wide variety of wet FGD materials should include careful identification of the sample type and location as well as factors that may impact the mercury and ATE concentrations and leaching behavior.

5.5.1.2 Arsenic

The ranges of arsenic leachate results by leaching test are reported for all project fly ash samples in Table 5-33, FGD–SDA samples in Table 5-34, and wet FGD samples in Table 5-35.

Table 5-32. Ranges of Wet FGD Material Mercury Leachate Results by Leaching Test, µg/L

Test	FGD Gypsum	Wet FGD Slurry	Wet FGD Filtercake	Fixated Wet FGD
18-hour SGLP	<0.01	0.047	0.404–0.476	0.237–0.289
30-day LTL	NT	NT	<0.01	<0.01
60-day LTL	<0.01	NT	<0.01	<0.01

Table 5-33. Range of Fly Ash Arsenic Leachate Results by Leaching Test, µg/L

Test	Fly Ash	Fly Ash + AC (pre-primary PCD)	Fly Ash + EA + AC (pre-primary PCD)	Fly Ash + EA	Fly Ash + AC (post-primary PCD)
18-hour SGLP	<2–266	<4–16.3	<2–15.2	NT	20.2–842
30-day LTL	<4–305	<2–9.9	<4–6.4	46.3	8.1–30.4
60-day LTL	<2–336	<2–11.7	<2–7.5	73.0–95.9	10.4–27.3

Table 5-34. Ranges of FGD–SDA Arsenic Leachate Results by Leaching Test, µg/L

Test	FGD–SDA	FGD–SDA + EA + AC (pre-primary PCD)
18-hour SGLP	2.10–3.50	4.30
30-day LTL	2.60–3.30	3.60
60-day LTL	2.20–2.30	3.80

Table 5-35. Ranges of Wet FGD Material Arsenic Leachate Results by Leaching Test, µg/L

Test	FGD Gypsum	Wet FGD Slurry	Wet FGD Filtercake	Fixated Wet FGD
18-hour SGLP	<4	<4	<4	4.90–7.00
30-day LTL	NT	NT	3.50	5.20–24.0
60-day LTL	<2	NT	<2	<2–19.1

Arsenic leachate concentrations of fly ash + AC (pre-primary PCD), fly ash + EA + AC (pre-primary PCD), and fly ash + EA all were measured to be within the range reported for leachates from fly ash only. Total arsenic (Appendix G) was not elevated in any samples with AC or EA present. However, for the fly ash + AC collected post-primary PCD, several samples collected from a lignite-fired system had arsenic leachate concentrations significantly higher than the fly ash only, even though total arsenic concentrations were similar. The leaching data from this paired sample set as noted in Figure 5-3.

The arsenic-leaching data for one set of paired fly ash samples is shown in Figure 5-3 with the individual data from the 18-hour SGLP and 30- and 60-day LTL leaching test indicated for each sample. These samples were all collected from a system demonstrating injection of AC after the primary PCD. These data show a leaching profile typical of alkaline fly ash samples for elements that are present as oxyanions (arsenic, boron, selenium, and others). As shown, the arsenic leachate concentration decreases with time. These specific samples also show an increase

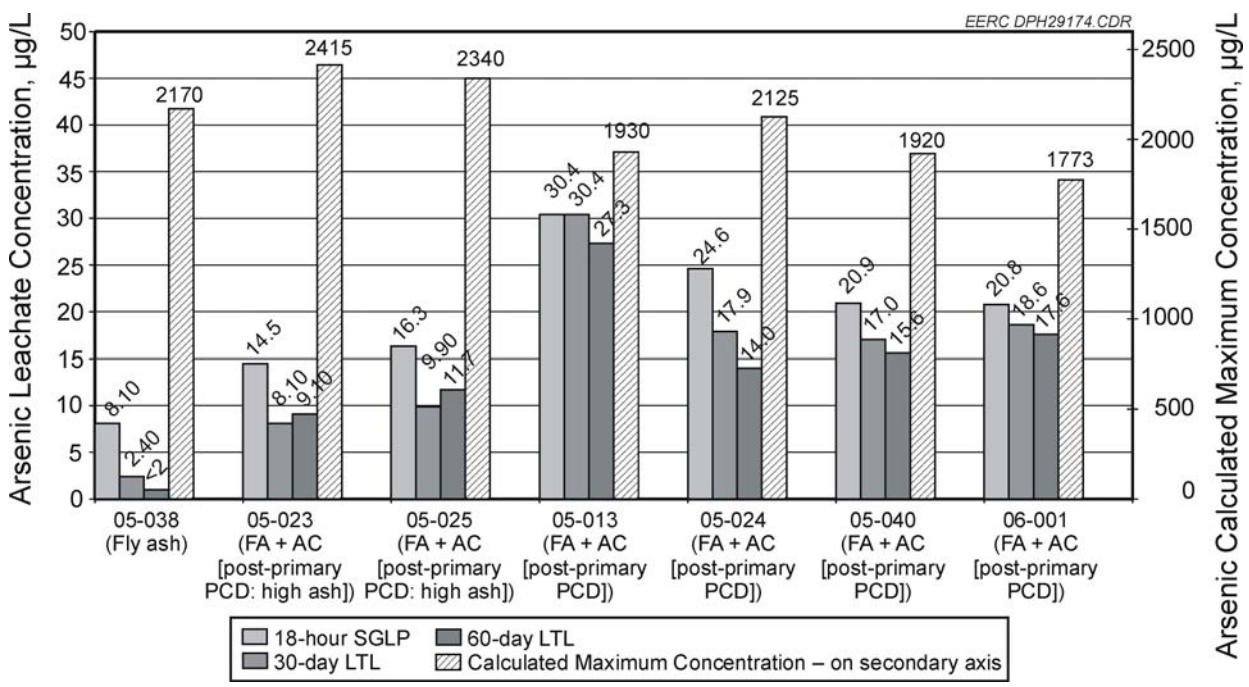

Figure 5-3. Arsenic 18-hour SGLP and 30- and 60-day LTL leaching data for a paired sample set.

in the arsenic leachate concentrations in the test samples as compared to the baseline sample even though the total arsenic concentrations in these samples were all similar. These data suggest that the AC may impact the leaching profile to facilitate increased arsenic release; however, other paired fly ash samples with AC injected post-primary PCD did not exhibit similar trends. This observation should be considered as various CCBs from mercury emission controls are evaluated for leaching characteristics, especially for arsenic since the arsenic limit for PDW was recently lowered to 10 µg/L.

Total arsenic concentrations were similar for FGD–SDA samples evaluated, and the arsenic leachate concentrations were also similar, as shown in Table 5-34. Arsenic mobility from all FGD–SDA samples evaluated was low.

The arsenic-leachate concentrations for the various wet FGD materials noted in Table 5-35 were also very low, with the highest values noted for the fixated wet FGD material. The LTL results also indicated an increase in arsenic leaching with time for the fixated wet FGD materials.

5.5.1.3 Cadmium

The ranges of cadmium leachate results by leaching test are reported in Tables 5-36 through 5-38 for fly ash samples, FGD–SDA samples, and wet FGD material samples, respectively.

For all sample types, cadmium leachate concentrations were generally low, but the highest cadmium leachate values were reported for the fly ash samples without any emission controls in place. No increase in total cadmium content was noted with the presence of AC or EA. Cadmium leachate data are similarly low, varying within the limits of the test and analysis, for all fly ash samples collected with mercury emission controls in place, all FGD–SDA materials, and all wet FGD materials. The cadmium leachate values for the fly ash samples collected under mercury emission control conditions fell within the range of cadmium leachate concentrations for fly ash only. As observed in previous work, no trend is noted for cadmium leachate concentrations over LTL.

Table 5-36. Ranges of Fly Ash Cadmium Leachate Results by Leaching Test, µg/L

Test	Fly Ash	Fly Ash + AC (pre-primary PCD)	Fly Ash + EA + AC (pre-primary PCD)	Fly Ash + EA	Fly Ash + AC (post-primary PCD)
18-hour SGLP	<0.2–8.08	<0.2–1.49	0.27–0.39	NT	0.99–1.87
30-day LTL	<0.2–7.64	<0.2–1.06	<0.2	2.40	0.85–1.99
60-day LTL	<0.2–8.30	<0.2–0.90	<0.2	<0.3–2.68	0.85–2.46

Table 5-37. Ranges of Fly Ash + FGD–SDA Material Cadmium Leachate Results by Leaching Test, µg/L

Test	FGD–SDA	FGD–SDA + EA + AC (pre-primary PCD)
18-hour SGLP	0.22–0.37	0.20
30-day LTL	<0.2–0.58	<0.2
60-day LTL	0.20–0.59	<0.2

Table 5-38. Ranges of Wet FGD Material Cadmium Leachate Results by Leaching Test, µg/L

Test	FGD Gypsum	Wet FGD Slurry	Wet FGD Filtercake	Fixated Wet FGD
18-hour SGLP	<0.2–0.46	<0.3	<0.2	0.43–0.44
30-day LTL	NT	NT	0.83	0.30–0.66
60-day LTL	<0.2	NT	0.47	0.37–0.50

5.5.1.4 Chromium

The ranges of chromium leachate results for all project sample types by leaching test are reported in Tables 5-39 through 5-41.

A comparison of all fly ash samples for total chromium versus leachate chromium was made (Appendix N), and results indicated that there may be an increased chromium leachate concentration for some fly ash samples with mercury control. However, the paired samples collected under this mercury emission control configuration do not provide any indication of increased total chromium concentrations in the test samples over the baseline sample (see Table 5-10). Additionally, the leaching results for these paired samples did not show any changes in the leaching profile for test samples compared to the baseline sample. Chromium leachate concentrations were generally similar for fly ash samples with and without mercury controls in place, but the samples of fly ash + AC did yield some leachates with higher chromium concentrations. For paired samples, it was typical that changes in leachate concentrations noted over the LTL series results were the same for baseline and test samples. In some cases, chromium leachate concentrations decreased with leaching time and, in some cases, the chromium leachate concentrations increased with leaching time. No general trend was identified. The decreases in chromium leachate concentrations with time were consistent with formation of secondary hydrated phases, but even though the pH of all samples in the paired sample set was typical for these reactions to occur, the data were inconclusive.

For FGD–SDA materials, the paired samples collected with mercury emission controls in place exhibited lower chromium leachate concentrations than those collected without mercury emission controls in place. For both the baseline and test samples, the 18-hour leachate had lower chromium concentrations than the long-term leachates.

Table 5-39. Ranges of Fly Ash Chromium Leachate Results by Leaching Test, µg/L

Test	Fly Ash	Fly Ash + AC (pre-primary PCD)	Fly Ash + EA + AC (pre-primary PCD)	Fly Ash + EA	Fly Ash + AC (post-primary PCD)
18-hour SGLP	1.4–174	<50–560	<2–67.6	NT	17.3–410
30-day LTL	<2–265	3.6–147	<2–133	203	152–650
60-day LTL	<2–277	5.2–138	2.1–134	182–211	155–680

Table 5-40. Ranges of FGD–SDA Chromium Leachate Results by Leaching Test, µg/L

Test	FGD–SDA	FGD–SDA + EA + AC (pre-primary PCD)
18-hour SGLP	34.6–116	21.8
30-day LTL	113–215	67.7–78.0
60-day LTL	132–223	87.7

Table 5-41. Ranges of Wet FGD Material Chromium Leachate Results by Leaching Test, µg/L

Test	FGD Gypsum	Wet FGD Slurry	Wet FGD Filtercake	Fixated Wet FGD
18-hour SGLP	<2	<2	<2	3.0–4.7
30-day LTL	NT	NT	<2	2.2–3.1
60-day LTL	<2	NT	<2	2.4–3.3

Chromium concentrations were significantly lower in the wet FGD material leachates, but all wet FGD materials leached chromium at similarly low levels.

5.5.1.5 Lead

The ranges of lead leachate results are reported for fly ash samples in Table 5-42, FGD–SDA samples in Table 5-43, and wet FGD material samples in Table 5-44.

Lead leachate data indicated that nearly all leachate lead concentrations were below the analytical reporting level. In one paired sample set, the baseline sample had long-term leachate. The lead leachate results were consistent with data from previous studies and were generally very low.

Table 5-42. Ranges of Fly Ash Lead Leachate Results by Leaching Test, µg/L

Test	Fly Ash	Fly Ash + AC (pre-primary PCD)	Fly Ash + EA +AC (pre-primary PCD)	Fly Ash + EA	Fly Ash + AC (post-primary PCD)
18-hour SGLP	<2	<2	<2–3.0	NT	<2
30-day LTL	<0.001–3.6	<2–3.0	<2	<2	<2
60-day LTL	<0.001–8.5	<2–2.4	<2	<2	<2

Table 5-43. Ranges of FGD–SDA Material Lead Leachate Results by Leaching Test, µg/L

Test	FGD–SDA	FGD–SDA + EA + AC (pre-primary PCD)
18-hour SGLP	<2	<2
30-day LTL	<2	<2
60-day LTL	<2	<2

Table 5-44. Ranges of Wet FGD Material Lead Leachate Results by Leaching Test, µg/L

Test	FGD Gypsum	Wet FGD Slurry	Wet FGD Filtercake	Fixated Wet FGD
18-hour SGLP	<2	<0.001	<2	6.60–14.3
30-day LTL	NT	NT	<2	<2
60-day LTL	<2	NT	<2	<2

5.5.1.6 Nickel

Nickel-leaching data are presented in Tables 5-45 through 5-47. Results are shown for fly ash samples, FGD–SDA samples and wet FGD material samples, and the SGLP–LTL tests used. An early evaluation of total nickel content (Appendix G) compared to leachate nickel content for all fly ash samples indicated that fly ash + AC samples exhibited reduced leaching of nickel (see Appendix N). Continued laboratory evaluations indicated that this observation was not supported by the nickel-leaching data on paired fly ash samples. Nickel concentrations generally decrease over leaching time. Nickel usually does not participate in reactions that form secondary hydrated phases.

Nickel-leaching results for FGD–SDA materials also indicated a decrease in leachate nickel concentrations with leaching time. The SGLP leachate nickel concentrations were higher than those reported for fly ash samples even though the total nickel content of fly ash samples and FGD–SDA materials was similar, and baseline fly ash samples exhibited the highest measured total nickel content.

Table 5-45. Ranges of Fly Ash Nickel Leachate Results by Leaching Test, µg/L

Test	Fly Ash	Fly Ash + AC (pre-primary PCD)	Fly Ash + EA + AC (pre-primary PCD)	Fly Ash + EA	Fly Ash + AC (post-primary PCD)
18-hour SGLP	<2–80.6	<2–23.1	<2–25.2	NT	<2–23.4
30-day LTL	<2–10.6	<2–5.4	<2–8.2	2.8	4.4–7.1
60-day LTL	<2–70.0	<2–5.3	<2–5.4	<4	2.9–5.1

Table 5-46. Ranges of FGD–SDA Nickel Leachate Results by Leaching Test, µg/L

Test	FGD–SDA	FGD–SDA + EA + AC (pre-primary PCD)
18-hour SGLP	16.4–39.1	29.3
30-day LTL	<4	<4
60-day LTL	<2	<2

Table 5-47. Ranges of Wet FGD Material Nickel Leachate Results by Leaching Test, µg/L

Test	FGD Gypsum	Wet FGD Slurry	Wet FGD Filtercake	Fixated Wet FGD
18-hour SGLP	<2–28.4	15.0	6.1–7.4	<2
30-day LTL	NT	NT	32.1	<2–4.0
60-day LTL	10.1–12.6	NT	25.4	2.1–3.7

Leachate nickel concentrations for wet FGD materials were similar to those for most fly ash samples and the FGD–SDA samples.

5.5.1.7 Selenium

Selenium was the only ATE other than mercury identified as having increased total concentration in some fly ash + AC samples. Specifically, fly ash + AC samples where the AC was injected post-primary PCD exhibited an elevated total selenium content compared to the baseline for the single paired sample set of that type. Other fly ash paired samples that had the AC injected before the primary PCD did not exhibit this increase in total selenium content; however, the increase noted for the fly ash/fly ash + AC (post-primary PCD) samples and the properties of selenium raised interest in the selenium-leaching data. The ranges of selenium leachate results by leaching test for fly ash, FGD–SDA, and wet FGD samples are reported in Tables 5-48 through 5-50, respectively.

Table 5-48. Ranges of Fly Ash Selenium Leachate Results by Leaching Test, µg/L

Test	Fly Ash	Fly Ash + AC (pre-primary PCD)	Fly Ash + EA + AC (pre-primary PCD)	Fly Ash + EA	Fly Ash + AC (post-primary PCD)
18-hour SGLP	2.1–412	8.4–147	19.9–47.2	NT	99.3–8620
30-day LTL	<2–489	<2–100	<2–27.2	97.0	47.7–312
60-day LTL	<2–514	3.8–114	<2–30.3	<4–50.9	45.2–199

Table 5-49. Ranges of FGD–SDA Selenium Leachate Results by Leaching Test, µg/L

Test	FGD–SDA	FGD–SDA + EA + AC (pre-primary PCD)
18-hour SGLP	11.3–65.8	24.3
30-day LTL	12.0–65.2	12.0–13.2
60-day LTL	14.4–53.1	17.0

Table 5-50. Ranges of Wet FGD Material Selenium Leachate Results by Leaching Test, µg/L

Test	FGD Gypsum	Wet FGD Slurry	Wet FGD Filtercake	Fixated Wet FGD
18-hour SGLP	3.3–18.7	65.0	41.0–71.2	2.1–2.70
30-day LTL	NT	NT	55.2	2.4–3.40
60-day LTL	2.7–8.2	NT	45.3	<2–2

5.5.2 Vapor-Phase Transport

Two types of vapor-phase transport (release) experiments were performed for this project: long-term ambient-temperature release experiments and elevated-temperature release experiments. These experiments only measured mercury releases. No other ATEs were determined.

5.5.2.1 Long-Term Ambient-Temperature Release

Over the course of this project, the experimental results and information obtained through the Year 1 field task, from documents assembled, and through discussions with other research groups and sponsors, it became apparent that the term "release" did not always describe the results of the ambient-temperature vapor-phase experimental results. The results of the ambient-temperature vapor-phase transport experiments were reported as either mercury released or sorbed by the solid sample tested.

All samples included in the ambient-temperature experiments and the results are included in Appendix O. The experimental results are presented in sample sets because the experimental protocol required significant physical space and, therefore, limited the number of samples that could be evaluated at one time. Four sample sets were evaluated for mercury captured in the

analytical traps typically measured three times over the course of the experiment. The experiments were usually run for approximately 200 days, but selected samples were allowed to run for longer durations because of sample characteristics or release profiles. In the summary tables for this section, results for paired samples are highlighted. The tables of summary data include results of the two replicates of each sample expressed in two ways:

- Cumulative % Hg sorption or release refers to the amount of mercury sorption or release based on the blank value measured over the entire experiment reported as a percentage of the total mercury concentration of the sample.

- Years to release 100% Hg on CCB at measured rate is a calculation of the number of years required to release 100% of the total mercury content on the CCB at the rate of release measured over the experiment.

The first sample set evaluated comprised 12 samples and included fly ash, fly ash + AC (pre-primary PCD), and FGD–SDA samples from eastern bituminous, Powder River Basin (PRB) subbituminous, and lignite coal. One paired sample set (Samples 03-061 and 03-060) was evaluated. The samples and a summary of the results are shown in Table 5-51.

The results collected from Sample Set 1 are also shown graphically in Figure 5-4. Over the entire 194-day period of the experiment, five samples showed overall mercury release and seven samples showed overall mercury sorption. The release of mercury, expressed as pg/g/day, was less for most samples in the final 90-day collection period than for the previous 90-day collection period. The observed variability was attributed to the variability inherent in the analysis of the extremely low concentrations of mercury captured by and desorbed from the gold-coated analytical traps.

Samples included in Sample Set 2 and a summary of the results obtained are included in Table 5-52, and results are presented graphically in Figure 5-5. The sample set comprised seven samples including fly ash, fly ash + AC (post-primary PCD), fly ash + EA + AC (pre-primary PCD), and wet FGD filtercake from eastern bituminous, western bituminous, and lignite coal. One paired sample set (Samples 04-035 and 04-036) was evaluated.

In Sample Set 2, all fly ash samples sorbed mercury regardless of the presence of AC. The results from Sample Set 2 indicated that the release of mercury from the wet FGD filtercake sample (03-082) was higher than any releases measured for fly ash samples. Evaluation of this sample continued past that of the fly ash samples.

Based on this observation, Sample 03-082 was reevaluated in Sample Set 3. Also included in Sample Set 3 were fly ash, fly ash + EA + AC (pre-primary PCD), FGD–SDA, FGD–SDA + EA + AC (pre-SDA), and FGD gypsum from eastern bituminous, PRB subbituminous, and lignite coal. Two paired sample sets were evaluated. These included a fly ash pair (Samples 05-001 and 05-003) and an FGD–SDA pair (Samples 05-002 and 05-004) from the same mercury control technology test. Results for Sample Set 3 are presented in Table 5-53. The results of the first 187 days of testing are displayed graphically in Figure 5-6.

Table 5-51. Long-Term Ambient-Temperature Sample Set 1 Summary (Positive values indicate release, and negative values indicate sorption of mercury. Duplicate bottles are represented.)

					Replicate 1		Replicate 2	
ID No.	Sample Type	Coal Type	Total Hg on CCB, µg/g	Exp. Duration, Days	Cumulative % Hg Sorption or Release	Years to Release 100% Hg on CCB at Measured Rate	Cumulative % Hg Sorption or Release	Years to Release 100% Hg on CCB at Measured Rate
01-002	Fly ash	E. bit.	0.187	194	−0.000153	NA – sorbing	−0.000157	NA – sorbing
03-006	Fly ash	E. bit.	0.194	194	−0.000110	NA – sorbing	−0.0000845	NA – sorbing
99-456	Fly ash	PRB sub.	1.39	194	−0.0000233	NA – sorbing	−0.0000109	NA – sorbing
01-008	Fly ash	PRB sub.	1.22	194	0.0000037	14,472,785	0.0000000	NA – no sorption or release
03-061*	Fly ash	PRB sub.	0.578	194	0.0000076	6,965,200	−0.0000330	NA – sorbing
03-060	Fly ash + AC (pre-primary PCD)	PRB sub.	1.86	194	0.0000007	74,619,320	0.0000021	25,587,175
03-017	Fly ash + AC (pre-primary PCD)	Lignite	0.225	194	0.0000045	118,14,972	−0.0000966	NA – sorbing
03-018	Fly ash + AC (pre-primary PCD)	Lignite	0.289	194	0.0000049	10,817,569	−0.000122	NA – sorbing
03-062	Fly ash + AC (pre-primary PCD)	Lignite	0.490	194	0.0000031	17,214,465	0.0000004	119,651,861
99-188	FGD–SDA	PRB sub.	0.112	194	0.0000026	20,144,056	-0.000657	NA – sorbing
00-048	FGD–SDA	Lignite	0.361	194	−0.0000674	NA – sorbing	0.0000018	29,229,517
01-011	FGD–SDA	Lignite	2.55	194	0.0000006	82,875,125	0.0000008	68,131,501

* Highlighted samples are paired samples.

Table 5-52. Long-Term Ambient-Temperature Sample Set 2 Summary (Positive values indicate release, and negative values indicate sorption of mercury. Duplicate bottles are represented.)

					Replicate 1		Replicate 2	
ID No.	Sample Type	Coal Type	Total Hg on CCB, µg/g	Exp. Duration, Days	Cumulative % Hg Sorption or Release	Years to Release 100% Hg on CCB at Measured Rate	Cumulative % Hg Sorption or Release	Years to Release 100% Hg on CCB at Measured Rate
04-054	Fly ash + AC (post-primary PCD)	E. bit.	17.7	188	−0.0000008	NA – sorbing	−0.0000012	NA – sorbing
04-006	Fly ash	W. bit.	0.144	188	−0.000126	NA – sorbing	−0.000235	NA – sorbing
04-007	Fly ash	W. bit.	0.521	188	−0.0000685	NA – sorbing	−0.0000168	NA – sorbing
04-035*	Fly ash	Lignite	0.159	188	−0.0000646	NA – sorbing	−0.0000763	NA – sorbing
04-036	Fly ash + EA + AC (pre-primary PCD)	Lignite	0.287	188	−0.0000392	NA – sorbing	−0.0000434	NA – sorbing
04-067	Fly ash + EA + AC (pre-primary PCD)	Lignite	0.640	188	−0.0000246	NA – sorbing	−0.0000280	NA – sorbing
03-082	Wet FGD filtercake	E. bit.	0.248	699	0.609	315	0.448	428

* Highlighted samples are paired samples.

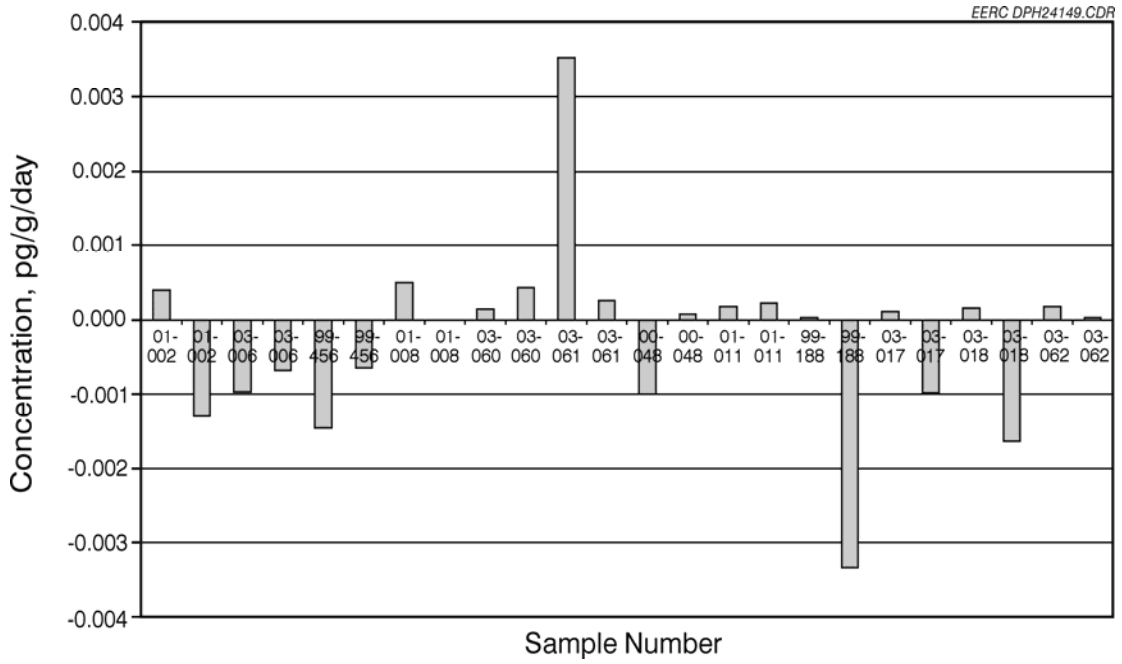

Figure 5-4. Sample Set 1 (194-day) long-term ambient-temperature mercury release or sorption as related to blank values, pg/g/day. Positive values indicate release, and negative values indicate sorption of mercury. Duplicate bottles are represented.

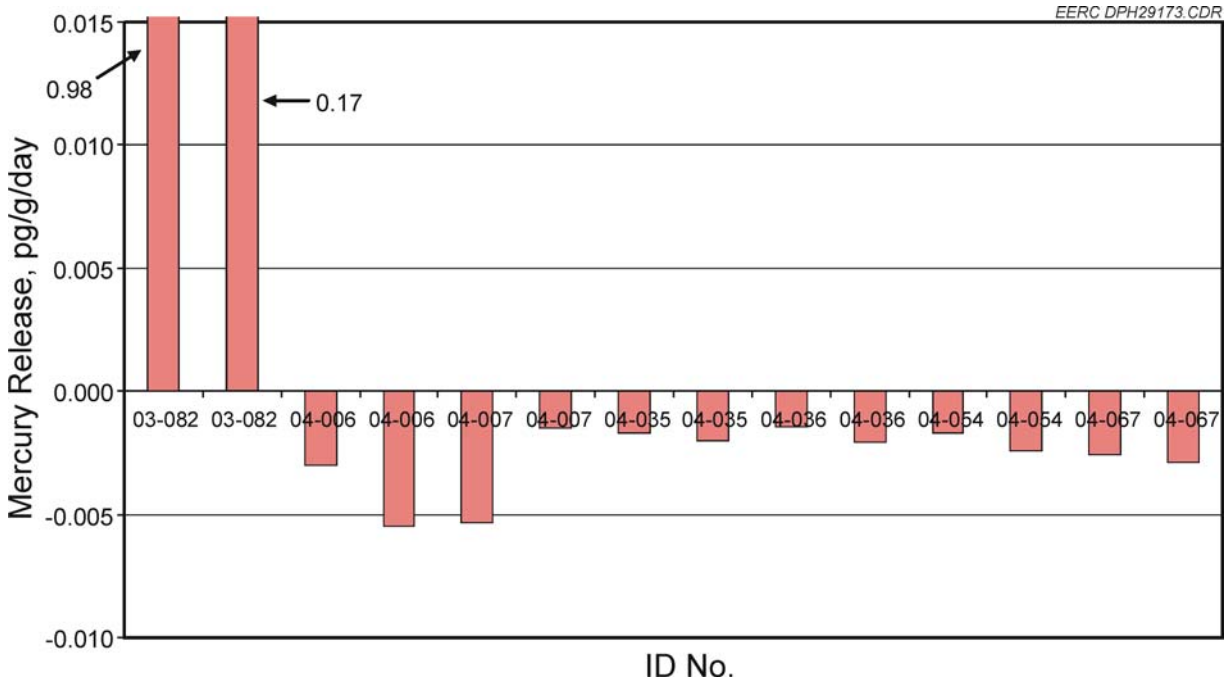

Figure 5-5. Sample Set 2 (188-day) long-term ambient-temperature mercury release or sorption as related to blank values, pg/g/day. Positive values indicate release, and negative values indicate sorption of mercury. Duplicate bottles are represented.

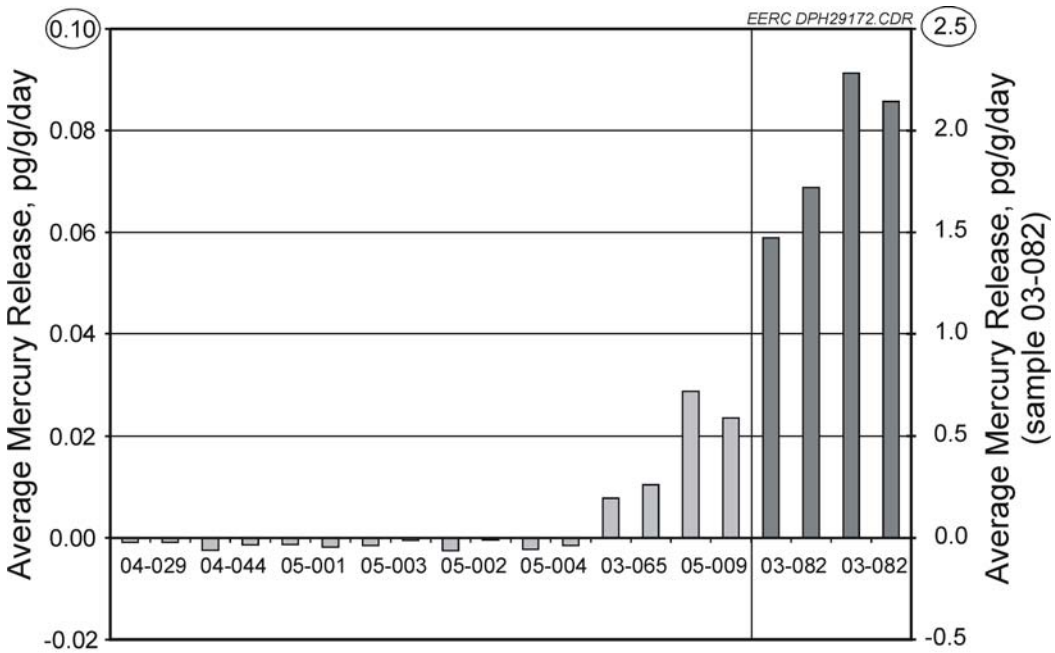

Figure 5-6. Sample Set 3 (187-day) long-term ambient-temperature mercury release or sorption as related to blank values, pg/g/day. Positive values indicate release, and negative values indicate sorption of mercury. Duplicate bottles are represented. Sample 03-082 is displayed on a secondary axis.

All fly ash samples in Sample Set 3 sorbed mercury. The FGD gypsum and wet FGD filtercake samples released mercury, with the wet FGD filtercake releasing at a rate of approximately over 100 times that of the FGD gypsum in the first 187 days of testing. The mercury determinations indicated that mercury release was continuing at that point, so the exposure to ambient air was continued on all FGD material samples and mercury release was determined approximately every 45–60 days.

The cumulative mercury release for all the wet FGD material samples was higher than for any other samples evaluated. The rate of mercury vapor release was also higher than fly ash samples. After extensive exposure to ambient air, some of the wet FGD material samples, showed an indication of sorption of mercury.

Results for Sample Set 4 are shown in Table 5-54. This sample set included a set of paired fly ash samples, with 05-038 being the baseline sample, collected from a system where AC was injected after the primary PCD. The paired fly ash + AC samples in the set were test samples that had high or low ash content and varying levels of AC present. The remaining two samples were FGD gypsum samples from the same plant, where Sample 04-082 was collected when the SCR was on and Sample 04-083 was collected when the SCR was off.

Table 5-53. Long-Term Ambient-Temperature Sample Set 3 Summary (Positive values indicate release, and negative values indicate sorption of mercury. Duplicate bottles are represented.)

					Replicate 1		Replicate 2	
ID No.	Sample Type	Coal Type	Total Hg on CCB, µg/g	Exp. Duration, Days	Cumulative % Hg Sorption or Release	Years to Release 100% Hg on CCB at Measured Rate	Cumulative % Hg Sorption or Release	Years to Release 100% Hg on CCB at Measured Rate
04-029	Fly ash	PRB sub.	0.261	187	−0.0000304	NA – sorbing	−0.0000333	NA – sorbing
04-044	Fly ash	Lignite	0.878	187	−0.0000245	NA – sorbing	−0.0000129	NA – sorbing
05-001*	Fly ash	Lignite	<0.01	187	−0.00238	NA – sorbing	−0.00392	NA – sorbing
05-003	Fly ash + EA + AC (pre-primary PCD)	Lignite	0.565	187	−0.0000234	NA – sorbing	−0.0000072	NA – sorbing
05-002	FGD–SDA	Lignite	<0.01	187	−0.00548	NA – sorbing	−0.00119	NA – sorbing
05-004	FGD–SDA + EA + AC (pre-SDA)	Lignite	0.332	187	−0.0000611	NA – sorbing	−0.0000409	NA – sorbing
03-065	FGD gypsum	E. bit.	0.044	473	0.00756	17,133	0.0111	11,678
05-009	FGD gypsum	E. bit.	0.032	473	0.0239	5,430	0.0190	6,833
03-082	Wet FGD filtercake	E. bit.	0.248	472	1.07	120	0.867	149
03-082	Wet FGD filtercake	E. bit.	0.248	476	0.866	151	0.963	135

* Highlighted samples are paired samples.

Table 5-54. Long-Term Ambient-Temperature Sample Set 4 Summary (Positive values indicate release, and negative values indicate sorption of mercury. Duplicate bottles are represented.)

					Replicate 1		Replicate 2	
ID No.	Sample Type	Coal Type	Total Hg on CCB, µg/g	Exp. Duration, Days	Cumulative % Hg Sorption or Release	Years to Release 100% Hg on CCB at Measured Rate	Cumulative % Hg Sorption or Release	Years to Release 100% Hg on CCB at Measured Rate
05-038*	Fly ash	Lignite	0.104	187	0.0000293	1,747,138	−0.0000531	NA – sorbing
05-013	Fly ash + AC (post-primary PCD)	Lignite	39.0	187	0.0000001	388,756,048	0.0000001	399,977,490
05-023	Fly ash + AC (post-primary PCD: high ash)	Lignite	12.7	187	0.0000003	173,663,704	0.0000004	125,457,465
05-024	Fly ash + AC (post-primary PCD)	Lignite	35.9	187	−0.0000001	NA – sorbing	−0.0000001	NA – sorbing
05-025	Fly ash + AC (post-primary PCD: high ash)	Lignite	12.6	187	−0.0000017	NA – sorbing	−0.0000019	NA – sorbing
05-040	Fly ash + AC (post-primary PCD)	Lignite	44.5	187	0.0000000	6,414,372,585	−0.0000005	NA – sorbing
06-001	Fly ash + AC (post-primary PCD)	Lignite	64.5	187	−0.0000003	NA – sorbing	−0.0000003	NA – sorbing
04-082	FGD gypsum	E. bit.	0.0427	200	8.41	6.51	8.38	6.54
04-083	FGD gypsum	E. bit.	0.103	200	0.381	144	0.282	194

* Highlighted samples are paired samples.

The fly ash and fly ash + AC samples in Sample Set 4 generally sorbed mercury or showed very low releases. Although Sample 04-082 (SCR on) had a lower total mercury concentration than Sample 04-083 (SCR off), it released a greater percentage of mercury. Sample 04-082 showed the highest mercury release in this project. Figure 5-7 graphically presents the rate of mercury release, pg/g/day, from Samples 04-082 and 04-083. This clearly shows that the release of mercury from Sample 04-082 is decreasing with time.

Review of the results of long-term ambient-temperature release tests indicated that mercury might be released from some CCBs at relatively low levels. Fly ash that had unburned carbon or AC generally tended to sorb mercury from the ambient air that was introduced into the sample container. For fly ash samples, the release of mercury was higher for each sample in the first period than in subsequent periods, indicating a reduced rate of release with time. This is due to the disruption of the sample and apparatus during sample addition to the container.

Wet FGD materials all released mercury at higher levels than any of the fly ash samples evaluated, and the calculated number of years to complete release of mercury was the lowest for the wet FGD material samples, ranging from 6 to 428 years, while the calculated years to complete release were greater than 50M years + for fly ash and FGD–SDA samples evaluated. Generally, the rate of release measured in the final testing period was decreasing compared to the prior testing period; therefore, the calculated years to release 100% of the total Hg on the CCB is likely low. The results indicate that the release or sorption of mercury from fly ash and FGD–SDA samples is very minute and would cause no adverse impact on the mercury loading to the atmosphere.

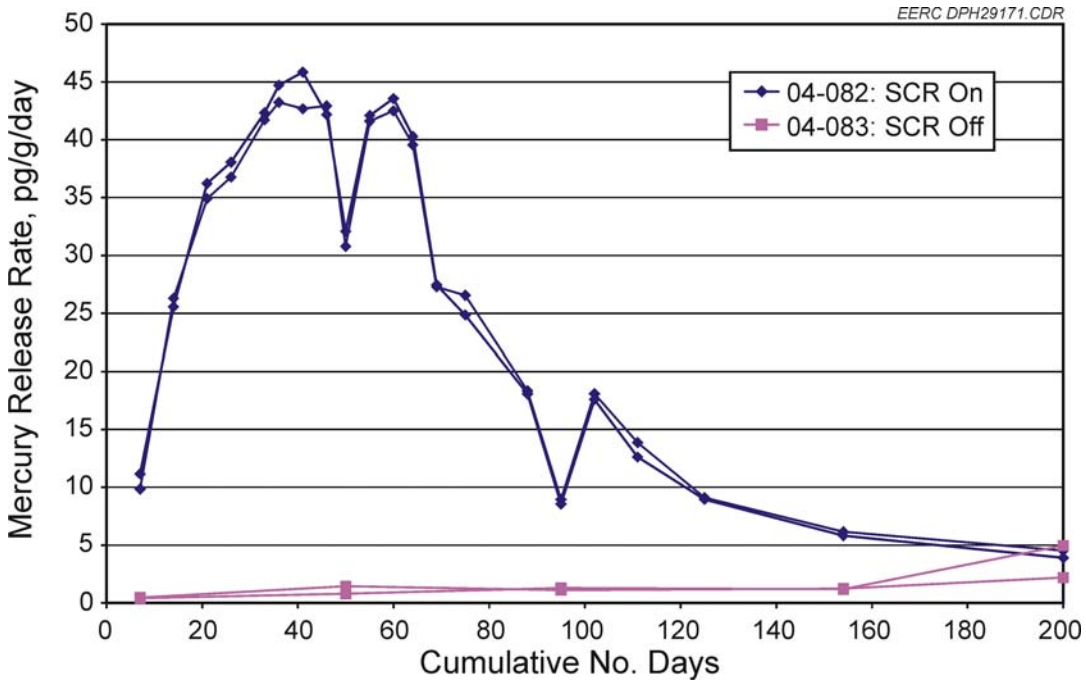

Figure 5-7. Long-term ambient-temperature mercury release rate, pg/g/day, from Samples 04-082 and 04-083. Duplicate bottles are represented.

5.5.2.2 Desorption at Elevated Temperatures

A variety of CCBs were evaluated for the real-time elevated-temperature release of mercury. The CCBs were primarily fly ash. Evaluation of FGD materials was limited because of analytical interference from the releases of sulfur compounds on sample exposure to elevated temperatures. The use of elevated-temperature release of mercury was evaluated as a means of determining the speciation of mercury present on CCBs. An elevated-temperature vapor-phase mercury release report was published in February 2006 and can be found in Appendix P. This report included a complete discussion of the work performed to evaluate the mercury releases from CCBs on exposure to elevated temperatures, and the results are summarized here. All results can be found in Appendix Q.

Thermal desorption curves provided a comparative means of evaluating the elevated-temperature release of mercury from a variety of CCBs. Mercury thermal desorption curves were generated for 65 CCBs, including 31 fly ash samples and 28 fly ash samples with mercury control, two FGD–SDA samples and one FGD–SDA sample with mercury control, and three wet FGD materials. Tables 5-55 and 5-56 list the samples evaluated indicating the coal source and mercury control. Although three wet FGD materials were tested, analytical interferences precluded continued work on FGD materials.

The fly ash samples subjected to the elevated-temperature regime typically generated either one or two mercury peaks, with four being the maximum number of peaks identified for fly ash. As also noted in Table 5-55, mercury was released at temperatures ranging from 256° to 750°C. Some samples continued to show increasing mercury release at 750°C, so the highest peak temperature at which the mercury was released could not be determined. Samples exhibiting this continued mercury release at 750°C were predominantly eastern bituminous fly ash samples with a LOI greater than 3% or fly ash + AC (post-primary PCD) samples. Samples with added AC were more difficult to replicate in part because the mercury was likely associated with the carbon particles, and it was more difficult to take a representative sample of fly ash + AC, especially with the sample size limitations of the method. Some samples were ground or sieved in order to obtain a more homogeneous sample for evaluation.

Although the lowest mercury absorbance peak occurred at 256°C for a fly ash sample, the initiation of the first mercury release peak was noted before 250°C. Representative mercury release curves generated under this task are shown in the report in Appendix P. Examples of replicate curves are also shown in the report. An example of a desorption curve with two peaks is shown in Figure 5-8. The relatively sharp first peak was typical of most first mercury peaks recorded. In curves where two or more peaks were noted, peaks after the initial peak tended to show slightly less definition and were usually broader, although the absorption could be higher.

Samples with AC were more difficult to evaluate for elevated-temperature mercury releases, but sorbents that contained other compounds, such as halogens or sulfur, also offered analytical challenges. While sample identifications did not always indicate the exact nature of the

Table 5-55. Summary of Fly Ash Samples Evaluated in Elevated-Temperature Mercury Release Experiments

Coal Type	Sample Type	No. of Samples Tested	No. of Peaks	Range of Temp. at Peaks, °C	Total Hg Content Range, µg/g	LOI Range, %
Eastern Bituminous	Fly ash	16	0–4	260–750	<0.01–0.685	0.47–8.46
	Fly ash + AC (post-primary PCD)	6	1–4	262–750	0.742–120	12.6–24.4
South American Bituminous	Fly ash	2	1–3	356–750	0.151–0.607	12.7–21.2
Western Bituminous	Fly ash	2	1	330–378	0.144–0.521	1.42–2.56
PRB Subbituminous	Fly ash	2	1	333–404	0.261–0.578	0.48–1.08
	Fly ash + AC (pre-primary PCD)	4	1–2	302–750	1.09–5.81	2.28–4.14
Fort Union Lignite	Fly ash	9	0–3	275–750	<0.01–0.785	0.22–7.48
	Fly ash + AC (pre-primary PCD)	4	1	323–702	0.225–2.22	0.96–4.21
	Fly ash + EA + AC (pre-primary PCD)	3	1–2	306–750	0.287–0.640	1.04–2.49
	Fly ash + EA	1	0–2	388–684	0.717	1.70
	Fly ash + AC (post-primary PCD)	10	0–3	256–750	0.147–64.5	0.59–13.2

AC used, samples of this type were expected to produce a thermal curve containing multiple peaks. Multiple peaks were noted in a significant number of fly ash samples and were likely due to the presence of multiple mercury compounds in the samples (mercury chloride, oxide, nitrate, or sulfate) because each compound would be expected to result in a discreet peak on vaporization.

Elemental mercury is known to sorb as an oxidized species on AC. Additives such as sulfur or iodine, for example, could lead to the formation of additional compounds such as

Table 5-56. Summary of FGD–SDA and Wet FGD Material Samples Evaluated in Elevated-Temperature Mercury Release Experiments

Coal Type	Sample Type	No. of Samples Tested	No. of Peaks	Range of Temp. at Peaks, °C	Total Hg Content Range, µg/g	LOI Range, %
PRB Subbituminous	FGD–SDA	1	2–3	270–695	0.0716–0.131	2.07
Fort Union Lignite	FGD–SDA	1	0	NA	<0.01	0.95
	FGD–SDA + EA + AC (pre-SDA)	1	1	312–487	0.332	1.12
Eastern Bituminous	FGD gypsum	2	1	298–329	0.044–0.096	1.22–1.94
	Fixated wet FGD	1	3	256–720	0.180	3.11–3.17

mercuric sulfide or mercuric iodide. The thermal desorption curves were indicative of the following mechanisms of desorption:

- Elemental mercury and mercuric chloride can desorb unchanged.
- Other mercury compounds can decompose into their components as would happen with mercuric oxide, which would decompose into oxygen and elemental mercury prior to desorption.

Table 5-57 shows comparative data for fly ash samples subjected to elevated temperature. The table shows ranges of the temperatures recorded for the initiation and peak of each mercury peak noted for fly ash samples evaluated. The data indicated that the addition of an EA may result in fewer peaks to be generated both when used alone or with AC for mercury control. This same phenomenon was noted for the FGD–SDA sample shown in Table 5-58. The wet FGD materials (results summarized in Table 5-58) produced fewer mercury peaks, and the mercury tended to desorb at lower temperatures than noted for samples of fly ash and FGD–SDA. Results for FGD–SDA samples tended to be more reproducible than results from fly ash samples.

5.5.2.3 Mercury Speciation Method

An effort was made to use the elevated-temperature apparatus to develop information on the species of mercury present on the CCBs tested. The presence of multiple peaks was potentially indicative of multiple mercury compounds being desorbed. The mercury speciation investigation was initiated with the use of quartz sand and pure quartz powder, spiked with

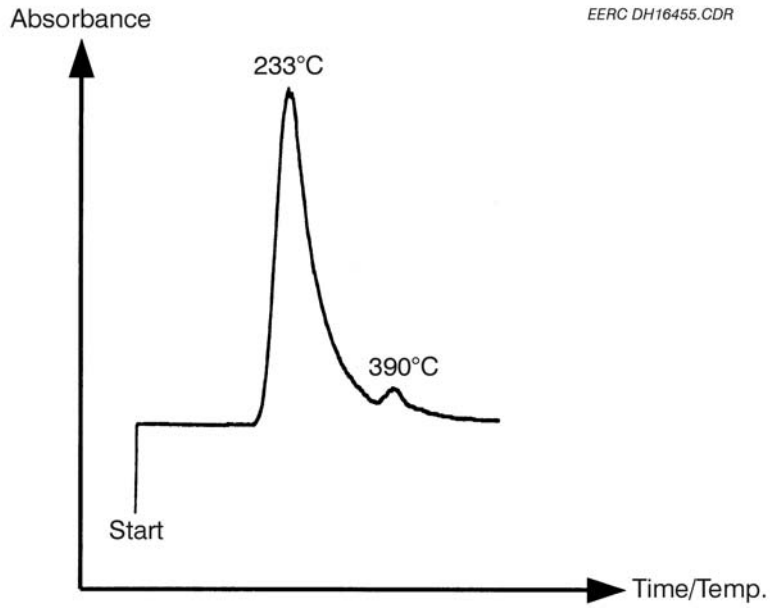

Figure 5-8. Typical two-peak mercury desorption curve for fly ash.

Table 5-57. Range of Fly Ash Peak Mercury Release Temperatures at Elevated Temperature, °C

Peak	Fly Ash	Fly Ash + AC (pre-primary PCD)	Fly Ash + EA + AC (pre-primary PCD)	Fly Ash + EA	Fly Ash + AC (post-primary PCD)
Peak 1 Start	173–645	226–433	275–371	339–372	135–540
Peak 1	273–750	302–702	324–433	388–406	262–750
Peak 2 Start	315–705	388–657	350	388	290–710
Peak 2	346–750	363–750	750	417–684	330–751
Peak 3 Start	454–709	687	NA	NA	362–750
Peak 3	551–750	704–750	NA	578	411–750
Peak 4 Start	629	NA	NA	NA	515–750
Peak 4	737–747	750	NA	NA	705–750

Table 5-58. Range of FGD–SDA and Wet FGD Material Peak Mercury Release Temperatures at Elevated Temperature, °C

Peak	FGD–SDA	FGD–SDA + EA + AC	FGD Gypsum	Fixated FGD
Peak 1 Start	200 (3 times)	264–280	170–250	157
Peak 1	275–280	312–354	298–329	256
Peak 2 Start	412–416	NA	NA	430
Peak 2	430–475	487	NA	460
Peak 3 Start	NA	NA	NA	670
Peak 3	695	NA	NA	720

mercuric chloride. Quartz was selected as an inert material. A single, sharp peak was recorded when the mercuric chloride was added to the quartz sand. However, when mercuric chloride was spiked onto pure quartz powder, a double peak was noted.

Additional elevated-temperature release experiments were also performed on CCB samples spiked with mercury. All samples used in this experiment were fly ash, some of which contained AC or EA plus AC from mercury emission control demonstrations. The addition of mercuric chloride or elemental mercury vapor to the CCBs resulted in a shift of the mercury release peaks noted previously from the samples without any added mercury. The peak temperatures measured for spiked CCB samples shifted to higher temperatures for some samples and to lower temperatures for other samples. This indicated that the temperature range for mercuric chloride in CCBs was too wide for positive identification of a peak as a particular compound.

Figures 10 and 11 in Appendix P are an example of a fly ash sample tested as described earlier compared to a separate aliquot spiked with mercuric chloride. This was done by mixing a single aliquot of the CCB, just less than 2 grams, and dividing it into two small, nearly equal portions. One portion was left untreated while the other portion was spiked with 50 µL of an ether solution of mercuric chloride containing 10 ng/µL of mercuric chloride. This is equivalent to the addition of 370 ng of mercury as mercuric chloride. Spiking was done in this manner to minimize nonhomogeneity between the two aliquots of sample. Mercuric chloride spiking of this fly ash sample produced an additional peak to those noted on the original fly ash sample. The reasons for an additional peak noted in the spiked sample are the same as why a fly ash sample may release multiple peaks of mercury.

Results indicated that the interaction of mercury and mercury compounds with the CCBs at elevated temperatures may preclude speciation using this method on these complex materials. It is hypothesized that the first peak that evolves from each CCB is sorbed elemental mercury, which can volatilize more readily than mercury compounds.

5.5.3 Microbiologically Mediated Leaching and Vapor-Phase Transport

A variety of CCB samples were evaluated for microbiologically mediated mercury releases using the methods described in the experimental section and in a report entitled "Microbiologically Mediated Mercury and Air Toxic Element Rereleases from Coal Combustion By-Products," and submitted to project sponsors in 2006. The report is included in its entirety in Appendix R. The report summarizes the bulk of the work performed under this subtask. The work included significant efforts to modify the experimental method and apparatus used to allow determination of mercury released from samples of CCB subjected to conditions conducive to microbial growth. The samples included in this subtask were primarily fly ash. A complete summary of the samples evaluated and identifying information is included in Appendix S.

As described in the report noted, six sets of microbiologically mediated experiments were completed, and a seventh set was run after preparation of that report. The experimental method was designed to determine the leaching and vapor-phase releases from the CCBs under aerobic and anaerobic conditions with appropriate buffer to keep the pH of the systems in a range that would allow the microbes to reproduce.

In keeping with the format used in the report included as Appendix R, a summary of the samples and results from Experiment 7 are included here. Table 5-59 provides information on the samples evaluated. The samples were all bituminous fly ash without any mercury emission controls in place. Results of Experiment 6 indicated that high-pH fly ash typically generated from North Dakota lignite or subbituminous coal, cannot be maintained at a pH level that will support microbial growth. For that reason, the final experiment focused on fly ash samples with near-neutral pH values.

Microbiological release Experiment 7 included aerobic and anaerobic glucose-fed conditions in triplicate similar to the earlier experiments. A 4-day initial elemental mercury release measurement was made for the samples, which was the period between sample and buffer addition and bacteria addition to the flask. Observations included possible fungal growth within three days of bacteria addition in most sample flasks and a moldy or musty odor in the air over the aerobic side of the experimental setup 10 days after bacteria addition. In some samples, a gray mold was clearly visible.

Analytical data were collected at the end of the monthlong experiment and are reported in Tables 5-60–5-62. Prior to preparations necessary for sample analyses, the condition of each flask sample was noted after settling of the solids. All anaerobic sample flasks contained a clear liquid and had no odor. All aerobic sample flasks contained a dark gray to black, opaque liquid. All but one of the aerobic sample flasks (Sample 04-003) had a slightly musty odor. Many of the aerobic sample flasks had varying amounts of small white specks or a film that were possibly fungus. One of the aerobic flasks for Sample 03-006 had a definite fungus or mold patch on the top of the liquid. The liquid samples from the aerobic side of the experiment required the use of a centrifuge to separate the liquid and solid enough to filter through a 0.45-µm filter. Eh and pH measurements of all filtered liquid samples are reported in Table 5-60.

Table 5-61 reports the elemental and organomercury vapor-phase release results in pg/g/day. The samples on the aerobic side released more vapor-phase mercury with one exception.

Results of the mercury and trace element leachate concentrations from that experiment are shown in Table 5-62. The aerobic trace element results were reported as the dissolved concentration versus the total concentration. Table 5-62 shows several clear differences in leachate concentrations of select trace elements between aerobic and anaerobic conditions. Under aerobic conditions, concentrations of arsenic, lead, and mercury with one exception, were

Table 5-59. Microbiological Release Experiment Sample Summary, Experiment 7

ID No.	Sample Type	Coal Type	24-hour pH	Total Hg, µg/g
03-006	Fly ash	Eastern bituminous	6.78	0.194
03-007	Fly ash	Eastern bituminous	5.52	0.141
04-003	Fly ash	Eastern bituminous	8.54	0.685
05-018	Fly ash	Eastern bituminous	8.49	0.123

Table 5-60. Microbiological Experiment 7 Eh and pH Results

Anaerobic			Aerobic		
ID No.	Eh, mV	pH	ID No.	Eh, mV	pH
03-006	209.0	6.98	03-006	98.3	8.87
03-006	177.3	7.00	03-006	196	8.78
03-006	167.7	6.87	03-006	83.8	8.70
03-007	207.5	6.71	03-007	126	8.64
03-007	178.3	6.64	03-007	195	8.72
03-007	163.5	6.69	03-007	103	8.65
04-003	95.3	6.95	04-003	156	8.77
04-003	51.4	8.49	04-003	119	8.60
04-003	62.3	8.49	04-003	98.5	8.61
05-018	14.2	7.91	05-018	149	8.60
05-018	11.5	7.86	05-018	97.0	8.63
05-018	2.4	8.06	05-018	116	8.54

Table 5-61. Vapor-Phase Mercury Release Results, pg/g/day, Experiment 7

Anaerobic			Aerobic		
ID No.	Elemental Mercury	Organomercury	ID No.	Elemental Mercury	Organomercury
03-006	0.130	0.164	03-006	17.9	1.91
03-006	0.255	0.095	03-006	5.36	0.524
03-006	0.178	0.075	03-006	6.08	0.752
03-007	0.253	0.050	03-007	5.89	0.206
03-007	6.17	0.104	03-007	1.11	0.215
03-007	0.388	0.180	03-007	13.6	1.51
04-003	0.068	0.046	04-003	15.6	0.035
04-003	0.249	0.057	04-003	4.17	0.085
04-003	0.285	0.039	04-003	10.3	0.174
05-018	12.1	0.763	05-018	17.7	1.07
05-018	0.797	0.120	05-018	21.3	0.717
05-018	1.74	0.212	05-018	34.9	3.24

elevated. Under anaerobic conditions, concentrations of chromium, nickel, and selenium were elevated. Under both conditions, concentrations of cadmium remained about the same. It could be hypothesized that since under aerobic conditions pH values were elevated, simple pH control of conditions would explain the leachate concentrations. However, the slightly depressed concentrations of cadmium in the aerobic experiments make that unlikely. Cadmium solubility over the pH range 6–9 would be expected to be much like that of lead and it was not. It is likely that in these experiments it was the differences in microbial and fungal populations that exerted a major influence in the final solution concentrations of trace elements.

Summaries of vapor-phase release information generated in all experiments in this subtask are included in Tables 5-63 for fly ash samples and 5-64 for FGD–SDA and wet FGD filtercake.

Table 5-62. Microbiologically Leached Total Trace Element Results, µg/L, Experiment 7

Anaerobic									Aerobic								
ID No.	As	Cd	Cr	Pb	Hg	Ni	Se	pH	ID No.	As	Cd	Cr	Pb	Hg	Ni	Se	pH
03-006	644	3.40	6.8	<2	0.134	128	608	6.98	03-006	2190	2.42	3.4	59.8	NT	8.6	216	8.87
03-006	663	3.37	6.8	<2	<0.01	122	617	7.00	03-006	2310	2.53	3.1	15.8	0.120	15.5	217	8.78
03-006	638	3.68	7.2	<2	<0.01	122	607	6.87	03-006	2160	2.25	<2	6.6	0.023	7.9	169	8.70
03-007	398	4.55	6.6	<2	<0.01	144	585	6.71	03-007	2010	2.67	<2	4.1	0.025	33.9	162	8.64
03-007	419	4.34	6.4	<2	<0.01	125	616	6.64	03-007	1320	3.13	3.5	8.4	<0.01	58.8	198	8.72
03-007	421	4.50	6.4	<2	0.247	125	602	6.69	03-007	1820	2.61	3.6	3.8	0.079	6.9	119	8.65
04-003	438	2.32	8.8	<2	0.009	111	655	6.95	04-003	1300	1.78	5.3	3.5	0.172	4.9	354	8.77
04-003	569	2.33	12.7	<2	<0.01	160	793	8.49	04-003	1170	1.70	3.1	3.2	0.157	8.1	300	8.60
04-003	596	2.38	12.9	<2	<0.01	160	823	8.49	04-003	1320	1.81	7.1	2.2	0.356	10.8	368	8.61
05-018	785	11.6	11.3	<2	NT	270	753	7.91	05-018	1290	7.96	4.1	5.1	0.191	58.1	378	8.60
05-018	726	10.9	10.4	<2	NT	249	723	7.86	05-018	1520	8.01	5.3	9.8	0.124	43.9	483	8.63
05-018	772	10.8	13.8	<2	NT	278	725	8.06	05-018	1370	8.51	4.0	3.3	0.164	259	471	8.54

Table 5-63. Summary of Vapor-Phase Mercury Releases from Microbiologically Mediated Experiments on Fly Ash Samples

					Vapor-Phase Hg Releases, pg/g/day			
					Anaerobic		Aerobic	
Experiment No.	ID No.	Sample Type	Coal Type	Total Hg, µg/g	Elemental Hg	Organo Hg	Elemental Hg	Organo Hg
2	01-002	FA	Bituminous	0.785	0.1 – 0.24	0.008 – 0.009	0.09 – 1.1	0.008 – 0.032
3	03-060	FA + AC	Subtuminous	0.689	0.03 – 0.09	0.002 – 0.008	0.65 – 1.7	0.007 – 0.010
4	03-079	FA	Lignite	0.160	0.56 – 1.06	1.00 – 1.34	2.26 – 3.96	0.50 – 6.16
4	04-043	FA	Lignite	0.287	0.26 – 0.44	0.12 – 0.22	0.08 – 9.30	0.26 – 0.90
5*	04-035	FA	Lignite	0.194	0.03 – 0.04	0.03 – 0.14	0.15 – 0.20	0.02 – 0.11
5	04-036	FA + AC	Lignite	0.41	0.03 – 0.52	0.02 – 0.14	0.26 – 0.45	0.07 – 0.11
7	03-006	FA	Bituminous	0.685	0.13 – 0.25	0.07 – 0.16	5.36 – 17.9	0.52 – 1.91
7	03-007	FA	Bituminous	0.123	0.25 – 6.17	0.05 – 0.18	1.11 – 13.6	0.21 – 1.51
7	04-003	FA	Bituminous	0.234	0.07 – 0.28	0.04 – 0.06	4.17 – 15.6	0.04 – 0.17
7	05-018	FA	Bituminous	1.86	0.80 – 12.1	0.12 – 0.76	17.7 – 34.9	0.72 – 3.24

* Shading indicates paired samples.

Key observations made based on the results of these experiments are as follows:

- Analysis of mercury was hindered by high analytical blanks and generation of hydrogen sulfide from high-sulfur samples that contaminated the analytical traps.

- Maintenance of neutral pH and associated microbial growth could not be achieved for samples with an initially high pH.

- Fungi was present in some samples under aerobic conditions and, when fungi was noted, the vapor-phase mercury releases were higher than in replicate sample flasks where no fungi was evident.

- Aerobic conditions resulted in increased vapor-phase mercury releases for both elemental and organomercury for all samples evaluated.

- The FGD–SDA and wet FGD filtercake exhibited significantly higher vapor-phase mercury release rates than the fly ash samples evaluated, and the FGD–SDA sample evaluated had the highest release rate of vapor-phase mercury.

- The formation of organomercury compounds was evident in all of the microbiologically mediated experiments. It was observed, however, that organomercury formation appears to be directly related to the amount of fungi present in the flasks at the end of the experiments.

- The mercury released from the CCB slurry was generally higher in the samples fed with glucose versus starved samples. The final experiments only included "fed" systems.

Sulfate-reducing bacteria in sulfur-rich samples such as FGD material tended to form large amounts of hydrogen sulfide in the anaerobic flasks. This hydrogen sulfide production required putting traps on the flasks in order to keep the hydrogen sulfide and its odor out of the lab. The

Table 5-64. Summary of Vapor-Phase Mercury Releases from Microbiologically Mediated Experiments on FGD–SDA and Wet FGD Filtercake Samples

					Vapor-Phase Releases, pg/g/day			
					Anaerobic		Aerobic	
Experiment No.	ID No.	Sample Type	Coal Type	Total Hg, µg/g	Total Hg	Organo Hg	Total Hg	Organo Hg
1	99-188	FGD–SDA	Subbituminous	0.131	31.5 – 43.5	NT	1090 – 2110	NT
4	03-082	Wet FGD Filtercake	Bituminous	0.218	0.14 – 2.54	0.52 – 20.4	97.2 – 130	18 – 22
5[1]	03-082	Wet FGD Filtercake	Bituminous	0.218	1.54	NT	4.64 – 9.69	0.94 – 1.62

[1] Microbes were not added.

hydrogen sulfide also made analyses impossible because of the formation of colloidal sulfur soon after the samples were harvested. Additionally, hydrogen sulfide collected in the Carbotrap™ tubes came off as elemental sulfur and precluded analyses of these traps in our normal manner. No solutions were developed to solve this analytical problem.

Highly alkaline ash samples generated from lignite have proven particularly difficult to maintain at near neutrality. Experiments performed in the absence of bacteria provide us with a neutralization capacity for acid addition, but in microbiological experiments, these neutralized solutions quickly rose to above pH 10.5, thus killing the bacteria. We had been using dilute sulfuric acid for neutralization and believe that after neutralization, a sulfate coating has deposited around individual particles. After bacteria were introduced, we believe that the bacterial action may have removed the protective sulfate coating from alkaline particles, thus releasing additional alkalinity. At this time, this is our only working hypothesis, and solutions based on this hypothesis are under investigation.

It is important to note that although methylation did predictably occur, the apparent rate and resultant concentrations of methylmercury were extremely small. Research on the issue of methylation of mercury and other trace elements such as selenium and arsenic are currently ongoing. Despite the extreme toxicity of methylated mercury species, there does not appear to be evidence that would lead to any need for special precautions at this time. Methylation of select trace elements is a phenomenon that should be expected to occur and which is known to occur in sites with natural sources of arsenic, mercury, and selenium. The research team's primary observation was that the presence of fungi under aerobic conditions appears to be a primary source of methyl mercury. It was expected at the onset of these experiments that the presence of sulfate-reducing bacteria under anaerobic conditions would be a primary source of methylation. This was not the case despite the presence of sulfate-reducing bacteria in samples with high concentrations of sulfate.

The presence of these specific bacteria was determined by the strong odor of hydrogen sulfide in samples with high concentrations of sulfate under anaerobic conditions. The presence of hydrogen sulfide was significant enough that scrubbers were added to the flasks in order to keep the air in the lab breathable.

5.6 Field Investigations

The goal of the field investigation task was to develop information to facilitate an understanding of how laboratory results could be used to understand the potential for releases of ATEs from CCBs in real-world management settings. As already stated, field concentrations of constituents released from CCBs by exposure to water cannot be predicted by laboratory leaching test results, but leaching can provide information that can be used to determine if the potential for mobility of one or more constituents is at a level that warrants further consideration prior to a material being placed in specific environmental settings or conditions. The field task focused on obtaining information on mercury concentrations in the air near and around CCB disposal facilities in order to make a preliminary determination on how to best use results from laboratory vapor-phase experiments to provide information valuable in an assessment of the potential for vapor-phase mercury release to impact atmospheric mercury loading. This task was

accomplished in two subtasks: 1) Evaluation of Vapor-Phase Mercury at CCB Disposal Sites and 2) Small-Scale Vapor-Phase Mercury Release from Soil–Ash Mixtures. On completion of the first field subtask, the data were reviewed and compared with other field data, and it was agreed by project sponsors that instead of performing another field site investigation, it would be more valuable to carry out a small-scale evaluation of vapor-phase mercury release from soil–ash mixtures since this was an ash utilization scenario that might fall under scrutiny by regulatory agencies and citizen groups.

5.6.1 Field Task 1

The first subtask of the field investigation task was performed at CCB management facilities associated with a lignite-fired power plant. The EERC contracted with UNR to perform the mercury flux measurements using a mercury flux chamber as reported previously by UNR (Engle et al., 2001; Xin et al., 2006). The field task consisted of three key activities: 1) collection of near-surface solid samples and water samples, where available; 2) mercury flux measurements taken at near-surface locations by UNR; and 3) collection of mercury samples from CCB landfill air at near-surface locations by the EERC. Air sampling was performed at a variety of locations as described in Table 4-3.

5.6.1.1 Measurement of Mercury in Field-Collected Solid Samples

Water samples and replicate solid samples (EERC and UNR) were obtained for laboratory testing. Solid composite samples were taken of the substrate on which the mercury air sampling was conducted. Composite samples are described in Table 4-3. Liquid samples were collected at disposal ponds where possible.

Averages of total mercury content of samples collected by both the EERC and UNR are noted in Table 5-65. Results from the two entities were similar for each jointly sampled substrate type. The total mercury concentrations for fly ash samples were low. The wet FGD material had the highest total mercury. The fly ash and bottom ash/mill rejects + wet FGD material total mercury contents were lower than the natural grasslands (background soil) and agricultural land.

Fundamental characterizations of the solid samples collected in the field by the EERC are noted in Table 5-66 and Appendix T. The stabilized FGD material (with fly ash) had the widest total mercury range. Moisture content and LOI in the bottom ash/mill rejects + wet FGD material samples exhibited the widest range of values. The range of pH values was similar in all samples.

5.6.1.2 Measurement of Mercury Flux by UNR

In situ mercury fluxes were measured under highly variable weather conditions ranging from bright, sunny days to cold, rainy days with strong wind. Measurements of relative humidity (24%–84%), solar irradiance (36–761 W/m^2), and temperature (8.6°–33.1°C) were made and varied widely depending on the weather conditions. Mercury flux measurements were performed at seven locations with varying substrates, and results are summarized in Table 5-67.

Table 5-65. Field Sample Composites and Associated CCB Mercury Analysis Results, average

Sample Type	Total Hg, µg/g EERC Results	Total Hg, µg/g UNR Results (Xin and Gustin, 2005)
Fly Ash	<0.01	<0.015
Vegetated Fly Ash with Soil Cover	NT	0.095
Wet FGD Material + Mill Rejects	0.197	0.179
Wet FGD Material	0.299	0.360
Bottom Ash/Mill Rejects + Wet FGD Material	0.014	NT
Stabilized Wet FGD Material (with fly ash)	0.114	0.23
Natural Grasslands (background soil)	0.050	0.05
Agricultural Land	NT	0.03

Table 5-66. Range of Fundamental Characterization Data in Field Samples Collected by the EERC

Sample Type	Total Mercury Content, µg/g	Moisture Content, %	LOI, %	10–15-min pH	Overnight pH
Fly Ash	<0.01	15.0	5.73	9.36	9.13
Wet FGD Material + Mill Rejects	0.188–0.207	19.3–21.3	2.18–3.31	8.62–8.68	8.51–8.53
Wet FGD Material	0.299	23.3	2.49	8.55	8.27
Stabilized Wet FGD Material (with fly ash)	0.011–0.250	10.1–23.5	2.68–3.68	8.72–10.33	8.63–10.81
Bottom Ash/Mill Rejects + Wet FGD Material	<0.01–0.044	7.02–28.8	1.99–13.0	8.77–9.78	9.29–10.33
Natural Grasslands (background soil)	0.050	12.6	6.88	8.57	8.40

Mercury flux was measured from eleven areas at the site. Five fly ash-sampling locations with low mercury emission fluxes (from 0.0 to 1.8 ng/m^2/hr) were measured, while two fly ash sites had higher emissions (4.5 ± 3.3 and 4.9 ± 2.5 ng/m^2/hr). For two other sites, the mean flux indicated deposition of atmospheric mercury to the fly ash during the day.

Mercury flux was also measured from three sites on a vegetated fly ash substrate. The fly ash was covered with a 2' clay cap and a 3' vegetated soil layer. Two of the measurement sites exhibited low mean mercury emission rates (0.9 and 1.3 ng/m^2/hr), and one site had an

Table 5-67. Summary of Mercury Fluxes Measured from Landfill Facilities (after Xin and Gustin, 2005)

Substrate Type	Number of Measurements on Substrate Surface	Range of Flux Measurements, ng/m^2/hr
Fly Ash	97	−0.2–4.9
Vegetated Fly Ash with Soil Cover	9	0.9–33.4
Wet FGD Material + Mill Rejects	12	6.9–15.9
Wet FGD Material	61	0.3–2.5
Stabilized Wet FGD Material (with fly ash)	61	0.7–22.2
Natural Grasslands (background soil)	9	−0.1–0.3
Agricultural Land	9	0.0–2.3

exceptionally high mercury mean emission rate (33.3 ng/m^2/hr). The high flux rate value was not used in further calculations because the sampling location was close to an active road and potentially had contaminated road dust or other road-related deposits to the soil surface.

For the wet FGD material substrate, which was disposed of in an ash pond, mercury emission flux was low. The mean daytime mercury flux was 1.3 ± 0.8 ng/m^2/hr and the mean nighttime mercury flux was 0.3 ± 0.3 ng/m^2/hr. The low emission for the saturated FGD material, as compared to that for wet but not saturated material, is similar to that reported for soils. Soils that are saturated have been shown to have low Hg emissions, but as soils dry, emissions increase (Gustin and Stamenkaric, 2005). Mercury emission rates were highest from the wet FGD materials.

For the stabilized wet FGD material (with fly ash) substrate, mercury flux varied significantly among measurement sites. Low mean mercury emission fluxes were measured at three sites (0.7–4.8 ng/m^2/hr), while higher mercury emission values were observed at two sites (10.9–22.2 ng/m^2/hr). The average daytime mercury flux was 11.5 ± 12.7 ng/m^2/hr, and the average nighttime mercury flux was 10.9 ± 7.2 ng/m^2/hr. The high variability of the data may be explained by the inhomogeneity of the wet FGD material and fly ash mixture within the disposal site. No correlation between mercury flux and light was observed for this substrate. The windy conditions when flux measurements were made on this substrate could also have affected the mercury flux (Gustin et al., 1997).

Mercury emissions were also measured for two types of soils in the surrounding area: a natural soil not obviously impacted by agriculture and a field. Mean flux ranged from −1–2.3 ng/m^2/hr during the day.

Observations can be summarized as follows:

- Wet FGD material (with fly ash) exhibited the highest release.

- Fly ash substrates exhibited very low mercury emissions, with the exception of one potentially contaminated site.

- Fly ash, vegetated fly ash with soil cover, and wet FGD material exhibited low mercury emissions similar to the background natural grasslands and agricultural land.

- No strong correlation was observed between mercury flux and total mercury concentration for the substrates evaluated.

The flux measurements were used to calculate an annual mercury release for each substrate, and those calculated releases are noted in Table 5-68 (Xin and Gustin, 2005). Based on calculations for this field site, about 20.6 g Hg/yr would be emitted from the five sites evaluated. For the same area of natural grassland, 0.4 g Hg/yr would be emitted, and 5.5 g Hg/yr would be emitted from the agricultural land.

Data from this work were compared with data collected from a CCB landfill facility in the eastern United States (Gustin and Ladwig, 2004) and a CCB landfill located in the Great Lakes area of the United States. The eastern site was a bituminous fly ash landfill visited in October 2002 and the Great Lakes site was a blended bituminous–subbituminous fly ash landfill visited in October 2003. The comparison data are shown in Table 5-69. Assuming a disposal area of 100,000 m^2 for all substrates at all disposal sites, annual mercury emissions were calculated. These are also included in Table 5-69.

The highest calculated mercury releases were noted for the lignite-based stabilized wet FGD material (with fly ash) and the wet FGD material + mill rejects. The lignite-derived barren fly ash had the highest mercury flux compared to bituminous and blended bituminous–subbituminous fly ash. Vegetated fly ash from the eastern United States and Great Lakes area acted as a mercury sink (mercury flux <0), whereas vegetated fly ash at the lignite site indicated

Table 5-68. Summary of Scaling of Emissions Using Field Site Data (Xin and Gustin, 2005)

Sample Type	Area[1], m^2	Mean Flux, $ng/m^2/hr$	Total Annual Flux, g/yr
Barren Fly Ash	141,642	1.1	1.4
Vegetated Fly Ash	56,657	1.1	0.5
Stabilized Wet FGD	141,642	11.2	13.9
Unstabilized Wet FGD	141,642	0.8	1.0
Wet FGD + Mill Rejects	40,469	10.9	3.9
TOTAL	522,050	-	20.6
Natural Grassland (background soil)	522,050	0.1	0.4
Agricultural Land	522,050	1.2	5.5

[1] Areas was estimated according to the field site landfill map.

Table 5-69. Comparison of Scaling of Hg Flux Using In Situ Data from Three Landfill Sites (Field site examined in this report, one site in Eastern United States, and one site in the Great Lakes area of the United States. Area used for scaling is 100,000 m^2 for each substrate. Mean flux was the average flux obtained from daytime and nighttime flux [Xin and Gustin, 2005])

Location	Coal Type	Sample Type	Mean Flux, ng/m^2/hr	Total Annual Flux, g/yr
Field Site Described in This Report	Lignite	Barren fly ash	1.1	0.9
		Vegetated fly ash	1.1	0.9
		Stabilized wet FGD	11.2	9.8
		Unstabilized wet FGD	0.8	0.7
		Wet FGD + mill rejects	10.9	9.5
		Natural grassland	0.1	0.1
		Agricultural land	1.2	1.1
Eastern United States	Bituminous	Barren fly ash	−0.2	−0.2
		Soil-covered fly ash	−9.5	−8.3
		Vegetated fly ash	−0.2	−0.2
Great Lakes Area in United States	Blended bituminous and subbituminous	Barren fly ash	0.9	0.8
		Vegetated fly ash	−0.1	−0.1
		Soil	0.5	0.5

a release of mercury. Xin et al. (2006) provides a detailed discussion of data collected in the eatstern United States and the Great Lakes region.

5.6.1.3 Measurement of Mercury in CCB Landfill Air by the EERC

Using the method described in the experimental section, sampling was performed at several locations at the CCB landfill site. Measurements were taken at locations near the UNR mercury flux measurement locations when possible. Results generated by the EERC at storage sites for elemental mercury captured on gold traps and organomercury captured on Supelco Carbotrap™-containing tubes are outlined in Table 5-70. The results are reported as ng/m^3, which refers to the amount of mercury captured on traps while a determined amount of CCB landfill air was drawn through the tubes.

The measured CCB landfill air mercury values were low and generally comparable to air measurements made at locations in the natural grasslands, which served as an undisturbed background site. The highest elemental mercury concentrations were measured near the wet FGD material + mill rejects. Most of the other elemental mercury air measurements were similar.

The measured organomercury concentrations, however, were all very low, with the stabilized wet FGD material (with fly ash) sampling location yielding the highest reading.

Table 5-70. Average CCB Landfill Mercury Readings and Standard Deviation, ng/m^3 (field blanks were subtracted)

Substrate Type	Elemental Mercury	n	Organomercury	n	Calculated Total Mercury
Fly Ash	1.021 ± 0.238	4	0.052 ± 0.038	2	1.073
Vegetated Fly Ash with Soil Cover	0.616 ± 0.277	4	0.019 ± 0.026	2	0.635
Wet FGD Material + Mill Rejects	1.459 ± 0.995	4	0.006 ± 0.002	2	1.465
Wet FGD Material	0.954 ± 0.413	4	0.045 ± 0.042	2	0.999
Bottom Ash/Mill Rejects + Wet FGD Material	0.541 ± 0.193	4	0.023 ± 0.011	2	0.564
Stabilized Wet FGD Material (with fly ash)	0.849 ± 0.378	4	0.354 ± 0.476	2	1.203
Natural Grasslands (background soil)	0.640 ± 0.270	4	0.017 ± 0.004	2	0.657

In Table 5-70, a calculated total mercury for air at each location is included. Using this value, the measurements can be listed from highest to lowest:

Wet FGD material + mill rejects
> Stabilized wet FGD material (with fly ash)
> Fly ash
> Wet FGD material
> Natural grasslands (background soil)
> Vegetated fly ash with soil cover
> Bottom ash/mill rejects + wet FGD material (sample not evaluated by UNR)

In comparison, the mercury flux measurements performed by UNR resulted in the following indication of high to low mercury associations by substrate:

Wet FGD material + mill rejects
> Stabilized wet FGD material (with fly ash)
> Fly ash
> Agricultural land (sample not evaluated by EERC)
= Wet FGD material
> Vegetated fly ash with soil cover
> Natural grasslands (background soil)

5.6.2 Alternate Field Task

The Phase 2 field investigation (alternate field task) was developed in response to project sponsor input on results of Field Task 1. It was agreed that a useful addition to this task would be to evaluate the impact of interaction between soil and CCBs on mercury release from CCBs, especially since CCBs are used in numerous soil applications. The interaction of greatest interest was that caused by inherent microbiological organisms typically found in soils. The CCB–soil laboratory experimental apparatus was designed to evaluate microbiologically mediated mercury release from CCB–soil mixtures, analogous to utilization management practices in the field. Elemental mercury and organomercury release measurements were evaluated. Fundamental characterization data of the soil used are in Appendix T.

The results of the elemental mercury release are shown in Table 5-71, reported in a manner similar to the long-term ambient-temperature release experiments for CCBs. The total mercury content of the CCB–soil mixtures was not measured; therefore, a calculation based on the total mercury content of the separate components and the mixture percentage is given in Table 5-71. Each sample bottle had a blank bottle measurement of elemental mercury prior to introduction of the CCB–soil mixture. Sorption or release of elemental mercury was determined by subtracting the blank value from the measurements. The calculations in the columns labeled "Cumulative % Elemental Hg Sorption or Release from Mix" and "Years to Release 100% Elemental Hg at Measured Rate" are based on the calculated mixture total mercury content. Paired samples (Samples 05-038 and 05-025) are highlighted; these samples are from the larger sample set of paired lignite fly ash samples.

During the duration of the experiment, the research team was unable to collect replicate data for two samples (Samples 05-038 and 06-014) because of apparatus difficulties that developed.

The results show that the soil–peat moss mixture (only one data point) used in this task sorbed elemental mercury. The CCB–soil mixtures exhibited low levels of elemental mercury release, with the exception of one replicate. On average, over 100,000 years of air movement over the CCB–soil mixtures is required to release all mercury from the system. Samples that had AC present released lower percentages of elemental mercury than those without AC present, even though the total mercury was higher in the samples with AC, especially those collected after the primary PCD. On average, the samples with AC present released mercury an order of magnitude lower percentage than the sample from a similar coal source without AC. However, as shown in Appendix U, the measured elemental mercury release rate was higher for the fly ash + AC (post-primary PCD) samples. The paired sample set provided a good comparison of a fly ash sample without and with AC present.

Organomercury results are reported in Table 5-72. No organomercury blank value measurements were performed since preparation of the experimental vessel (heating to >500°C) was expected to eliminate any organomercury from the container. Therefore, the organomercury collected from the soil-only bottle served as the blank for the experiment. This allowed for a determination of the impact of each CCB in each CCB–soil mixture.

Table 5-71. Alternative Field Task (CCB–soil) Elemental Mercury Results Summary. Positive values indicate release and negative values indicate sorption of elemental mercury. Duplicate bottles are represented.

					Replicate 1		Replicate 2	
ID No.	Sample Type	Coal Type	Calculated Mixture Total Hg, µg/g	Cumulative No. Days	Cumulative % Elemental Hg Sorption or Release from Mix	Years to Release 100% Elemental Hg at Measured Rate	Cumulative % Elemental Hg Sorption or Release from Mix	Years to Release 100% Elemental Hg at Measured Rate
04-003	Fly ash	Eastern bituminous	0.190	167	0.00105	43,693	0.000590	77,517
04-054	Fly ash + AC (post-primary PCD)	Eastern bituminous	3.60	167	0.000288	158,678	0.000295	154,928
04-029	Fly ash	PRB subbituminous	0.106	167	0.00529	8,650	0.00414	11,056
03-060	Fly ash + AC (pre-primary PCD)	PRB subbituminous	0.426	166	−0.000195	NA – sorbing	0.000123	368,455
05-038[1]	Fly ash	Lignite	0.0740	166	0.00266	17,075	NQ[2]	NQ
05-025	Fly ash + AC (post-primary PCD: high ash)	Lignite	2.58	167	0.000205	222,968	0.000266	172,319
05-009	FGD gypsum	Eastern bituminous	0.0598	166	0.00181	25,189	0.00101	45,221
06-014	Soil	None	0.0666	166	NQ	NQ	−0.00205	NA – sorbing

[1] Shading indicates paired samples.

[2] Not quantitated.

Table 5-72. Alternative Field Task (CCB–soil) Organomercury Results Summary. Results are expressed as a comparison to the soil used as blank. Positive values indicate release, and negative values indicate sorption of organomercury. Duplicate bottles are represented.

					Replicate 1		Replicate 2	
ID No.	Sample Type	Coal Type	Calculated Mixture Total Hg, µg/g	Cumulative No. Days	Cumulative % Organomercury Sorption or Release from Mixture Compared to Soil	Years to Release 100% Organomercury at Measured Rate Compared to Soil	Cumulative % Organomercury Sorption or Release from Mixture Compared to Soil	Years to Release 100% Organomercury at Measured Rate Compared to Soil
04-003	Fly ash	Eastern bituminous	0.190	168	0.00134	34,465	0.000977	47,396
04-054	Fly ash + AC (post-primary PCD)	Eastern bituminous	3.60	171	−0.0000123	NA – below soil release	−0.0000207	NA – below soil release
04-029	Fly ash	PRB subbituminous	0.106	169	−0.000531	NA – below soil release	−0.000481	NA – below soil release
03-060	Fly ash + AC (pre-primary PCD)	PRB subbituminous	0.426	167	−0.000248	NA – below soil release	−0.000261	NA – below soil release
05-038[1]	Fly ash	Lignite	0.074	168	−0.00124	NA – below soil release	NQ	NQ
05-025	Fly ash + AC (post-primary PCD: high ash)	Lignite	2.58	172	0.0000297	1,588,470	−0.0000109	NA – below soil release
05-009	FGD gypsum	Eastern bituminous	0.0598	168	−0.000418	NA – below soil release	0.00358	12,858

[1] Shading indicates paired samples.

The results indicated that more organomercury was released from four of 13 replicate CCB–soil mixture bottles than from the soil-only bottle. All organomercury releases were low. Again, the samples with AC generally exhibited a lower-percentage release of mercury than those without AC present, although the difference was not as consistent as that observed for elemental mercury releases. The fly ash alone from the paired sample set released a lower-percentage organomercury by two orders of magnitude when compared to the fly ash + AC in the paired set.

The CCB sample elemental mercury vapor profiles for this task versus long-term ambient-temperature release and microbiologically mediated vapor-phase transport task profiles are provided in Table 5-73. The FGD gypsum sample evaluated in this task (Sample 05-009) exhibited elemental mercury release whether analyzed alone or when mixed with soil. Generally, fly ash samples that exhibited an overall elemental mercury sorption in the long-term ambient-temperature release experiment released mercury in the alternate field task when combined with soil. It was hypothesized by the project team during performance of the microbiologically mediated mercury release experiments that carbon (either unburned or activated) would provide a source of food for the microbes present in the system and might promote release of mercury. These limited results support that hypothesis.

5.7 Data Reduction and Interpretation

The standard analysis techniques used in the project indicate acceptable performance criteria. The repeatability of the data was within the expected ±20%, with the exception of the data produced in the microbiological experiments. In this case, the experiments are still a work in progress, with much improvement yet needed on the technique. This is nearing completion. Despite more variability than had been hoped for, the data still proved useful.

Data reduction and interpretation was performed on a task basis for the release and field tasks, incorporating information from the method and sample selection tasks. Data interpretation incorporated information from real-world ash management scenarios in an attempt to draw conclusions on Hg ATE releases under disposal and use scenarios.

6.0 CONCLUSIONS AND RECOMMENDATIONS

This project achieved its stated objectives, and based on the results of the laboratory and field experiments conducted in this project, the following conclusions were drawn:

- Results for “paired” baseline and test fly ash and FGD–SDA samples indicated that total mercury content was higher in the test samples. Test samples contained AC injected as mercury sorbent with one exception, where an EA only was injected. The higher total mercury content was also generally noted for all fly ash samples collected from systems without mercury emission controls as compared to fly ash that was collected from systems with mercury emission controls in place. No similar trend was noted for the limited nonpaired FGD–SDA samples.

Table 5-73. Overall Elemental Mercury Vapor Profiles in Noted Tasks

ID No.	Sample Type	Coal Type	Total Mercury Content, µg/g	LOI, %	Long-Term Ambient-Temperature Release: CCB Only	Alternate Field Task: CCB–Soil Mixture	Microbiologically Mediated Vapor-Phase Transport: CCB in Buffer
04-003	Fly ash	Eastern bituminous	0.685	8.45	NT	Release	Higher release under aerobic conditions
04-054	Fly ash + AC (post-primary PCD)	Eastern bituminous	17.7	18.6	Sorption	Release	NT
04-029	Fly ash	PRB subbituminous	0.261	0.48	Sorption	Release	NT
03-060	Fly ash + AC (pre-primary PCD)	PRB subbituminous	1.86	2.37	Release	Sorption	Higher release under aerobic conditions
05-038[1]	Fly ash	Lignite	0.104	0.22	Sorption	Release	NT
05-025	Fly ash + AC (post-primary PCD: high ash)	Lignite	12.6	3.19	Sorption	Release	NT
05-009	FGD gypsum	Eastern bituminous	0.032	1.92	Release	Release	NT
06-014	Soil	None	0.067	44.2	NT	Sorption	NT

[1] Shading indicates paired samples.

- The total selenium content of "paired" baseline and test fly ash samples with post-primary PCD ACI was higher for the test samples than the baseline samples. This trend was not noted for "paired" samples with pre-primary PCD ACI or generally for the nonpaired samples.

- Total concentrations of arsenic, cadmium, chromium, lead, and nickel were similar for all fly ash samples and FGD–SDA samples collected from systems with or without mercury emission controls in place. This was true for "paired" and nonpaired samples.

- Direct leaching tests indicated that mercury was not readily leached from fly ash or FGD materials. 87% of samples leached had at least one leachate mercury concentration below the 0.01 µg/L analytical reporting limit. Mercury leachate concentrations did not correlate to total mercury concentrations. In particular, the samples with the highest total mercury content showed no detectable leachate mercury. These conclusions were consistent for both paired and nonpaired samples.

- When exposed to ambient-temperature air in laboratory experiments, fly ash samples either released or sorbed small amounts of mercury. Samples containing unburned carbon or AC tended to sorb mercury in ambient-temperature vapor-phase experiments. For fly ash samples that release mercury, the rate of release generally decreased with time. For those that sorbed mercury, the rate of sorption was generally increased over the duration of the experiments. All wet FGD material, including FGD gypsum released mercury in ambient-temperature laboratory experiments. When releases were noted, they were extremely low, both in total released over extended laboratory tests and in rate released. Laboratory data indicated that the potential for ambient-temperature vapor-phase mercury releases from CCBs is unlikely to impact atmospheric mercury loading.

- Mercury was not released to the vapor-phase at temperatures below 250°C in elevated-temperature experiments. For some samples, the presence of AC with fly ash increased the temperature at which mercury was released when exposed to elevated temperature, but these samples were too limited in number to draw a final conclusion on the effect of AC on the initial release temperature for fly ash + AC. For most fly ash samples with and without AC present, all mercury was released from the sample before the sample reached 750°C. Interferences from sulfur compounds precluded the use of the method developed for FGD materials.

- Under microbiologically mediated conditions, elemental and organomercury were released both to the vapor phase and the leachate. While the levels of elemental and organomercury were low in both leachate and vapor, more elemental mercury was released. Fly ash samples with high pH values did not support microbial growth because the buffering capacity of the samples was too great. Samples of FGD material released hydrogen sulfide so mercury releases could not be quantitated. Very low amounts of elemental and organomercury releases were measured from soil–CCB mixtures in simulated field experiments. The results were consistent between the two experiments.

- Field experiments evaluated vapor-phase releases at a CCB disposal site. Results indicated low-level vapor-phase mercury releases, as was generally noted in laboratory experiments for lignite fly ash samples. Releases from FGD materials were noted both in laboratory and field measurements.

- Laboratory methods were developed to evaluate the potential for mercury releases under several release mechanisms.

Based on the results of this project, the following recommendations were made:

- Further work is needed on fly ash + noncarbon sorbents, fly ash + EAs, and fly ash + carbon and noncarbon sorbents with EAs.

- Further investigations are required to better quantitate mercury releases from FGD materials and understand the mechanisms of release.

- Highly alkaline fly ash samples with or without sorbent or additives do not need to be subjected to microbiologically mediated release experiments. Future work could include samples of alkaline fly ash mixed with other CCBs such as FGD material that might provide adequate neutralization to support microbial growth.

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APPENDIX A

SAMPLE IDENTIFICATION FORM

SAMPLE IDENTIFICATION FORM
Mercury and Air Toxic Element Impacts of Coal Combustion Byproduct Disposal and Utilization

Company:

Station: Unit:

Contact Name (to relay data):

Date Sample Collected:

SYSTEM INFORMATION

BURNER TYPE
☐ Pulverized Coal-Fired
☐ Cyclone
☐ Stoker
☐ Fluidized-bed combustion (FBC)

☐ Low-NO_x Burners

PARTICULATE COLLECTION
☐ Fabric Filter (FF)
☐ Electrostatic Precipitator (ESP) Cold Side
☐ ESP Hot Side
☐ ESP/Mechanical
☐ FF/Mechanical
☐ Other: _____

SO_2 CONTROL
☐ None
☐ Wet Flue Gas Desulfurization (FGD) (calcium based)
  ☐ Lime
  ☐ Limestone sorbents
  ☐ Forced oxidation
  ☐ Natural or in situ oxidation
☐ Dry FGD (calcium based)
☐ Spray Dryer Atomizer
☐ Wet FGD (alkali based)
☐ Dry FGD (alkali based)
☐ Other:_____

AMMONIA-BASED SYSTEM
☐ None
☐ Ammonia Injection
☐ Selective Catalytic Reduction
☐ Selective Noncatalytic Reduction

MERCURY CONTROL

☐ None
☐ Carbon Injection Injection Rate: _____
☐ Noncarbon Sorbent Injection Injection Rate: _____
☐ Modified FGD
☐ Fine Particulate Control
☐ Fly Ash from Carbon Removal Technologies
☐ Other: _____

SAMPLE INFORMATION

FUEL TYPE

☐ Bituminous
☐ Subbituminous
☐ Lignite
☐ Bituminous–Subbituminous Blend: ___% Bituminous/___% Subbituminous
☐ Subbituminous–Lignite Blend: ___% Subbituminous/___% Lignite
☐ Oil
☐ Other_____

SAMPLE TYPE(S)

☐ Fly Ash
☐ FGD
☐ Blend: ___% _____/ ___% _____
☐ Filtrate
☐ Other: _____

COLLECTION POINT(S)

☐ FF
☐ ESP Field
Specify: _____
☐ ESP Hopper
Specify: _____
☐ Silo
☐ Pond/Landfill
☐ Other: _____

OTHER INFORMATION

_____

Project ID	Sample Type	Collection Point	Other Description
03-321 EXAMPLE	Fly Ash	ESP Row 2	Composite 03/21/03–04/02/03; Activated Carbon Injection 5 lb/MMacf

Return this form and samples to:
Loreal Heebink
Energy & Environmental Research Center
15 N 23rd Street
Grand Forks, ND 58203

lheebink@undeerc.org
Phone: (701) 777-5116
Fax: (701) 777-5181

APPENDIX B

DRAFT STANDARD METHOD FOR SYNTHETIC GROUNDWATER LEACHING PROCEDURE

APPENDIX A

DRAFT ASTM STANDARD METHOD FOR SYNTHETIC GROUNDWATER LEACHING PROCEDURE

DRAFT ASTM STANDARD METHOD FOR SYNTHETIC GROUNDWATER LEACHING PROCEDURE

1. Scope

1.1 This method determines the leachability of constituents in wastes, products, or materials using a leaching solution designed to simulate leachate anticipated in field conditions. The method allows for prediction of changes in leachability brought about as a result of the formation of secondary hydrated phases and new minerals through interaction of the waste and water over extended periods of time.

1.2 his method consists of the agitation of waste and a synthetic groundwater solution over an extended period of time (greater than 60 days) with sampling at regular intervals.

1.3 This method allows a comparison of maximum leachate concentration with actual concentrations of leachate at time intervals of from 18 hours to 2 months or greater. The method allows for determination of mass of analyte mobilized based on a leachate concentration and percent of total element leached and provides information to estimate leachate concentration trends with respect to time.

1.4 This method may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this method to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Applicable Documents

2.1 American Society for Testing and Materials (ASTM) Standards:
D1129 Definitions of Terms Relating to Water
D1193 Specification for Reagent Water
D3987 Shake Extraction of Solid Waste with Water
D2216 Method for Laboratory Determination of Moisture Content of Soils

2.2Toxicity Characteristic Leaching Procedure (TCLP) EPA Method 1311

3. Definitions

3.1 For definitions of terms in this test method, see Definitions D1129.

3.2 Ettringite: Ettringite is a mineral having the nominal composition $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$. Ettringite is also the family name for a series of related compounds as is the case for many mineral families. Ettringite has characteristic structural features that are fairly unique. The structure comprises of calcium aluminate columns $\{Ca_6Al_2(OH)_{12}24H_2O\}^{6+}$ with the channels between these columns containing the other components, which include an oxyanion such as sulfate with hydroxide and water $\{(SO_4)_{2\text{-}4}\ (OH)_{0\text{-}4}\ (H_2O)_{0\text{-}6}\}^{6-}$. Ettringite is unique in that several elements that exist as oxyanions can substitute for the sulfate in the structure. These elements include but are not limited to arsenic, boron, chromium, molybdenum, selenium, and vanadium. Ettringite is known to form in the hydration of low-rank coal conversion solid residues

(CCSRs) and in CCSRs from advanced coal combustion processes such as fluidized-bed combustion (FBC) and limestone injection modified burner (LIMB).

3.3 Synthetic Groundwater: Synthetic groundwater as used in this application refers to a solution prepared in the laboratory containing the major geochemical parameters that would be found in water likely to contact the disposed CCSR. In the case of rainwater contact, this solution would be Type IV water, while with groundwater, a typical solution might contain calcium, magnesium, sodium, sulfate, and bicarbonate. Groundwater collected at the site of disposal could also be used, although if that were the case, corrections would have to be made for concentrations of trace elements already present in the water. It has been found with most CCSRs that it is the CCSR that regulates the equilibrium concentrations of major constituents in a synthetic groundwater leaching procedure; thus the inclusion of major geochemical constituents of actual groundwater may be unnecessary in many cases.

4. Significance and Use

4.1 This test is intended as a means for determining the mass of analyte readily mobilized by leaching with groundwater and also provides a means of determining the trend of leachate concentration change, if applicable. This test is intended for use with CCSRs and other materials formed under conditions of high temperature. The long-term nature of the test allows the determination of changes in concentrations of leached constituents as materials react with water to form secondary hydrated phases and other materials not present in the original material.

4.2 This test method is not intended to provide an accurate means of determining actual leachate concentrations under field conditions. The test does provide information about leaching under field conditions, however, and is useful in predicting the mobility of leachable constituents of CCSRs. The information provided from this test is an estimation of the mass of analyte that can be solubilized and trend of concentration change with respect to time. It should be noted that not all analytes will increase in concentration to an equilibrium level. Numerous elements, especially those trace elements that exist as oxyanions in aqueous solution, can exhibit a decrease in solution concentration after an initial and normally rapid increase in concentration. Additionally, major constituents can change solution concentration in a manner that would not be predicted on the basis of solubility calculations based on common mineral types, especially in CCSRs that form ettringite.

4.3 Since CCSRs are produced under conditions of high temperature, reactions with water during leaching can be expected. If these reactions produce ettringite, the concentrations of analytes present in solution as oxyanions can be expected to decrease with respect to time as ettringite forms. Other mineral formation can be expected to control leachate concentrations of additional analytes in ways not expected from simple solubility calculations based on the composition of ash before leaching. Additionally, the formation of secondary hydrated phases can be expected to affect the concentrations of major components.

5. Apparatus

5.1 For a complete description of the apparatus, see ASTM Standard Test Method for Shake Extraction of Solid Waste with Water. Any apparatus that can provide conditions of end-over-end agitation at 30 plus or minus 2 rpm as specified in the protocol for the TCLP can be used in this procedure.

6. Reagents

6.1 Purity of Reagents – Reagent-grade chemicals can be used, provided they do not contain appreciable amounts of elements to be determined in the extraction test. Reagents must be of sufficient purity so they do not interfere with the accuracy of the test or introduce bias in the results of analyses of leachates.

6.2 Purity of Water – Unless otherwise indicated, references to water shall be understood to mean Type IV reagent water at 18° to 27°C (Specification D1193). The method by which the Type IV water is prepared (distillation, ion exchange, reverse osmosis, etc.) should remain constant throughout the test.

6.3 Synthetic Groundwater – Synthetic groundwater is a leaching solution containing the major geochemical parameters important to groundwater likely to contact disposed CCSRs. As previously stated, in the case of CCSRs disposed above the water table and where the likely water to contact the disposed materials is rainwater, Type IV water can be used as the leaching solution. Where the water likely to contact disposed material is highly mineralized, either a sample of the water itself or a synthetic mixture prepared in the lab will be used. A typical North Dakota synthetic groundwater can be prepared by dissolving 0.50 grams of sodium sulfate and 1.00 grams of sodium bicarbonate in one liter of Type IV water. The analysis of this solution is as follows:

Na	436 mg/L
SO_4	338 mg/L
HCO_3	726 mg/L
pH	8.3–8.7

This sodium sulfate bicarbonate buffered water is typical for central and western North Dakota. Used for leaching low-rank coal ash, calcium was omitted since the ash itself ultimately determined the final calcium concentration.

Other formulas for synthetic groundwater can be prepared as needed for site-specific conditions. Care is required when preparing formulations containing calcium and magnesium that carbonates not be allowed to precipitate. This can be overcome by adding the reagents in the proper order, being certain that all carbonate is buffered to bicarbonate before adding the calcium and magnesium. Since sulfuric acid is used for sulfate and acid buffering, having excess sulfuric acid acidity will ensure this. A lotus spreadsheet is available for the calculations necessary to select reagents for synthetic groundwater formulations, but with the limited components, the calculations can also be easily carried out manually.

7. Sampling

8. Sample Preparation

8.1 For sample preparation, see D3987 Standard Test Method for Shake Extraction of Solid Waste with Water.

9. Procedure

The laboratory protocol is similar to the U.S. Environmental Protection Agency (EPA) TCLP and ASTM D3987 Standard Test Method for Shake Extraction of Solid Waste with Water. The primary difference is in the selection and preparation of the extraction fluid and the extension of test equilibration time over the prescribed 18-hour period. The long-term leaching aspect of this test is especially important since CCSRs can form secondary hydrated phases upon contact with water that can have a profound impact on leachate concentration of trace elements, especially elements that tend to exist as oxyanions in solution. The formation of secondary hydrated phases is known to take time, depending on the source of reactants in the leaching system. Time for complete formation of secondary hydrated phases can be from days to months. The test is not intended to carry the leaching to complete equilibrium but rather to extend the leaching time long enough for prediction of leachate concentration trends. For specifics related to the test, see D3987 Standard Test Method for Shake Extraction of Solid Waste with Water, or EPA Method 1311 TCLP, Federal Register, Vol 55, No. 126, June 29, 1990.

9.1 Record the physical description of the sample to be tested including particle size as known.

9.2 Solids Content – Determine the solids content of the sample as described in D3987 Standard Test Method for Shake Extraction of Solid Waste with Water, Sections 9.2.1 through 9.2.4.

9.3 Shake Procedure – Prepare the apparatus and begin the test as described in D3987 Standard Test Method for Shake Extraction of Solid Waste with Water, Sections 9.4 through 9.7, except that multiple shake test containers are prepared for each sample, the number depending on the duration of long-term leaching. Leaching solution shall be prepared as described in the following section. Long-term leaching intervals for this procedure are 18 hours, 1 week, 1 month, and 2 months. Longer times can be used if desired, although trends are usually identified within the 60-day duration of this long-term leaching procedure. An alternative to the use of 2 liters of leaching solution involves the use of 225-mL polysulfone bottles. To each bottle, 10 grams (dry weight) of ash is added along with 200 mL of leaching solution. Multiple bottles prepared in this manner provide at least 150 mL of leachate and allow for the simultaneous extraction of a large number of samples with minimal space and equipment. It has been found that the standard equipment used for TCLP leaching will generally hold four of the polysulfone containers in the same position usually reserved for one 2-liter container.

9.4 Preparation of Leaching Solution: Leaching solution shall be prepared as recommended by an evaluation of field conditions. Where material disposed in a monofill is above the water table, the leaching solution shall be Type IV water (D1193 Specification for Reagent Water). Where the disposed material will likely be contacted by groundwater,

either a sample of groundwater from the site or a synthetic groundwater shall be used for leaching. The synthetic groundwater if prepared in the lab shall contain all of the primary mineralization parameters as determined from an analysis of groundwater from the site or from an evaluation of data from analysis reports of water representative of the area of disposal.

9.5 Long-Term Leaching Sampling – Long-term samples are taken from containers prepared for the shake test in an identical manner to the specimen for the 18-hour sampling period. These containers are sampled at the end of 1 week, 1 month, and 2 months. Longer sampling intervals can be added as required. A convenient method for doing this procedure is to prepare the samples at time intervals so that all of the samples are finished at the same time. For example, one sample is prepared, a second is prepared 1 month later, a third sample 1 month later, and a final sample 18 hours before the other samples are due to be terminated. This saves considerable lab time and expedites the entire procedure.

9.6 Sampling of Leachate – Leachate is sampled for analysis as specified in D3987 Standard Test Method for Shake Extraction of Solid Waste with Water, Section 9.8.

9.7 Analysis

9.7.1 Selection of Analytes to Be Included in the Report. Analytes include all elements present in the ash in high enough concentrations to be problematic in disposal. These can be determined through screening procedures such as proton-induced x-ray emission (PIXE), instrumental neutron activation analysis (INAA), or plasma emission such as inductively coupled argon plasma (ICAP) spectroscopy or ICAP–mass spectrometry. Analytes for ash screening generally include the eight Resource Conservation and Recovery Act (RCRA) elements for regulatory purposes.

9.7.2 Determination of Total Concentration of Select Analytes. Analytes selected on the basis of screening (9.6.1) are determined on a bulk sample prepared by digestion of sample in a microwave heated-sealed Teflon bomb. Analyses can be performed according to methods for trace analyses in SW846.

9.7.3 Determination of Analyte Concentrations in Leachates. Concentrations of analytes in leachates shall be determined using methods as described in SW846 or by approved analytical techniques using EPA or other approved techniques. All data shall be validated using good laboratory practice and approved quality assurance/quality control (QA/QC) procedures.

10. Calculation

10.1 Calculate the solids content as specified in D3987 Standard Test Method for Shake Extraction of Solid Waste with Water, Section 10.1.

10.2 Calculation of maximum analyte concentration is determined by dividing the total mass of analyte in a sample by the volume of liquid used for leaching. C = M/V where
C = Concentration of analyte
M = Mass of sample leached
V = Volume of leaching solution used

For this procedure the M:V ratio should be 1:20 as specified in the leaching protocol.

11. Report

11.1 The report shall include the following:

11.1.1 Source of CCSR, date of sampling, and preservation method used for leachates.
11.1.2 Description of CCSR including coal source, combustion technique, and method of sample collection (electrostatic precipitator, baghouse, etc.)
11.1.3 Solids content (see Method D2216)
11.1.4 A table of maximum analyte concentrations as determined by the method described in Section 10.2. (bulk chemical analysis)
11.1.5 A table of analyte concentrations as determined from analysis of 18-hour, 1-week, 1-month, 2-month, and any additional extended time intervals selected.

12. Precision and Bias

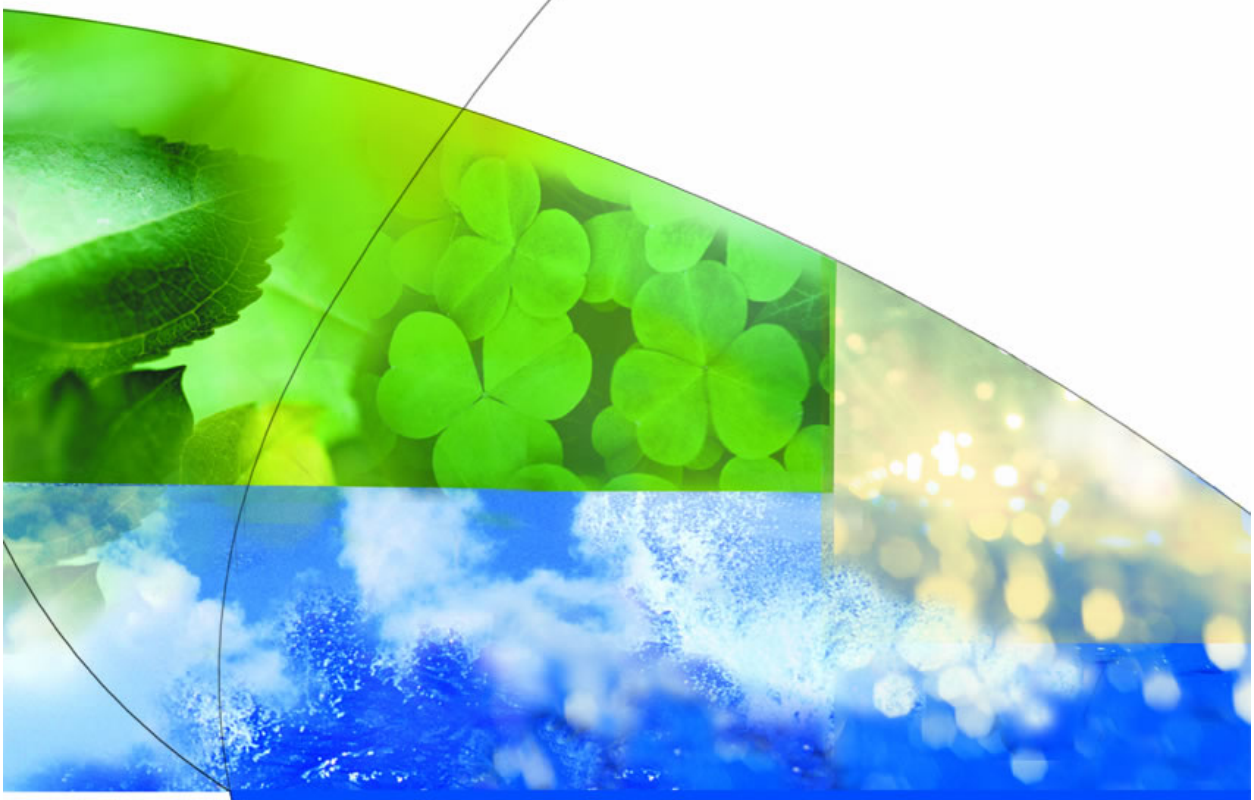
12.1 No information is presently available on the precision and accuracy or bias of this standard practice. It is recommended that standard QA/QC procedures such as analysis of duplicate samples and spiking of analyte be used for verification.

12.2 The precision of this test will vary depending on the material being leached.

APPENDIX C

MERCURY INFORMATION CLEARINGHOUSE REPORTS

MERCURY INFORMATION CLEARINGHOUSE



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

October 2004

Canadian Electricity Association
Association canadienne de l'électricité

EERC
Energy & Environmental Research Center

Center for Air Toxic Metals

MERCURY INFORMATION CLEARINGHOUSE

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

ACKNOWLEDGMENT AND DISCLAIMERS

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

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

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

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

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

2) Stimulate and encourage early implementation of new technology.

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

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

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

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

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

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

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

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

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

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

BACKGROUND

Mercury and CCBs

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

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

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

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

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

Anticipated Impacts of Proposed Mercury Control Technologies on CCBs

Proposed mercury emission controls have the potential to impact fly ash and FGD materials because mercury is highly volatile and should leave the combustion zone in the flue gas. As noted in Figure 1, mercury should be volatilized and emitted fully in the vapor phase in combustion systems. Mercury in the vapor phase in the flue gas has the potential to be sorbed onto the fly ash, carbon (either unburned carbon or sorbent), other sorbents, and the FGD reagent, or it may be emitted. The highest potential for mercury controls to impact CCBs is through the use of sorbent injection technologies that will incorporate the sorbent into the fly ash stream. The most likely sorbent candidate is activated carbon, even though other sorbents have been and are being tested. Testing at four full-scale boilers that measured mercury across particulate control devices gives some insight to the importance of particulate control in mercury removal and indicates that increased carbon relates to increased mercury removal. Even though no sorbent injection or other add-on mercury control technology was in place during these tests, the unburned carbon present in the fly ash provided significant mercury removals. Mercury removals ranged from a low of 28% for an ESP to between 61% and 99% for units equipped with reverse-gas baghouses (22). The highest mercury removals were observed where there was a high level of unburned carbon in the fly ash (high loss on ignition [LOI]). Pilot tests reinjecting power plant fly ashes ahead of a reverse-gas baghouse indicated removals between 13% and 80% at temperatures in the range of l35°–l60°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.

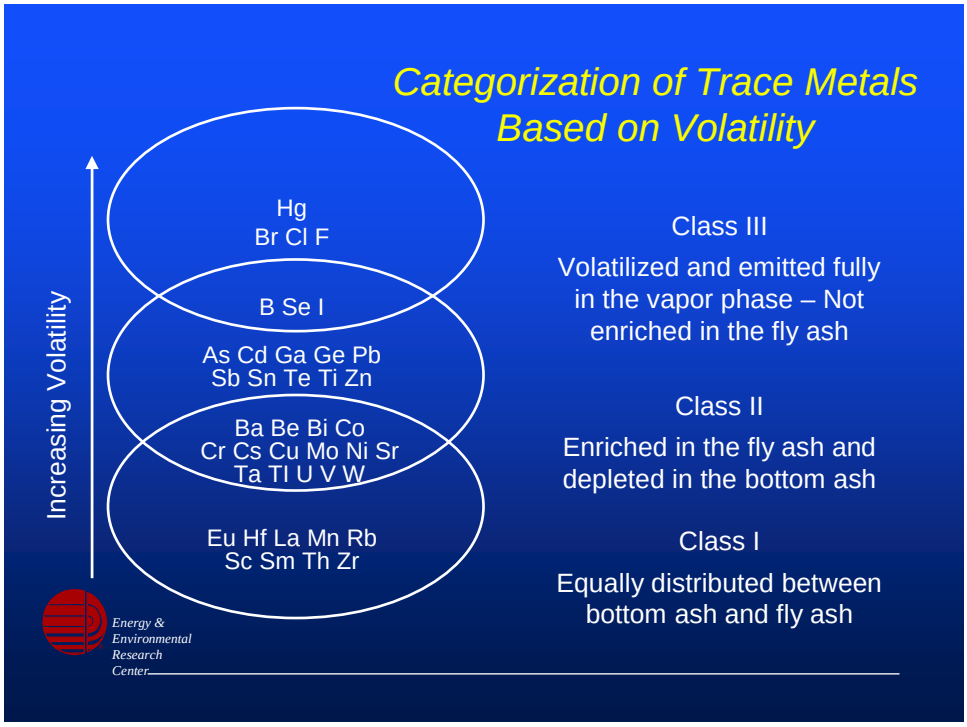

Figure 1. Categorization of trace elements based on volatility.

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 SO_2 controls for DOE Phase II (39) and new fine-particulate control standards. It has been shown that FGD material generated from wet systems can be oxidized to produce gypsum and that mercury present in the WFGD material is partitioned into the gypsum, implying that the mercury is not readily leached from the gypsum (40). The primary effort in the area of mercury emission control using FGD systems has been performed using wet systems, although other types of calcium-based FGD systems also are expected to remove oxidized mercury from flue gas at varying efficiency levels.

STABILITY OF MERCURY ON CCBs

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

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

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

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

Leaching[1]

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

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

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

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

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

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

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

[1] Sorbent injected downstream of the old ESP.
[2] Not applicable.

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

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

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

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

[a] Replicated measurements.
[b] Not detected.

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

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

[a] Not applicable.

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

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

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

The effect of 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 µg/L, while the single FGD material from a system using inhibited oxidation gave a mercury leachate concentration of 0.34 µg/L. Withum et al. (53, 54) leached a variety of Hg control technology CCBs with both TCLP and American Society for Testing and Materials (ASTM) D3987 tests. All samples had Hg leachate concentrations of <1.0 µg/L.

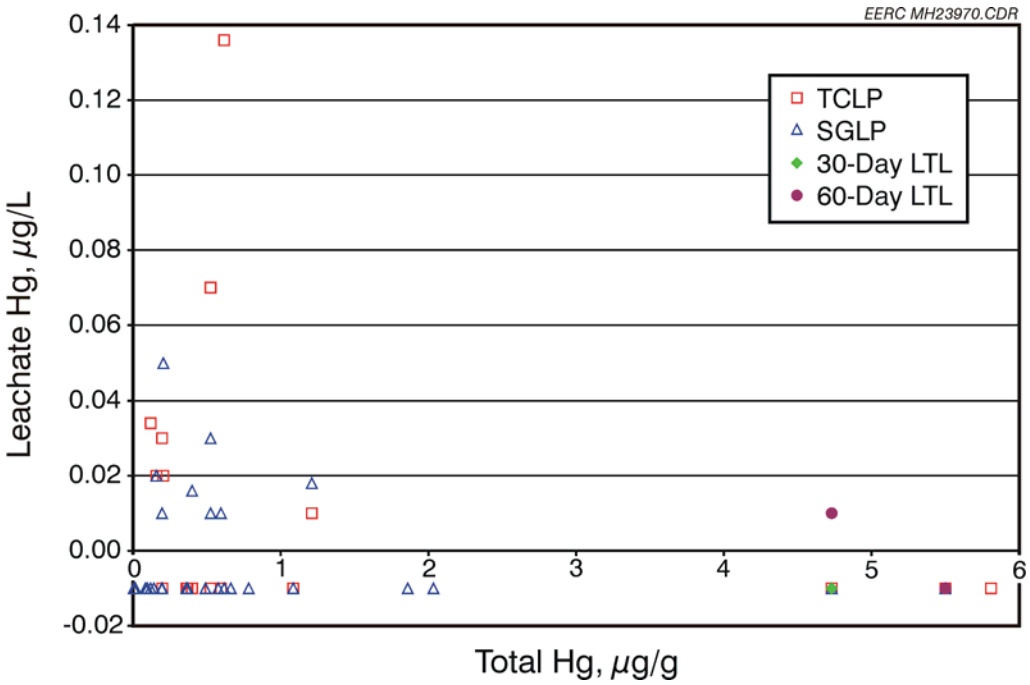

Figure 2. Leachate vs. total Hg; nondetects are shown as negative values.

Table 4. Mercury and Sulfur in Ash (50)

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

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

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

Vapor Release[2]

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

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

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

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

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

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

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

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

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

Microbiological Vapor-Phase Release

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

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

INTERPRETATION AND CONCLUSIONS

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

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

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

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

UPCOMING EVENTS

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

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

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

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

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

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

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

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

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

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

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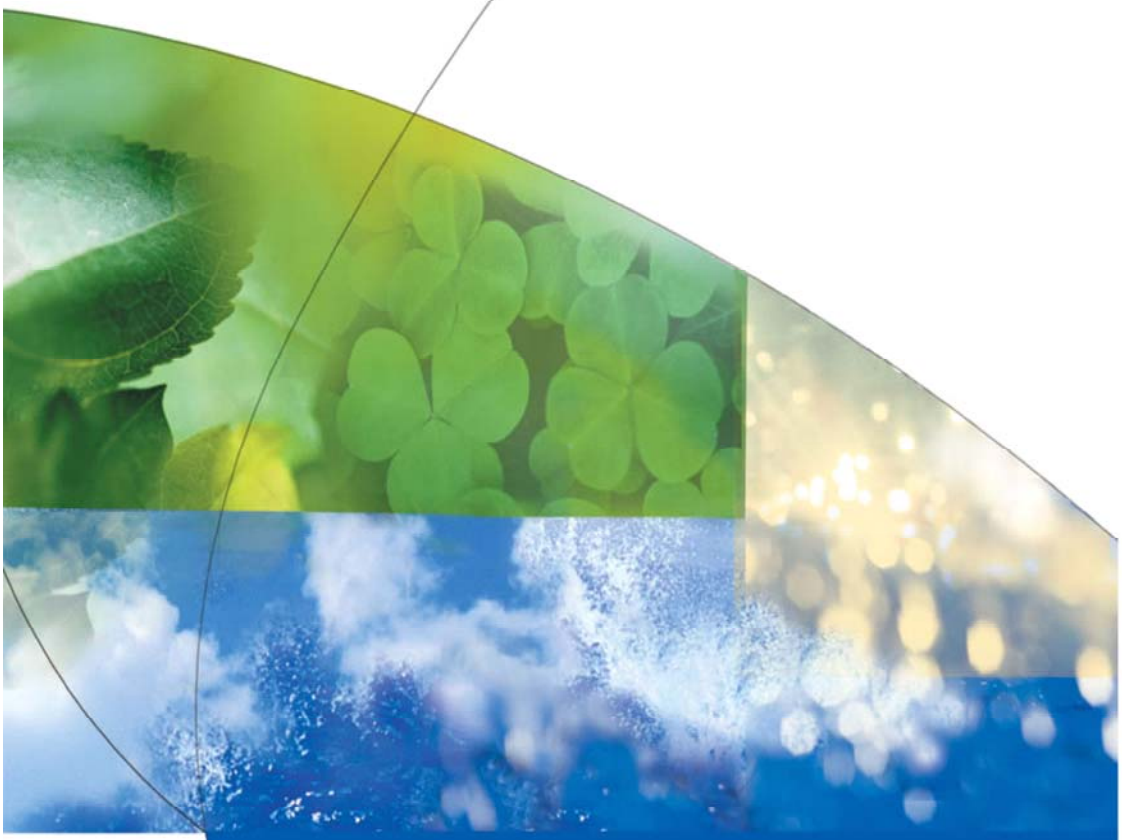
MERCURY INFORMATION CLEARINGHOUSE



Quarter 9 – Mercury Information Clearinghouse Final Report

December 2005

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MERCURY INFORMATION CLEARINGHOUSE

QUARTER 9 – MERCURY INFORMATION CLEARINGHOUSE FINAL REPORT

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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 9 – MERCURY INFORMATION CLEARINGHOUSE FINAL REPORT

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

QUARTER 9 – MERCURY INFORMATION CLEARINGHOUSE FINAL REPORT

INTRODUCTION

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

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

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

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

[1] Quarterly Data Reports

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

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 $\mu g/Rm^3$. NSPI's Point Aconi (only continuous fluidized-bed combustor tested) measured a stack gas mercury concentration of 0.32 $\mu g/Rm^3$ (one of the lowest measured) and, showed a relatively high mercury content in the ash, indicating that significant mercury capture is occurring across the FF. A similarly low stack mercury concentration was measured at OPG's Lambton Unit 4, indicating mercury capture is occurring across the ESP and/or FGD.

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

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

Mercury Policy

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

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

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

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

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

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

Table 2. CEA Mercury Program Ash Data

					BOTTOM ASH ANALYSIS				FLY ASH ANALYSIS			
Power Plant	MW	Coal Type	Blend Ratio	Bottom Ash: Fly Ash Ratio	Moisture, %	Carbon, % (dry)	Mercury[1], mg/kg (dry)	Mercury, Min/Max. 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: Concentration, µg/Rm^3	Total Hg Emissions: Emission Rate, g/h	Speciation of Mercury Emissions: Particulate, %	Speciation of Mercury Emissions: Oxidized, %	Speciation of Mercury Emissions: 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 SO_2 control and selective catalytic reduction (SCR) for NO_x control. Mitchell Baer of DOE added that, although the second phase of the rule will require addition mercury controls, it is expected that a number of mature economical technologies will be available to meet CAMR requirements (5).

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

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

Field Demonstrations of Carbon Injection

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

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

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

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

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

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

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

Table 4 summarizes 42 large-scale mercury control projects. This information identifies the lead contractor for each project, the demonstration site, boiler type and size, fuel type, air pollution control device (APCD) employed, mercury control technology being evaluated, and project status. The demonstration sites represent utility boilers across the United States and one

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

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 ft^2/kacfm). Results showed that 60%–70% removal is achievable at 4.5 lb/MMacf, improving to 70%–80% at 6.5 lb/MMacf, with no further improvement at the higher injection rate. In addition to demonstrating mercury removal, another purpose for the test was to determine the effects of ACI on ESP performance. At low loads there

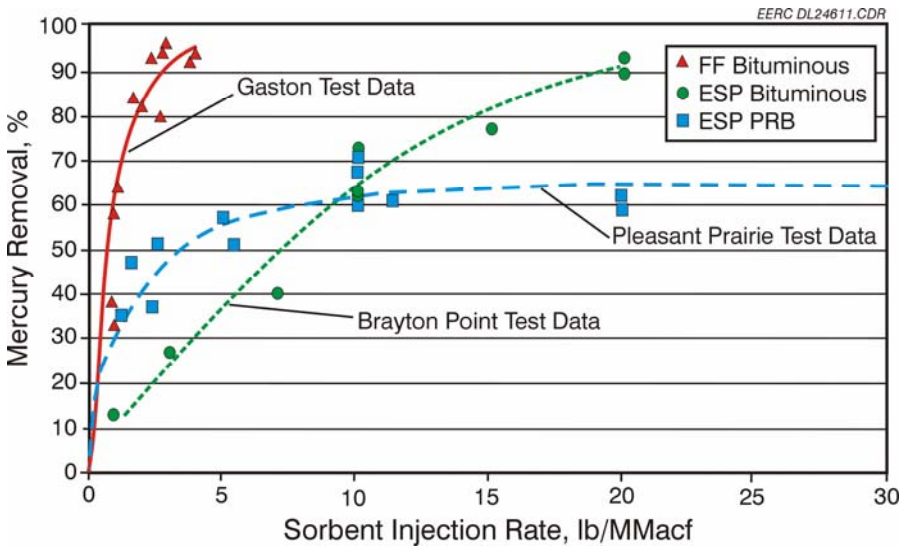

Figure 1. Mercury removal as a function of ACI rate at three sites.

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 powered activated carbons (B-PACs) that have proven very effective at removing mercury at a variety of power plants (7). Some plants have achieved >90% mercury removal at a cost that is <50% of DOE's baseline estimate. Based on this and other work, it appears that halogenated carbons can improve mercury capture for low-chloride coals but provide less benefit for eastern fuels.

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

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

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

Economics of ACI

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

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

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

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

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

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

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

[1] O&M costs are based on a report to DOE (11).
[2] Belldune is already achieving 70% mercury control (w-FGD).
[3] Point Aconi is already achieving 60%–90% mercury control (CFB).

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MERCURY MEASUREMENT (QUARTER 2 REPORT)

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

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

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

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

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

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

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

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

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

QA/QC Requirements for Mercury Measurement RATAs

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

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

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

or

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

Additional Experience Gained with Next-Generation Continuous Mercury Monitors

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

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

An Instrument-Based Reference Method for Mercury Measurement

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

gas cylinders is approximately 6%, which is an order of magnitude higher than they usually get with other types of gas cylinders and not acceptable as a standard. A new equation for the mercury vapor pressure curves is also being proposed by NIST. Currently NIST, PS Analytical, and Tekran all use slightly different equations for Hg vapor pressure. NIST also plans to look at the long-term stability of the gas cylinders and mercury generators.

ADVANCED AND DEVELOPMENTAL MERCURY CONTROL TECHNOLOGIES (QUARTER 3 REPORT)

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

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

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

Pretreatment of the Coal to Remove Mercury

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

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

marketplace. The success of the first full-scale plant as well as the strength of the market will determine how fast new capacity is developed to meet demand.

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

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

Combustion Modification and in Situ Generation of Sorbents

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

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

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

The EPRI process offers flexibility with the raw feed materials which may offer an opportunity to generate a very highly reactive, high-capacity sorbent. Since the generated sorbent material does not have to be collected and reinjected, the process may offer an opportunity to generate a very fine particle-size material. If so, in-flight capture would be

enhanced, making it an attractive application for ESP-controlled units. This process, however, has not been substantially tested, so near-term development is unlikely.

Non-Carbon-Based Sorbent, Amended Silicates™

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

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

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

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

Stationary Mercury Traps Positioned in the Flue Gas Stream

MerCAP™

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

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

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

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

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

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

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

EnviroScrub Pahlman Process

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

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

The concept has moved beyond the bench-scale level and has been tested with a 1000-acfm trailer-mounted slipstream device at a number of coal-fired power stations. However, only the collection step has been demonstrated. The fairly complex regeneration and recycling

steps have not been tested. Much longer-term and larger-scale testing needs to be completed to address all aspects of the process, but little additional development work has been done within the last year.

Combined Oxidation of NO_x and Mercury

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

LoTOx™

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

ECO/Powerspan

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

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

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

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

Mercury Control with the *Advanced Hybrid*™ Filter

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

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

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

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

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

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

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

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

Stability of Mercury on CCBs

Total mercury concentrations for CCBs are of interest because these data are valuable in developing mercury balances across emission control systems. Additional data have been reported by several groups primarily on those CCBs most directly impacted by potential mercury emission controls. Table 6 provides a summary of data on fly ash and FGD materials collected

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

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

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.

Leaching[1]

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

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

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

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

Vapor Release[2]

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

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

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

Elevated Temperature Vapor-Phase Rerelease

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

Ambient-Temperature Vapor-Phase Rerelease

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

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

Microbiologically Mediated Release

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

Field Studies of Mercury Releases

Disposal Site Water Evaluations

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

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

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

Field Vapor-Phase Releases

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

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

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

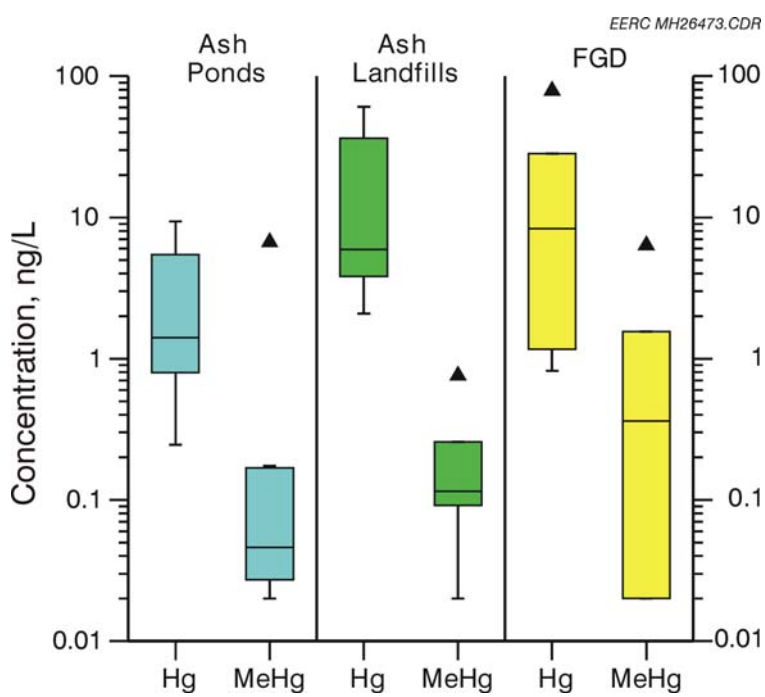

Figure 2. Field leachate – mercury speciation (15).

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^2hr
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/m^3 (FGD + fly ash); however, the value measured for the FGD + fly ash was significantly higher than other values (0.006–0.052), and the standard deviation was also high.

Rerelease of Mercury from CCBs in Select Utilization Applications

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

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

Table 8. Mercury Emission from Dry-Curing Concretes

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

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

Summary

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

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

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

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MERCURY FUNDAMENTALS (QUARTER 5 REPORT)

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

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

Flue Gas Effects

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

Carbon Structure Effects

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

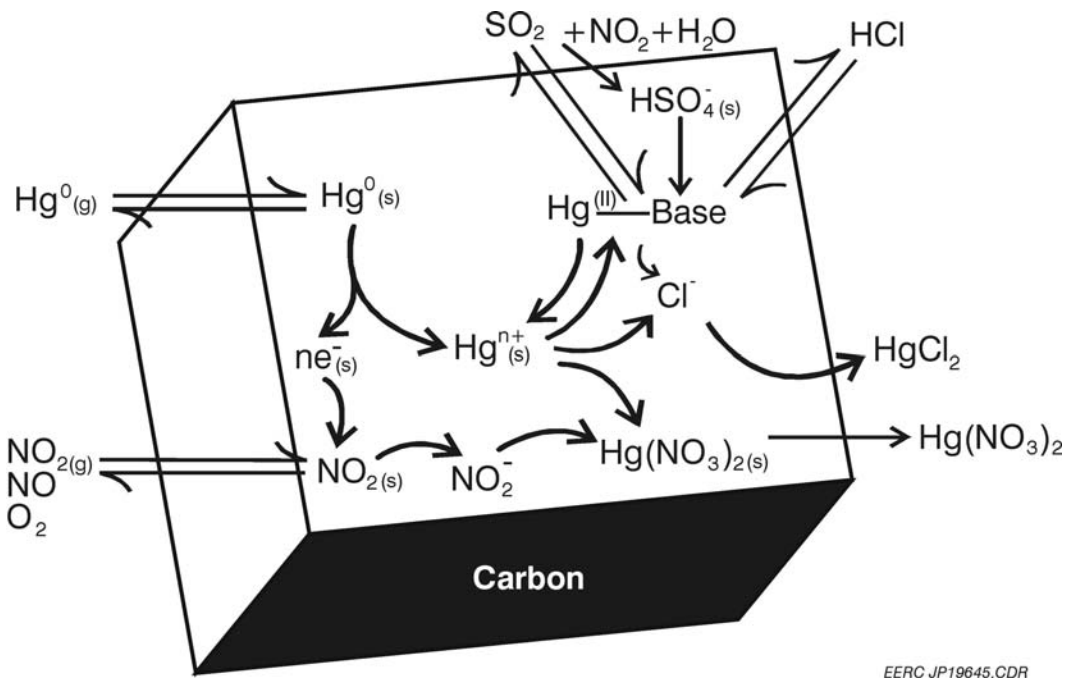

Figure 3. Overview of mercury flue gas interactions on an activated carbon sorbent.

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 SO_2 on the sorbent.
The model, shown in Figure 5, uses the concept of zigzag carbene edge structures recently proposed by Radovic and Brockrath (12). The zigzag carbon flanked by the aromatic rings has an electron pair and is the basic binding site for which the HCl, H_2SO_4, and Hg(II) compete, as shown on the left side of the figure, forming a positive carbenium ion intermediate in each case.

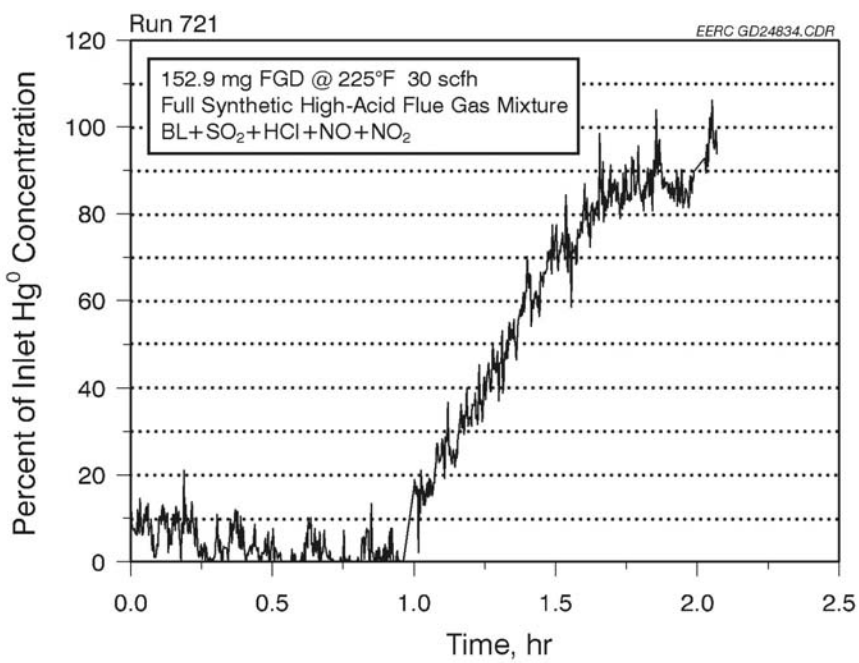

Figure 4. Breakthrough curves for high and low acid gas.

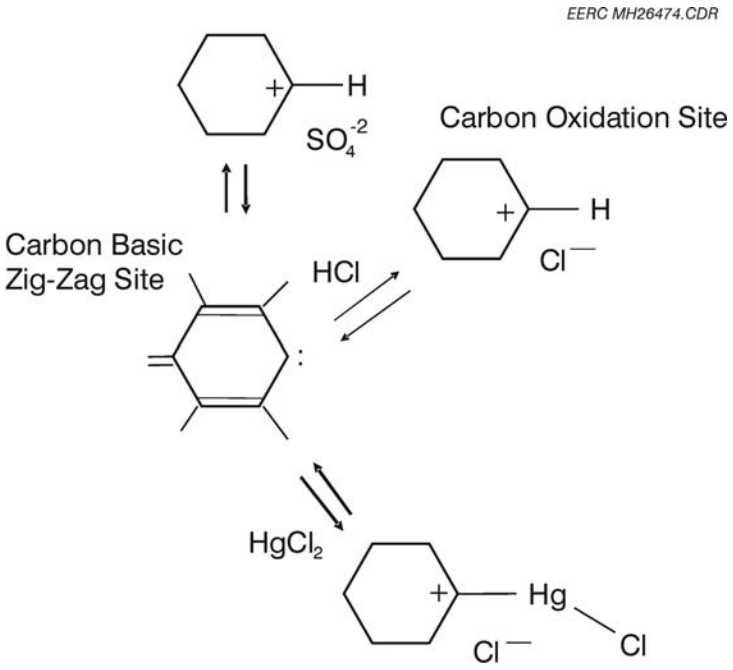

Figure 5. Mercury and acid gas-binding mechanism at carbon edge.

Mercury Oxidation Mechanism

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

Halogenated Carbons

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

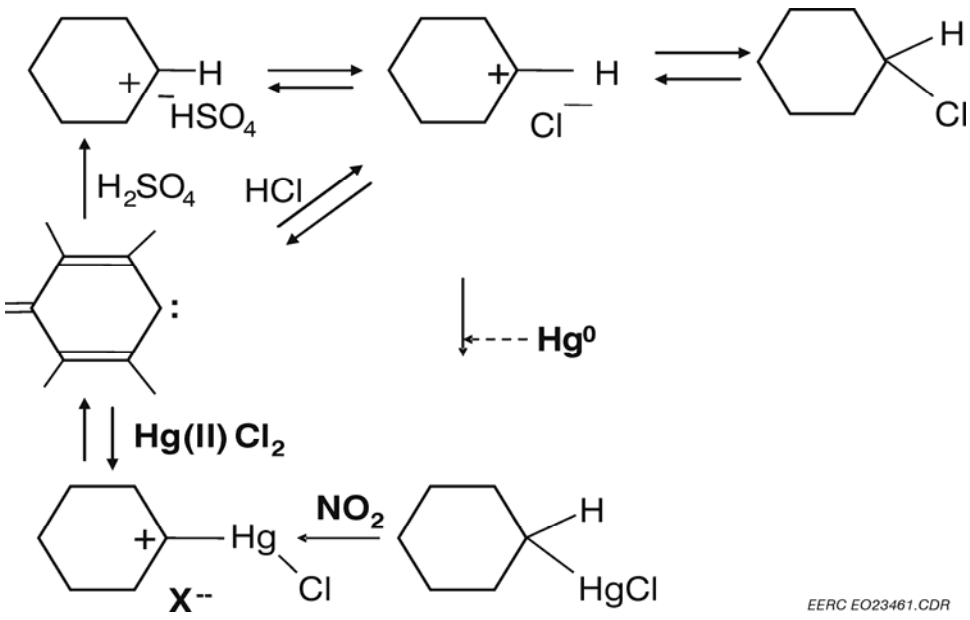

Figure 6. Oxidation mechanism – carbenium ion oxidant.

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 Hg^0, but a considerable amount of chemical evidence (19) showed that the halogens that are impregnated into carbon react with the carbon and are strongly bound to the carbon. So it is more likely that the halogens promote the reactivity of the carbon, as we have demonstrated for HCl, rather than react as such with the Hg^0.

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

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

carbon by a strong acid. Further exposure to flue gas resulted in further loss of both organochlorine and inorganic chloride. Although these chlorine spectra indicate the structures of the chlorine but not the mercury, the results contribute to our understanding of the reactive sites and allow us to extend the model to the chlorinated sorbents with little modification (see Figure 5).

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

Potential for More Effective Capture

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

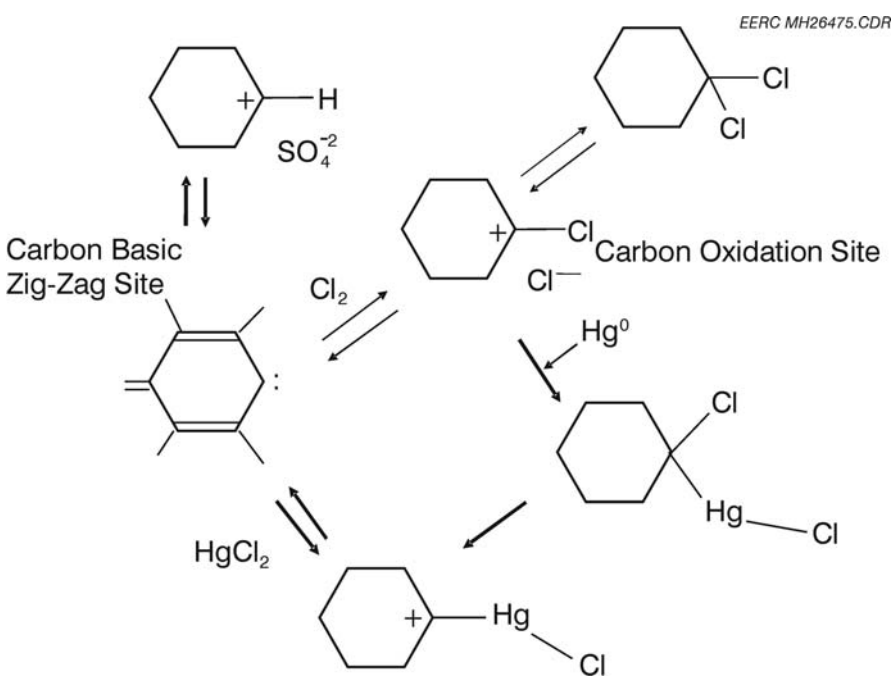

Figure 7. Mercury oxidation mechanism for chlorinated carbon.

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

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HEALTH ASPECTS OF MERCURY EMISSIONS (QUARTER 5 REPORT)

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

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

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

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

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

In the Faroe Islands (10, 11), adverse associations from prenatal CH_3Hg exposure have been found. Although adult Faroe Islanders consume ~72 g of fish a day, the fish they consume

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

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

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

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

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

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

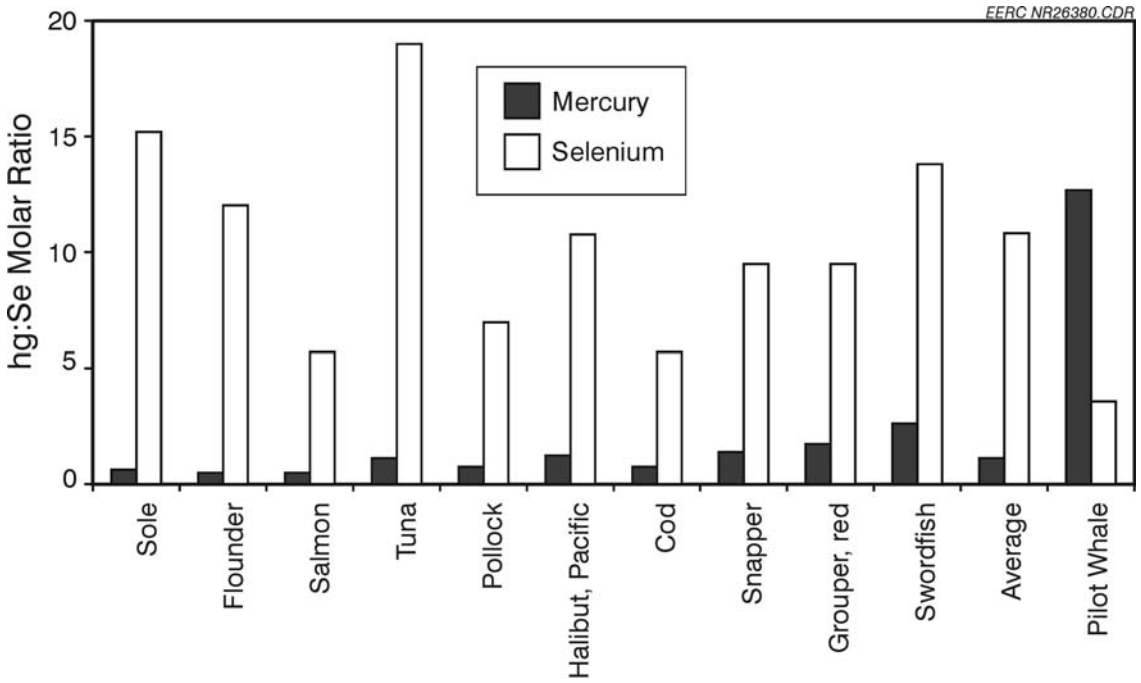

Figure 8. Molar relationships between mercury and selenium concentrations in seafood.

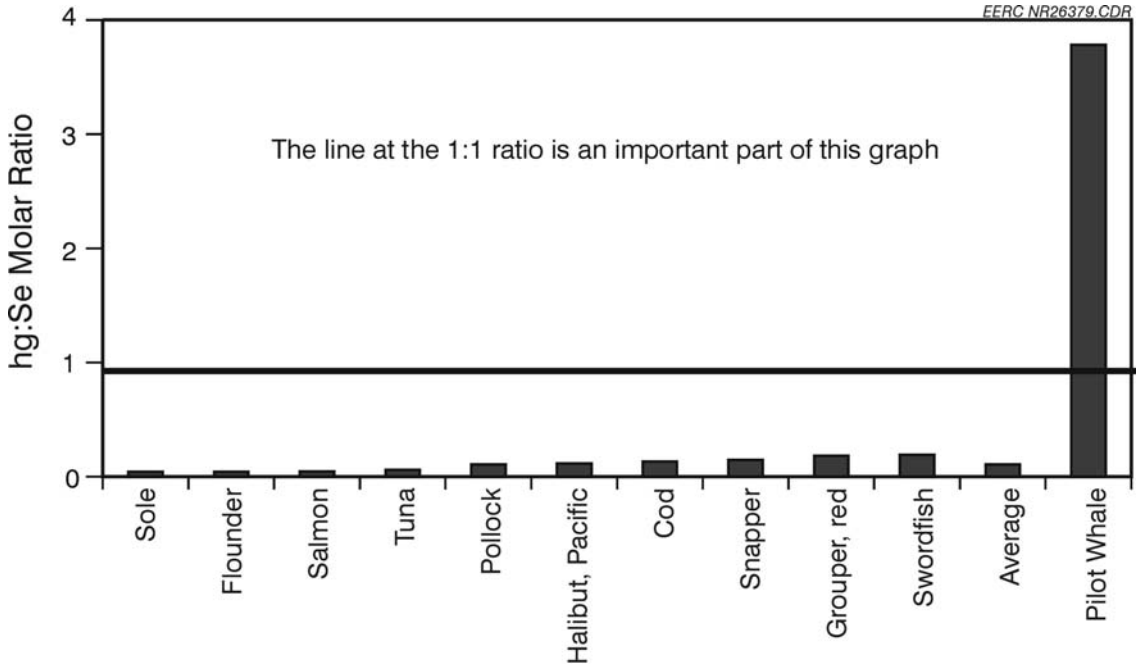

Figure 9. Molar ratio of mercury:selenium concentrations in seafood.

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

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

Recent work indicates the problem of excessive Hg exposure from whale meat consumption is not limited to the Faroes. Concentrations of MeHg in 160 samples of red meat products from small cetaceans sold for human consumption in markets throughout Japan from 2000–2003 all exceeded the provisional permitted levels in fish and shellfish set by the Japanese Government,

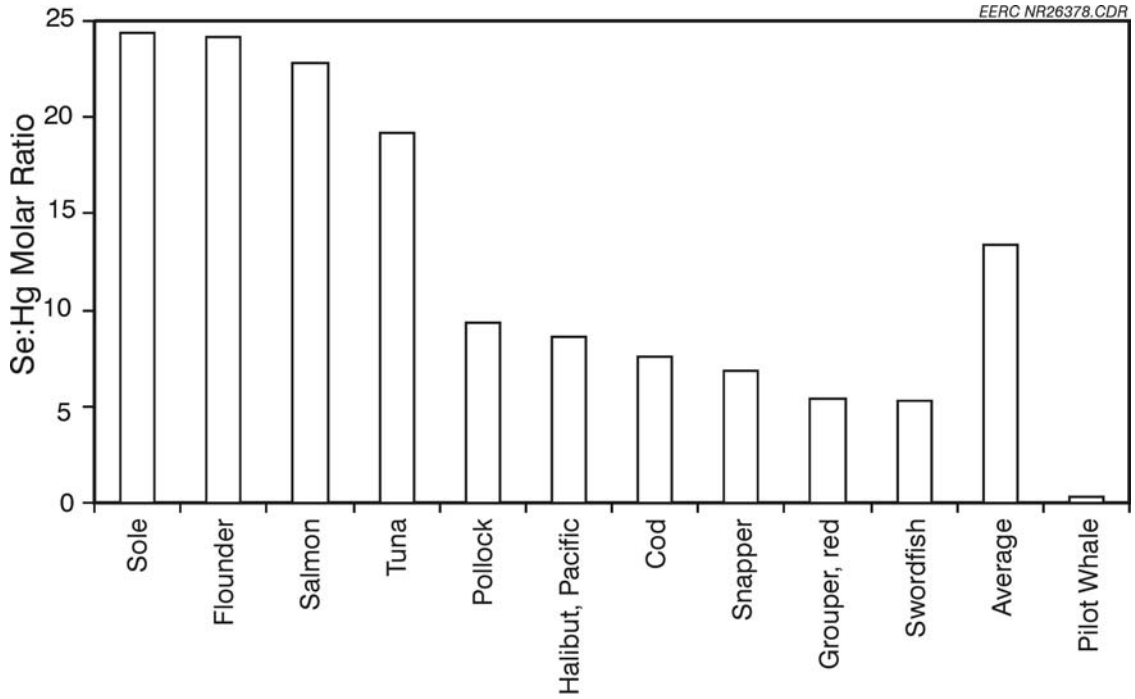

Figure 10. Molar ratio of selenium:mercury concentrations in seafood.

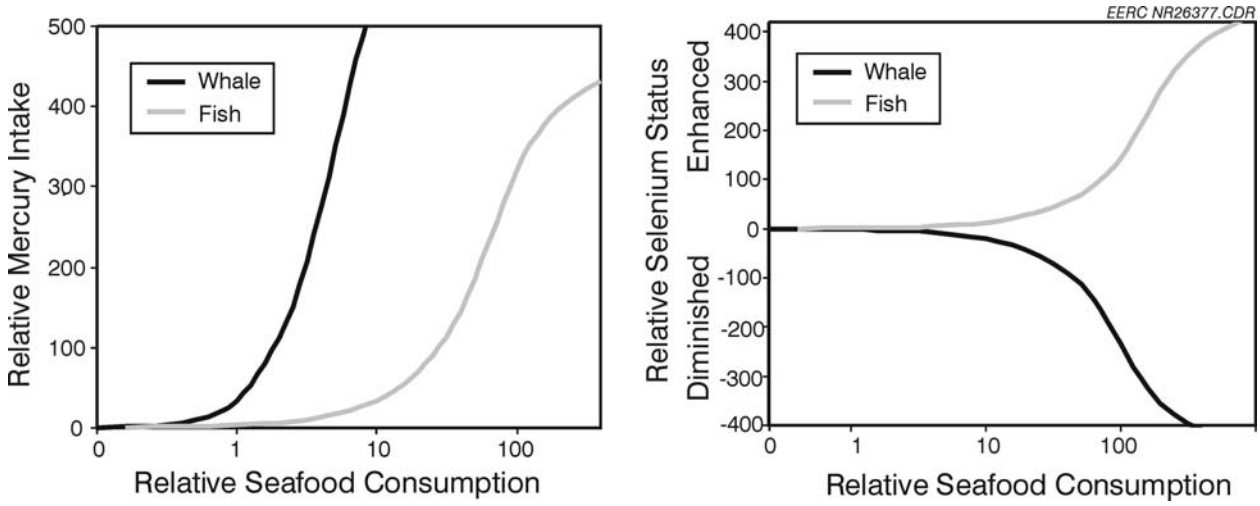

Figure 11. Relative effects of whale vs. fish consumption.

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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APPENDIX D

LABORATORY METHODS FOR THE EVALUATION OF POTENTIAL RELEASE OF MERCURY FROM COAL UTILIZATION BY-PRODUCTS

LABORATORY METHODS FOR THE EVALUATION OF POTENTIAL RELEASE OF MERCURY FROM COAL UTILIZATION BY-PRODUCTS

Topical Report

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LABORATORY METHODS FOR THE EVALUATION OF POTENTIAL RELEASE OF MERCURY FROM COAL UTILIZATION BY-PRODUCTS

EXECUTIVE SUMMARY

Under a 3-year effort funded by the U.S. Department of Energy (DOE) and industry entitled "Mercury and Air Toxic Element Impacts of Coal Combustion By-Product Disposal and Utilization," the Energy & Environmental Research Center (EERC) is evaluating the impact of mercury and other air toxic elements on the management of coal utilization by-products (CUBs). The EERC is measuring the release of mercury and other air toxic elements under different controlled laboratory conditions and investigating the release of these same air toxic elements in select field settings. Results will be used to determine if mercury release from CUBs, both as currently produced and as produced with mercury and other emission controls in place, will potentially impact CUB management practices. In order to adequately address the potential for release of mercury from CUBs, sorbents, and combinations, release mechanisms that must be evaluated include 1) leaching, 2) elevated- and ambient-temperature vapor-phase releases, and 3) microbiologically mediated releases. The EERC initiated research on the potential release of mercury from CUBs in 1999 and found that methodologies for evaluating the release of mercury from CUBs using these mechanisms were not documented in the scientific literature, with the exception of leaching. As a result, method development work was initiated under the U.S. Environmental Protection Agency (EPA) Center for Air Toxic Elements and the Coal Ash Resources Research Consortium.

The EERC concluded Year 2 of this effort in April 2005, and this report details the results to date from Task 2: Analytical Methods Selection. As noted in several forums in recent years, the methods used to evaluate CUBs must be relevant to the material and the management of CUBs where possible. EERC researchers reviewed methods currently being used at the EERC and elsewhere to determine the best possible methods for this effort.

Laboratory methods were selected based on early work performed at the EERC but method development and modification continued. The methods being employed to evaluate the release of mercury from CUBs by direct leaching, exposure to ambient and elevated temperatures, and exposure to biota are described, and method limitations are discussed.

LABORATORY METHODS FOR THE EVALUATION OF POTENTIAL RELEASE OF MERCURY FROM COAL UTILIZATION BY-PRODUCTS

INTRODUCTION

The stability of mercury associated with coal utilization by-products (CUBs) has become a prominent question as the coal-fired utility industry develops and tests mercury emission controls that may consequently increase the mercury associated with CUBs. The reasons for evaluating the release of mercury from CUBs are 1) to determine if mercury captured on CUBs is stable or if it will be released, thus negating the purpose of the removal of the mercury from the emissions, and 2) to aid utilities in determining and understanding changes in CUBs associated with mercury control and associated CUB management.

Under a 3-year effort funded by the U.S. Department of Energy (DOE) and industry entitled "Mercury and Air Toxic Element Impacts of Coal Combustion By-Product Disposal and Utilization," the Energy & Environmental Research Center (EERC) is evaluating the impact of mercury and other air toxic elements on the management of CUBs. The EERC is measuring the release of mercury and other air toxic elements under different controlled laboratory conditions and investigating the release of these same air toxic elements in select field settings. Results will be used to determine if mercury released from CUBs, both as currently produced and as produced with mercury and other emission controls in place, will impact CUB management practices.

The EERC concluded Year 2 of this effort in April 2005, and this report details the results to date from Task 2: Analytical Methods Selection. As noted in several forums in recent years, the methods used to evaluate CUBs must be relevant to the material and the management of CUBs where possible. EERC researchers reviewed methods currently being used at the EERC and elsewhere to determine the best possible methods for this effort. A summary of research in this area was published in 2004 (1).

BACKGROUND

Recent projections from the Energy Information Administration indicate that U.S. demand for energy will increase from 97.3 quadrillion to 130.1 quadrillion Btu between 2001 and 2020, reflecting an annual growth rate of 1.5%. By 2025, total energy consumption is projected to reach 139.1 quadrillion Btu (2). Fossil fuel combustion, including the burning of coal, natural gas, or oil, provides about 85% of the present energy production in the United States. Of this amount, over 50% is provided by coal-fired utilities (2). As a result of energy production from coal, CUBs are generated, and CUBs, as produced in the United States, are primarily a result of emission control technologies installed to meet emission regulations.

Emission regulations first mandated reduction of particulate matter released to the atmosphere by utilities, which required utilities to install collection devices for generated fly ash. Later emission regulations significant to CUB production mandated limits on SO_x emissions. As

a result, utilities using high-sulfur coal could change coal sources, resulting in a different by-product character, or scrub the flue gas using sorbents to remove the SO_x gases. The result of flue gas desulfurization (FGD) was high volumes of spent FGD sorbent material. There is a wide range of FGD technologies, so FGD materials have broadly varied characteristics, but generally contain high concentrations of calcium and sulfur. Currently, utilities are responding to regulation placing limits on NO_x emissions, which also impacts the character of ash by-products, including potentially increasing the amount of unburned carbon in fly ash or adding ammonia to the fly ash. Issues related to air toxic emissions, including mercury, are currently under technical and regulatory scrutiny.

Figure 1 includes an excerpt from a U.S. Environmental Protection Agency (EPA) Fact Sheet titled "EPA Proposes Options for Significantly Reducing Mercury Emissions from Electric Utilities," in which some of the concerns about mercury are summarized. On December 14, 2000, EPA announced that it would regulate mercury emissions from coal- and oil-fired electric utility steam-generating power plants (3); propose regulations by December 15, 2003; and finalize regulations by December 15, 2004. On December 15, 2003, EPA signed the Utility Mercury Reductions proposal, which seeks comments on two approaches for reducing mercury by up to nearly 70%. On March 15, 2005, the EPA issued the first federal rule to permanently cap and reduce mercury emissions from coal-fired power plants (a power plant is defined as an electrical generating facility that provides >25 MW_e). The rule is a market-based cap-and-trade program (Section 111 of the Clean Air Act) and is similar to the program in place for SO_2. The rule is to be administered in two phases. The first phase places a cap of 38 tons per year of mercury beginning in 2010. The second phase sets a final cap of 15 tons by 2018. Coal-fired power plants currently emit about 48 tons per year; therefore, the reduction in mercury emissions will be 21% and 69%, respectively.

Mercury Emissions – Both Naturally Occurring and Man-made Sources

- Mercury is a toxic, persistent pollutant that accumulates in the food chain. Fossil fuel-fired utilities are the largest source of human-generated mercury emissions in the United States.

- Concentrations of mercury in the air are usually low and of little direct concern. However, atmospheric mercury falls to Earth through rain or snow and enters lakes, rivers, and estuaries. Once there, it can transform to its most toxic form, methylmercury, and accumulate in fish and animal tissues.

- Americans are exposed to mercury primarily by eating contaminated fish. Because the developing fetus is the most sensitive to the toxic effects of mercury, women of child-bearing age are regarded as the population of greatest concern. Children who are exposed to low concentrations of methylmercury prenatally are at increased risk of poor performance on neurobehavioral tasks, such as those measuring attention, fine motor function, language skills, visual-spatial abilities, and verbal memory.

EXCERPTED FROM EPA FACT SHEET:
EPA Proposes Options for Significantly Reducing Mercury Emissions from Electric Utilities
December 15, 2003

Figure 1. Information from EPA on mercury emissions (4).

The reduction of emissions at coal-fired power plants has historically impacted the quantity and character of resulting CUBs. The removal or reduction of mercury emissions at coal-fired power plants has high potential to do the same because several proposed mercury emission control technologies involve the use of solid sorbents that will likely be introduced in the flue gas and collected with the fly ash. Other candidate emission control technologies focus on increasing the mercury sorbed on FGD materials. These mercury emission control technologies will impact the mercury content of CUBs. The question that this project was designed to answer is, "Will the changes in CUBs associated with mercury emission controls change the management options for those CUBs as they relate to the potential release of mercury?"

Since the large volumes of CUBs produced annually in the United States are managed either by disposal or utilization, the design of various tasks in this project focused on simulating potential behavior of CUBs in environments where they are typically managed. Examples of utilization scenarios include:

- The use of fly ash in concrete, soil stabilization, or fills that could be exposed to natural waters or to microbial action.

- The use of FGD gypsum in wallboard, where it may be exposed to high temperatures in production or to natural water under disposal.

- The use of fly ash in cement clinker production, where it would be exposed to extremely high temperatures.

- The use of FGD gypsum or fly ash as an agricultural soil amendment or mine fill, where it would be exposed to natural water and, potentially, microbial action.

In order to adequately address the potential for release of mercury from CUBs, sorbents, and combinations, release mechanisms that must be evaluated include leaching, elevated- and ambient-temperature vapor-phase releases, and microbiologically mediated releases. The EERC initiated research on the potential release of mercury from CUBs in 1999 and found that methods for evaluating the release of mercury from CUBs using these mechanisms were not documented in the scientific literature, with the exception of leaching. As a result, the EERC initiated a program under EPA's Center for Air Toxic Metals® and the Coal Ash Resources Research Consortium® to develop laboratory methods that would provide information on the potential for CUBs to release mercury and other air toxic elements under conditions associated with the proposed release mechanisms of direct leaching, direct ambient- and elevated-temperature vapor-phase release, and microbiologically mediated leaching and vapor-phase release.

OBJECTIVES

The goal of the methods selection task was to select or develop appropriate laboratory methods to evaluate the potential for release of mercury from CUBs under conditions that are relevant to management options applied to CUBs. Supporting objectives were as follows:

- Select and apply one or more leaching procedures appropriate for environmental characterization of CUBs.

- Select, develop, and apply a method to evaluate the release of mercury through offgassing from CUBs at elevated temperatures.

- Select, develop, and apply a method to evaluate the release of mercury through offgassing from CUBs exposed to ambient temperature air.

- Select, develop, and apply a method to evaluate the release of mercury through leaching and offgassing from CUBs exposed to biota commonly found in natural settings.

- Select and apply laboratory analytical methods required to determine mercury in solutions, collected on analytical traps, and in solid materials.

METHODOLOGIES – ANALYTICAL AND CHARACTERIZATION METHODS

Chemical and Physical Characterization

Chemical characterization of samples included total mercury and total bulk chemical composition on major, minor, and trace constituents. Physical characterization included carbon forms, pH, moisture, and loss-on-ignition (LOI) measurements. Eh measurements were taken on samples used for microbiological experiments. Methodologies used for these characterizations are further described below.

Total Mercury

The total mercury content of solid samples was determined using a direct mercury analyzer or digestion followed by cold-vapor atomic absorption spectrometry (CVAAS).

Total Air Toxic Elements

The total concentration of the other air toxic elements of arsenic, cadmium, chromium, lead, nickel, and selenium was determined using standard methods. Acid digestion was used on the CUB followed by detection using inductively coupled atomic emission spectroscopy (ICP–AES) or ICP mass spectroscopy (ICP–MS).

Total Bulk Chemical Composition

The major bulk composition, reported as percent oxides, was determined using x-ray fluorescence spectrometry. American Society for Testing and Materials (ASTM) D4326-04 Standard Test Method for Major and Minor Elements in Coal and Coke Ash by X-Ray Fluorescence was used (5).

LOI and Moisture

Standard characterization techniques were used to measure LOI and moisture content. ASTM C311-04 Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete was used (6).

pH

The pH of samples was determined using distilled water and/or 1 M KCl. The method employing 1 M KCl is required for many types of solid samples that exhibit a double electric layer that impacts the determination of pH. For this task, a slurry of 25 mL of 1 M KCl solution was mixed with 10 g of CUB, and the resulting pH was measured and recorded. As previously noted, the pH was also determined in slurry of distilled, deionized water. Where both methods were employed in this effort, it was noted that the pH values were similar. A comparison of these data for a relatively broad range of CUB types led researchers to conclude that it is not necessary to use 1 M KCl in determining the pH of CUB; therefore, remaining samples were evaluated using distilled, deionized water slurries. It is likely that the high concentration of total dissolved solids generated in the pH determination eliminated the double electric-layer effect that requires the use of KCl solution in the determination of pH in other types of solid samples.

Carbon Forms

Dominant carbon forms were identified in a select group of project samples. The samples on which carbon forms were determined were prepared by mounting them in epoxy resin. The sample was dispersed in the bottom of a 1-inch-diameter rubber cup mold. The epoxy was stained using Sudan black, which results in a high contrast between the particles of interest and the mounting medium. The surfaces to be analyzed were polished with incrementally smaller grits with ¼ µm being the final polishing grit used. The samples were then examined using a reflected-light microscope.

Eh

Eh was determined using a platinum electrode with a standard reference electrode.

Method Used to Measure Mercury on Gold-Coated Quartz Traps

Gold-coated quartz mercury collection traps were desorbed for analysis by heating to approximately 500°C, and the mass of mercury released was determined using double-gold amalgamation with atomic fluorescence (AF) detection. A Brooks Rand Model III cold-vapor atomic fluorescence spectrophotometer (CVAFS) was utilized for mercury concentration determination.

Method Used to Measure Mercury on Carbotraps

Supelco Carbotrap™ collection traps were analyzed for total mercury by heating them to approximately 300°C, passing the released organomercury through a tube held at about 800°C, and collecting the mercury on a gold-coated quartz trap, which was analyzed as described above.

METHODS FOR THE EVALUATION OF THE RELEASE POTENTIAL OF MERCURY AND OTHER AIR TOXIC ELEMENTS FROM CUB

Direct Leaching

Leaching is the most likely mechanism of transport of constituents from disposed or utilized CUBs contacted by water. Leaching is typically performed on CUBs to characterize them for management purposes. The leaching tests performed on the samples in this project were the toxicity characteristic leaching procedure (TCLP [EPA Method 1311 (7)]), the synthetic groundwater leaching procedure (SGLP), and long-term leaching (LTL) with 30- and 60-day equilibration periods.

TCLP is a leaching procedure designed for the evaluation of leaching of wastes when codisposed in a sanitary landfill. Leaching with TCLP utilizes a 20:1 liquid-to-solid ratio, end-over-end agitation at approximately 30 rpm, an 18-hour equilibration time, and one of two extraction fluids. The extraction fluid used is dictated by the pH of the material being leached. Extraction Fluid 1, used when the pH is below 5, is prepared by adding glacial acetic acid and sodium hydroxide to reagent water, and has a fluid pH of 4.93 ± 0.05. Extraction Fluid 2, used when the pH of the material is above 5, is prepared by adding glacial acetic acid to reagent water, resulting in a fluid pH of 2.88 ± 0.05.

The SGLP batch-leaching procedure is a relatively simple test that follows many of the conditions of TCLP. The test utilizes a 20:1 liquid-to-solid ratio, end-over-end agitation at approximately 30 rpm, an 18-hour equilibration time, and usually employs a leaching solution consisting of water from the site, water that has been prepared in the lab similar to water likely to contact the CUB, or distilled deionized water. When distilled water is used as the leaching solution for SGLP, the method is equivalent to the ASTM D3987 Standard Test Method for Shake Extraction of Solid Waste with Water (8). Distilled deionized water was used in this effort. For the long-term component of this procedure, multiple bottles are set up and analyzed at different time intervals. A typical SGLP–LTL test might consist of 18-hour, 30-day, and 60-day equilibration times. Although 60 days is often not adequate to achieve complete equilibrium, it is generally long enough to determine the concentration evolution of individual parameters. The most important factor when performing LTL is to have at least three equilibration times to determine a true trend. A draft of the SGLP–LTL method prepared for consideration by ASTM is in Appendix A.

For all leaching procedures, the solids were filtered from the leaching solution through a 0.45-µm filter, the pH of the resulting leachate was measured, and the leachate was preserved with HCl for mercury determination and with HNO_3 for determination of other trace elements.

Mercury leachate concentrations were determined using CVAAS and CVAFS as noted in the analytical methods section. Other trace elements were determined using inductively coupled argon-plasma spectrometry, ICP–MS, or graphite furnace atomic absorption spectroscopy.

The SGLP method was used preferentially for the project samples, and where TCLP was applied, SGLP was also applied. TCLP was included because some regulatory groups continue to use TCLP results to determine whether a "waste" is hazardous. The SGLP short-term leaching procedure was applied to all samples, but for samples with a pH >10, the LTL option was also used. CUBs exhibiting a high pH have the potential to undergo hydration reactions that can change the leaching profile with time. The EERC documented the impact of ettringite formation on leachate concentrations of several elements that are frequently present in CUBs such as selenium and boron (9–12). The elements that are most likely to be incorporated into the ettringite structure and exhibit a change in leaching profile with time are those that are present as oxyanions at high pH. Examples of leaching profiles of high pH CUBs for some trace constituents commonly found in CUBs are shown in Figures 2 and 3.

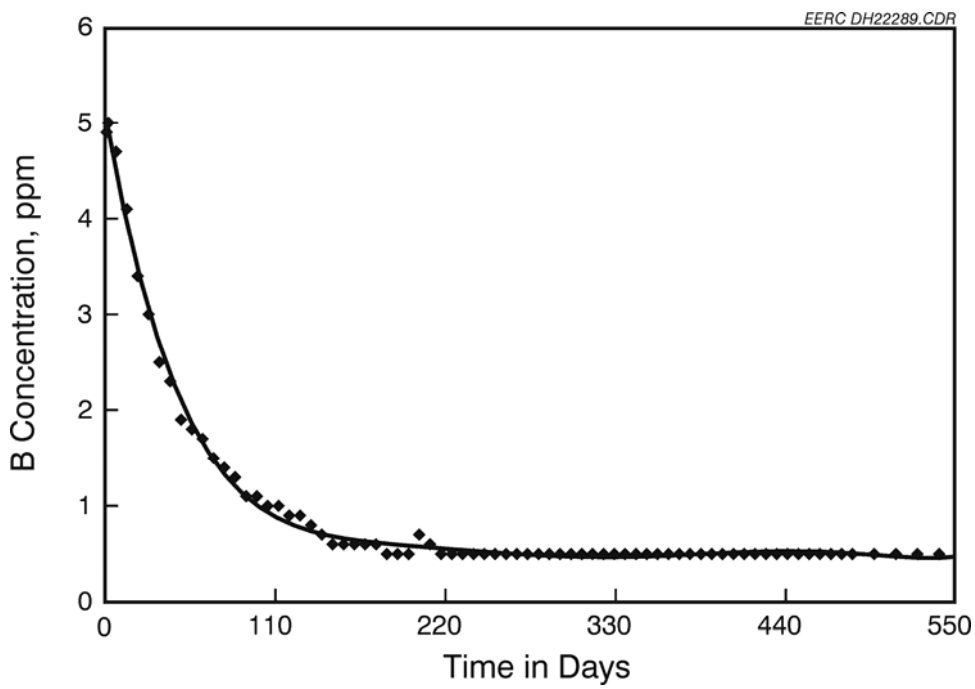

Figure 2. Long-term leaching results for boron.

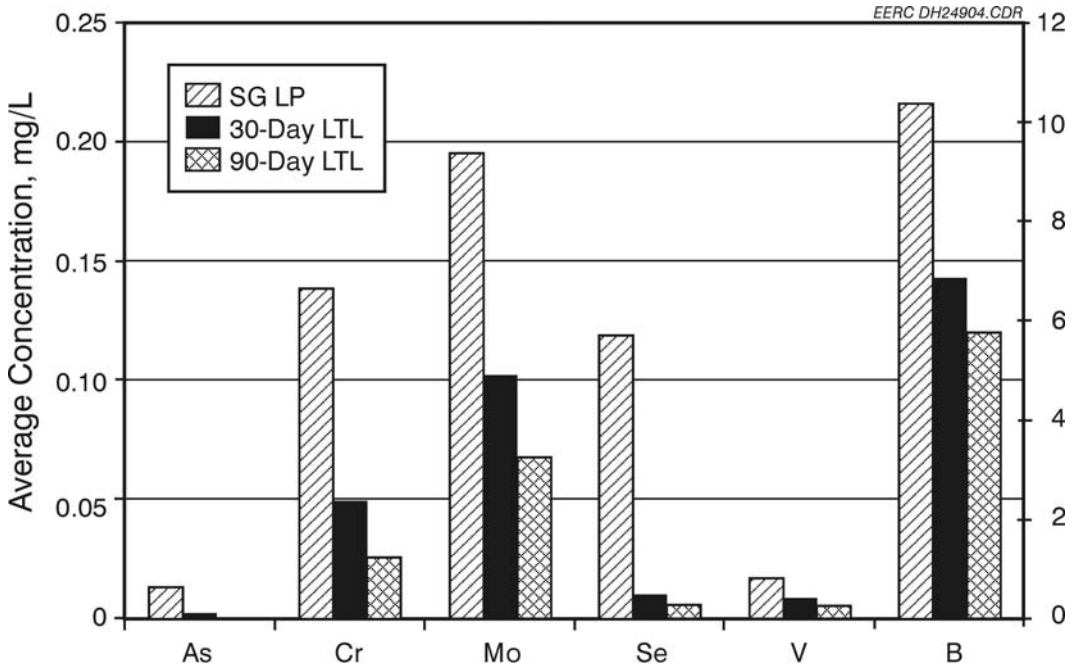

Figure 3. Indirect evidence of ettringite formation using SGLP and LTL (note: boron is on a secondary axis).

Vapor-Phase Transport

Long-Term Ambient Temperature Release

In order to develop a method to evaluate the potential for release of mercury from CUBs at ambient temperatures, several preliminary decisions were made based on the practicality of performing this type of evaluation in the laboratory, as follows:

- In order to measure mercury releases from CUBs, most of which have very low concentrations of mercury, samples with relatively high concentrations of mercury would be evaluated first.

- In order to evaluate multiple samples with available equipment and instrumentation, released mercury would be collected on analytical gold-coated quartz traps.

- Because very low release of mercury was anticipated, it was decided to expose a column of CUB to low-mercury air rather than expose only the surface of a CUB to the ambient temperature low-mercury air.

Using these preliminary premises, 250-mL wide-mouth glass test containers were designed with bonded Teflon liner caps. Two holes were drilled in the caps to accommodate a silicone tube for gas inlet and a Teflon outlet bulkhead fitting. The gas inlet tube extended nearly to the bottom of the container while the outlet tube extended only slightly into the container.

Using these test containers, approximately 150-g aliquots of CUB provided a column of material through which the low-mercury air could be transported. Breathing-quality air from a cylinder was passed through several sets of gold-coated quartz traps for mercury removal and admitted to each of the bottles through a gas distribution manifold that routed the gas through 0.25-mm-ID gas chromatography (GC) capillary tubing to each of the individual bottles. The pressure drop across the GC capillary tubing allowed for the regulation of air flow through each bottle by simply adjusting the length of tubing to each bottle. The length of tubing was a nominal 65 cm. This length of tubing, when pressurized to between 1 and 2 psig through a gas distribution manifold, provided a convenient means of regulating gas flow to approximately 2 cm^3/min. Because of the variability of particle sizes between different ash samples, the sample with the initial highest gas flow was left with a 65-cm length of GC tubing, and other samples had their tubing lengths shortened until all samples had approximately the same flow rate. The air exiting the GC tubing was given a final scrubbing to remove mercury vapor using a gold-coated quartz trap just prior to entering the bottle containing the CUB. After entering the bottles, the air passed through the ash and exited to a central mercury collection tube containing two separate gold-coated quartz traps. The second outlet or top trap was used to prevent mercury contamination from atmospheric mercury. This setup is illustrated in Figure 4.

The gold-coated quartz trap nearest the exit bulkhead fitting was analyzed multiple times with the most typical sampling scheme being one 7-day period followed by two consecutive 90-day periods. The gold-coated quartz analytical traps were evaluated according to the method described in the analytical method section. In order to determine the total mercury released over the duration of the experiment, the mercury results from all experimental time segments needs to be combined, and the container blank needs to be subtracted. The container blank was determined on the empty bottles used to hold the samples.

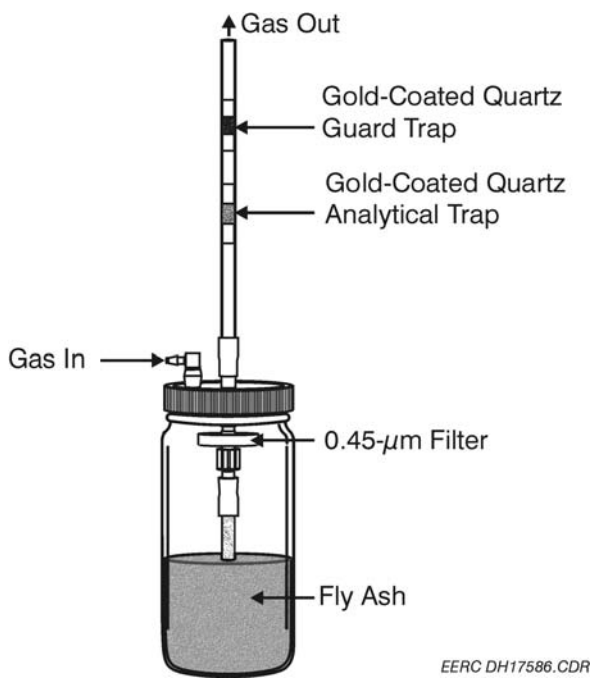

Figure 4. Mercury vapor release collection apparatus.

Examples of replicate data from a variety of CUB samples are shown in Figure 5.

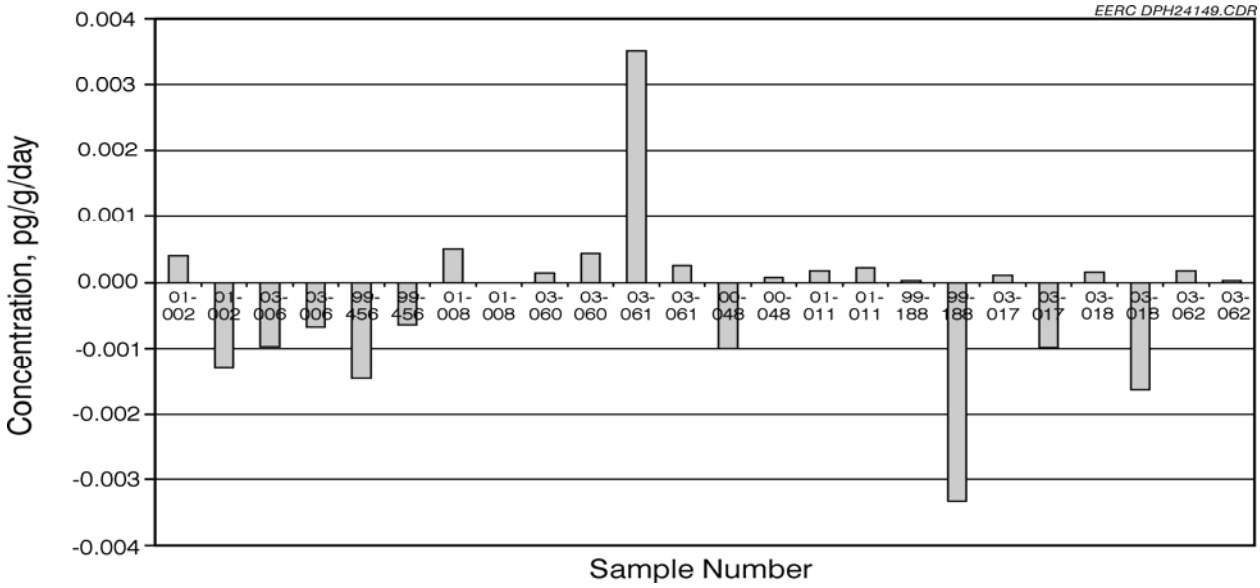

Figure 5. Average total long-term ambient-temperature mercury release or sorption as related to blank values, pg/g/day. Positive values indicate release and negative values indicate sorption of mercury.

Vapor-Phase Transport

Thermal Desorption at Elevated Temperature

Since mercury and mercury compounds are highly volatile, mercury was expected to be released from CUBs when they were exposed to elevated temperatures. Even mercury that is sorbed on fly ash, FGD material, or sorbents developed to remove mercury in flue gas is expected to have high potential to be released if exposed to high enough temperatures. Instrumental and equipment constraints existed for the physical testing of elevated temperature release of mercury from CUBs. These constraints included the following:

- Furnaces available for the experimental apparatus could only achieve maximum temperatures of 750°C.
- Fittings and connecting tubing needed to be heated in order to minimize the loss of mercury in the system.
- Gas flow to remove the mercury from the heated sample cell to the analytical cell needed to be constant.
- Temperature ramping needed to be controlled and consistent between sample runs.

The apparatus was constructed as shown in Figure 6. The CUB sample was weighed into a quartz tube with quartz wool used to keep the sample in place in the tube. Nominal sample size was approximately 1 g. The sample tube was placed into a small tube furnace capable of achieving a maximum of 750°C. A programmed temperature controller ramped the furnace from ambient to maximum temperature at 25°C per minute. In preliminary experiments, the maximum temperature achievable was 700°C, but an improved furnace was incorporated into the apparatus to increase the maximum to 750°C. A nitrogen gas flow of 5 cm^3/min was introduced into the tube furnace. As the mercury and mercury compounds desorbed from the CUB in the sample tube, the nitrogen flow carried them though the system to the electrically heated quartz analytical cell. The quartz analytical cell was operated at 800°C, allowing the detection of mercury compounds by thermally decomposing compounds to form elemental mercury, which can be detected by atomic absorption (AA). The analytical cell at the top of the diagram was placed in the center-focused beam path of an AA spectrophotometer (AAS). A mercury hollow cathode lamp was used as the light source, and the AAS detector was set to the 253.7 nm line for mercury. A Hewlett Packard 3395 integrator was used for data collection.

Examples of thermal desorption curves generated with this method are shown in Figures 7 and 8.

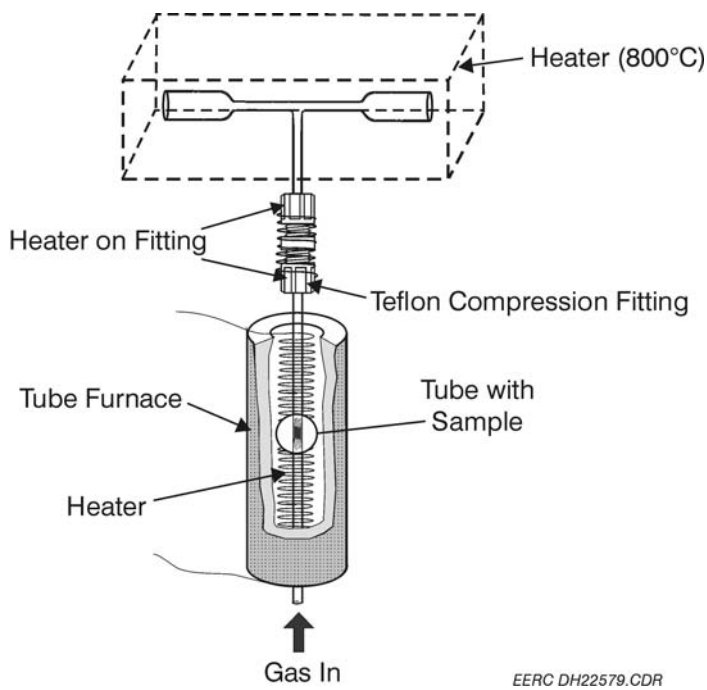

Figure 6. Mercury thermal desorption apparatus.

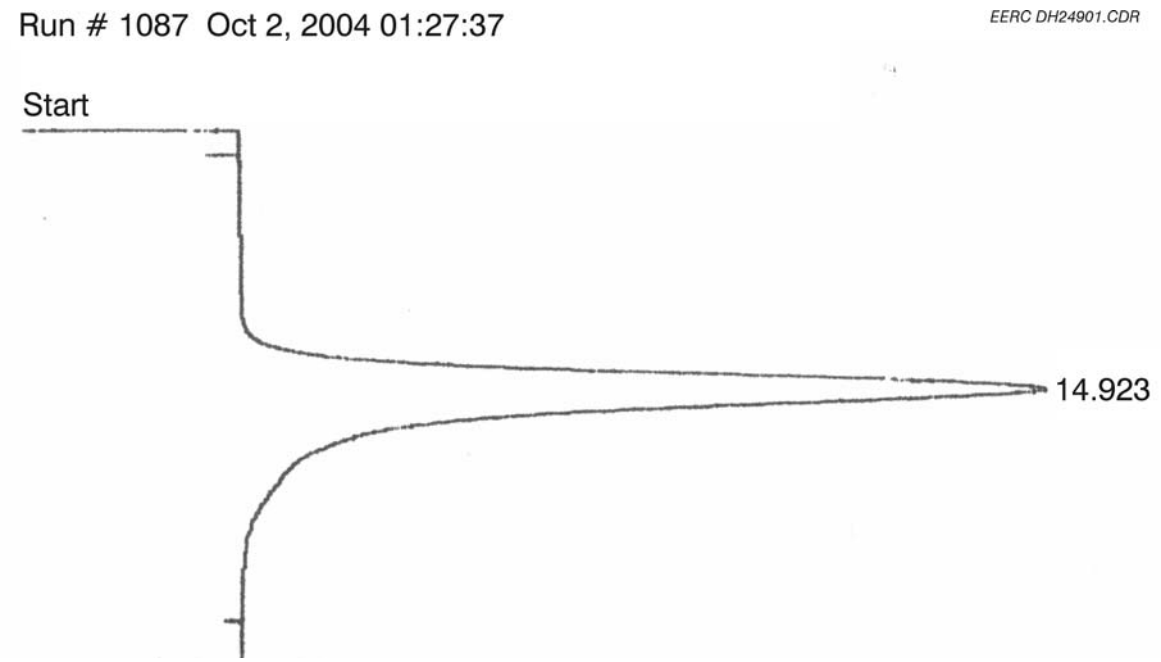

Figure 7. Typical thermal desorption curve for fly ash.

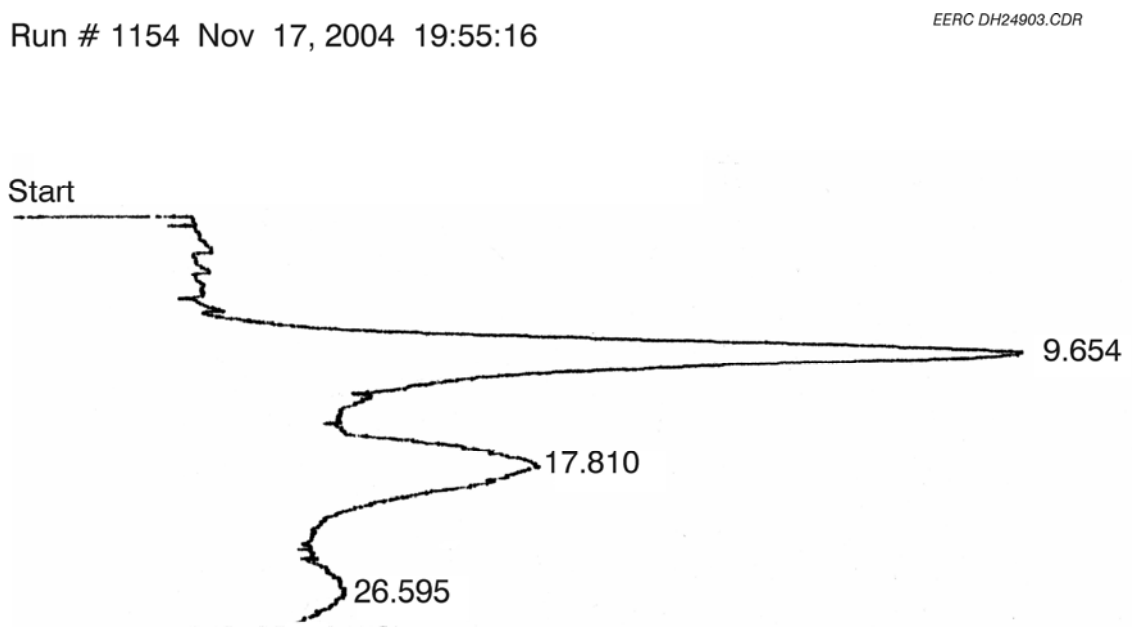

Figure 8. Example of thermal desorption curve for an FGD material.

Microbiologically Mediated Leaching and Vapor-Phase Transport

The EERC review of published data on the release of mercury from CUBs (1) reported that the only published method demonstrated for use in evaluating the release of mercury from CUBs on exposure to natural biota was developed by the EERC. The EERC method has been under development since approximately 1999 and has undergone numerous modifications to achieve the goal of evaluating the mercury release potential by leaching and offgassing when CUBs are under microbiologically mediated conditions. The first experiments performed using early versions of the apparatus focused on mercury releases by offgassing.

The first apparatus assembled to conduct microbiologically mediated vapor-phase mercury release used a 250-mL Erlenmeyer flask fitted with an impinger inlet/outlet tube with the inlet center shortened to 6 cm below the standard taper. Cylinder gas was passed through several sets of gold-coated quartz traps for mercury removal and admitted to each of the flasks through a gas distribution manifold that routed the gas through 0.25-mm GC capillary tubing to each of the individual flasks. A GC capillary length of approximately 60 cm, when pressurized to between 1 and 2 psig through a gas distribution manifold, provided a convenient means of regulating gas flow to approximately 2 cm^3/min. The gas passed mercury vapor from the head space of the flasks to a mercury vapor collection system at the outlet of the flasks, consisting of two traps. The nearest trap contained Supelco Carbotrap™, which collected organomercury compounds, followed by a gold-coated quartz trap, which collected elemental mercury.

The flasks were placed on a 16-flask wrist-action shaker. The experimental matrix consisted of eight flasks under anaerobic conditions (using argon) and eight flasks under aerobic conditions (using breathing-quality air). In each set of eight flasks, two contained only buffer, three contained the CUB with buffer (starved), and three contained the CUB with buffer and glucose (fed). An 80-g aliquot of CUB was placed in the flasks, and 100 mL of a phosphate buffer (with or without glucose as appropriate) was added to create a neutral pH. The CUB-containing flasks also had 100 µL of mixed bacterial culture added. The source of bacteria was a mixed bacterial inoculum from a brackish wetland. This setup is illustrated in Figure 9.

This apparatus underwent several iterations as difficulties were identified and solved. The wrist-action shaker was abandoned because it was unable to provide adequate suspended sample. Instead of the wrist-action shaker, a 9-place stir plate was introduced. This was operated for about 20 minutes every 3 hours to maintain sample agitation over the 30-day period of the experiment. Additionally, the sample size was reduced to 20 g, and the buffer was increased to 150 mL to provide adequate sample volume for additional trace element analyses. The buffer composition was also altered. It was found that phosphate and nitrate interfered with a derivitization step in the determination of organomercury compounds in the solid-phase microextraction (SPME) determination using GC separation followed by detection of the mercury compounds by atomic fluorescence. This technique is described later. The original buffer utilized nominal concentrations of phosphate and nitrate salts. The improved buffer used only 100 ppm of phosphate and substituted potassium glutamate as the nitrogen source. This simple change appeared to remove the interferences. Additionally, later experiments did not involve the use of starved control samples. In current experiments, all samples are fed with glucose. This setup is illustrated in Figure 10.

Figure 9. Microbiologically mediated mercury vapor-phase collection apparatus utilizing a wrist action shaker to facilitate mixing.

Figure 10. Microbiologically mediated mercury vapor-phase collection apparatus utilizing a stir plate to facilitate mixing.

Analyses of mercury and air toxic element releases were performed after a 30-day period. The gold-coated quartz traps and Carbotraps™ were analyzed as described in the analytical methods selection. Total mercury concentrations of the leachate were determined using CVAFS. Total air toxic element concentrations were determined using ICP–AES or ICP–MS.

Bacterial counts were performed upon completion of the experiment. A 1-mL aliquot of solution was taken from each flask. The aqueous supernate was serially diluted in 0.1% sodium pyrophosphate buffer (pH 7) and then used to inoculate a series of tubes containing 1% PTYG (peptone, tryptone, yeast extract, glucose) broth. The tubes were incubated at 30°C and growth, as turbidity, was monitored over a 3-week period.

SPME was used in the determination of organomercury species in the liquid portions of the samples. SPME is a sample collection technique in our case utilizing a fiber coated with polydimethylsiloxane. Samples containing organomercury compounds are first derivatized to increase the volatility of organomercury halides such as methylmercuric chloride. The derivitization reagents used were sodium tetraethyl borate, sodium tetrapropyl borate, and sodium tetraphenyl borate. Sodium tetraethyl borate was most commonly used. In the derivitization procedure, derivatizing agent, acetate buffer, an internal standard (usually propyl mercuric chloride), and sample were mixed in a septum-capped vial. In a relatively fast reaction, the halide is replaced with the appropriate alkyl or aryl group, depending on which derivatizing agent is chosen. A SPME fiber was inserted through the septum cap, and the sample was stirred using a Teflon-coated stir bar for 20 minutes. After this equilibration time, the SPME fiber was introduced into the heated inlet zone of a GC. Sample separation can be accomplished using a 0.53-mm capillary column 15 or 30 meters in length. The exit end of the column was connected to a heated (800°C) quartz tube, and makeup helium gas was added to increase the total flow to 25–30 mL per minute. The gas was then routed to an AF detector for determination of the separated mercury compounds. An example of a SPME chromatogram generated with this method is shown in Figure 11.

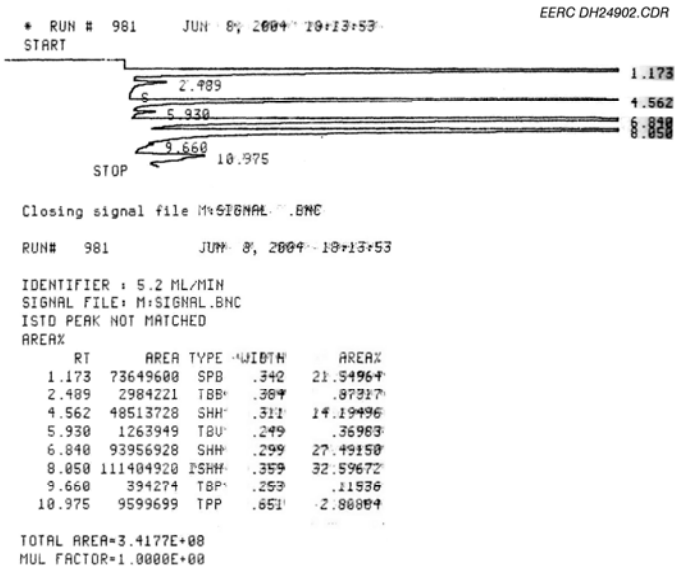

Figure 11. Example of a SPME chromatogram.

SUMMARY

Analytical methods were selected based on project needs and the sample types requiring analysis. Standard analytical methods were selected and used as frequently as possible. Replicate analyses were performed on a regular basis as part of the laboratory quality assurance/quality control program.

The leaching method selected, the SGLP–LTL, was selected based on EERC experience and familiarity with a large number of leaching procedures used to characterize CUBs and the appropriate application of those tests. The SGLP–LTL meets the criteria that EERC researchers have identified for leaching procedures to provide scientifically valid information. These criteria are as follows:

- Reactivity or other properties of the material being leached that may influence the leaching profile.

- The setting where the material is to be placed and the water that will most likely contact that material in that setting.

- The leaching time required to allow adequate time for hydration reactions to occur in reactive materials, such as high calcium coal fly ash.

The elevated-temperature vapor-phase release method underwent minor modifications early in the project but has been shown to provide reproducible data. The remaining technical challenge with the method as employed for this project is the limitations associated with the maximum achievable temperature to be applied to the CUB under investigation; and this cannot be addressed under this project.

The ambient-temperature vapor-phase release method developed for this work also presents technical challenges, but they are related to the quantitation limitations for mercury. The extremely low levels of mercury released at ambient temperatures are frequently near the levels of detection for the analytical system being used. The physical nature of the CUB samples also results in variable data and the need to modify the method. As an example, using the apparatus to evaluate the potential for release of mercury from a wet FGD material required modification of the apparatus to shorten the gas inlet tube to above the level of the sample because gas could not be forced through the material when the inlet was near the bottom of the sample container.

The method developed to evaluate the microbiologically mediated release of mercury underwent a relatively high degree of modification method over the first 2 years of the project. The final apparatus description and method now meets the project goals to produce reliable and relatively reproducible vapor and leachate samples. An evaluation of the particle-size reduction associated with the use of magnetic stir bars in the reaction vessels will be performed, and results of that evaluation will be included in future project reports.

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APPENDIX A

DRAFT ASTM STANDARD METHOD FOR SYNTHETIC GROUNDWATER LEACHING PROCEDURE

DRAFT ASTM STANDARD METHOD FOR SYNTHETIC GROUNDWATER LEACHING PROCEDURE

1. Scope

1.1 This method determines the leachability of constituents in wastes, products, or materials using a leaching solution designed to simulate leachate anticipated in field conditions. The method allows for prediction of changes in leachability brought about as a result of the formation of secondary hydrated phases and new minerals through interaction of the waste and water over extended periods of time.

1.2 his method consists of the agitation of waste and a synthetic groundwater solution over an extended period of time (greater than 60 days) with sampling at regular intervals.

1.3 This method allows a comparison of maximum leachate concentration with actual concentrations of leachate at time intervals of from 18 hours to 2 months or greater. The method allows for determination of mass of analyte mobilized based on a leachate concentration and percent of total element leached and provides information to estimate leachate concentration trends with respect to time.

1.4 This method may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this method to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Applicable Documents

2.1 American Society for Testing and Materials (ASTM) Standards:
D1129 Definitions of Terms Relating to Water
D1193 Specification for Reagent Water
D3987 Shake Extraction of Solid Waste with Water
D2216 Method for Laboratory Determination of Moisture Content of Soils

2.2Toxicity Characteristic Leaching Procedure (TCLP) EPA Method 1311

3. Definitions

3.1 For definitions of terms in this test method, see Definitions D1129.

3.2 Ettringite: Ettringite is a mineral having the nominal composition $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$. Ettringite is also the family name for a series of related compounds as is the case for many mineral families. Ettringite has characteristic structural features that are fairly unique. The structure comprises of calcium aluminate columns $\{Ca_6Al_2(OH)_{12}24H_2O\}^{6+}$ with the channels between these columns containing the other components, which include an oxyanion such as sulfate with hydroxide and water $\{(SO_4)_{2\text{-}4}\ (OH)_{0\text{-}4}\ (H_2O)_{0\text{-}6}\}^{6-}$. Ettringite is unique in that several elements that exist as oxyanions can substitute for the sulfate in the structure. These elements include but are not limited to arsenic, boron, chromium, molybdenum, selenium, and vanadium. Ettringite is known to form in the hydration of low-rank coal conversion solid residues

(CCSRs) and in CCSRs from advanced coal combustion processes such as fluidized-bed combustion (FBC) and limestone injection modified burner (LIMB).

3.3 Synthetic Groundwater: Synthetic groundwater as used in this application refers to a solution prepared in the laboratory containing the major geochemical parameters that would be found in water likely to contact the disposed CCSR. In the case of rainwater contact, this solution would be Type IV water, while with groundwater, a typical solution might contain calcium, magnesium, sodium, sulfate, and bicarbonate. Groundwater collected at the site of disposal could also be used, although if that were the case, corrections would have to be made for concentrations of trace elements already present in the water. It has been found with most CCSRs that it is the CCSR that regulates the equilibrium concentrations of major constituents in a synthetic groundwater leaching procedure; thus the inclusion of major geochemical constituents of actual groundwater may be unnecessary in many cases.

4. Significance and Use

4.1 This test is intended as a means for determining the mass of analyte readily mobilized by leaching with groundwater and also provides a means of determining the trend of leachate concentration change, if applicable. This test is intended for use with CCSRs and other materials formed under conditions of high temperature. The long-term nature of the test allows the determination of changes in concentrations of leached constituents as materials react with water to form secondary hydrated phases and other materials not present in the original material.

4.2 This test method is not intended to provide an accurate means of determining actual leachate concentrations under field conditions. The test does provide information about leaching under field conditions, however, and is useful in predicting the mobility of leachable constituents of CCSRs. The information provided from this test is an estimation of the mass of analyte that can be solubilized and trend of concentration change with respect to time. It should be noted that not all analytes will increase in concentration to an equilibrium level. Numerous elements, especially those trace elements that exist as oxyanions in aqueous solution, can exhibit a decrease in solution concentration after an initial and normally rapid increase in concentration. Additionally, major constituents can change solution concentration in a manner that would not be predicted on the basis of solubility calculations based on common mineral types, especially in CCSRs that form ettringite.

4.3 Since CCSRs are produced under conditions of high temperature, reactions with water during leaching can be expected. If these reactions produce ettringite, the concentrations of analytes present in solution as oxyanions can be expected to decrease with respect to time as ettringite forms. Other mineral formation can be expected to control leachate concentrations of additional analytes in ways not expected from simple solubility calculations based on the composition of ash before leaching. Additionally, the formation of secondary hydrated phases can be expected to affect the concentrations of major components.

5. Apparatus

5.1 For a complete description of the apparatus, see ASTM Standard Test Method for Shake Extraction of Solid Waste with Water. Any apparatus that can provide conditions of end-over-end agitation at 30 plus or minus 2 rpm as specified in the protocol for the TCLP can be used in this procedure.

6. Reagents

6.1 Purity of Reagents – Reagent-grade chemicals can be used, provided they do not contain appreciable amounts of elements to be determined in the extraction test. Reagents must be of sufficient purity so they do not interfere with the accuracy of the test or introduce bias in the results of analyses of leachates.

6.2 Purity of Water – Unless otherwise indicated, references to water shall be understood to mean Type IV reagent water at 18° to 27°C (Specification D1193). The method by which the Type IV water is prepared (distillation, ion exchange, reverse osmosis, etc.) should remain constant throughout the test.

6.3 Synthetic Groundwater – Synthetic groundwater is a leaching solution containing the major geochemical parameters important to groundwater likely to contact disposed CCSRs. As previously stated, in the case of CCSRs disposed above the water table and where the likely water to contact the disposed materials is rainwater, Type IV water can be used as the leaching solution. Where the water likely to contact disposed material is highly mineralized, either a sample of the water itself or a synthetic mixture prepared in the lab will be used. A typical North Dakota synthetic groundwater can be prepared by dissolving 0.50 grams of sodium sulfate and 1.00 grams of sodium bicarbonate in one liter of Type IV water. The analysis of this solution is as follows:

Na	436 mg/L
SO_4	338 mg/L
HCO_3	726 mg/L
pH	8.3–8.7

This sodium sulfate bicarbonate buffered water is typical for central and western North Dakota. Used for leaching low-rank coal ash, calcium was omitted since the ash itself ultimately determined the final calcium concentration.

Other formulas for synthetic groundwater can be prepared as needed for site-specific conditions. Care is required when preparing formulations containing calcium and magnesium that carbonates not be allowed to precipitate. This can be overcome by adding the reagents in the proper order, being certain that all carbonate is buffered to bicarbonate before adding the calcium and magnesium. Since sulfuric acid is used for sulfate and acid buffering, having excess sulfuric acid acidity will ensure this. A lotus spreadsheet is available for the calculations necessary to select reagents for synthetic groundwater formulations, but with the limited components, the calculations can also be easily carried out manually.

7. Sampling

8. Sample Preparation

8.1 For sample preparation, see D3987 Standard Test Method for Shake Extraction of Solid Waste with Water.

9. Procedure

The laboratory protocol is similar to the U.S. Environmental Protection Agency (EPA) TCLP and ASTM D3987 Standard Test Method for Shake Extraction of Solid Waste with Water. The primary difference is in the selection and preparation of the extraction fluid and the extension of test equilibration time over the prescribed 18-hour period. The long-term leaching aspect of this test is especially important since CCSRs can form secondary hydrated phases upon contact with water that can have a profound impact on leachate concentration of trace elements, especially elements that tend to exist as oxyanions in solution. The formation of secondary hydrated phases is known to take time, depending on the source of reactants in the leaching system. Time for complete formation of secondary hydrated phases can be from days to months. The test is not intended to carry the leaching to complete equilibrium but rather to extend the leaching time long enough for prediction of leachate concentration trends. For specifics related to the test, see D3987 Standard Test Method for Shake Extraction of Solid Waste with Water, or EPA Method 1311 TCLP, Federal Register, Vol 55, No. 126, June 29, 1990.

9.1 Record the physical description of the sample to be tested including particle size as known.

9.2 Solids Content – Determine the solids content of the sample as described in D3987 Standard Test Method for Shake Extraction of Solid Waste with Water, Sections 9.2.1 through 9.2.4.

9.3 Shake Procedure – Prepare the apparatus and begin the test as described in D3987 Standard Test Method for Shake Extraction of Solid Waste with Water, Sections 9.4 through 9.7, except that multiple shake test containers are prepared for each sample, the number depending on the duration of long-term leaching. Leaching solution shall be prepared as described in the following section. Long-term leaching intervals for this procedure are 18 hours, 1 week, 1 month, and 2 months. Longer times can be used if desired, although trends are usually identified within the 60-day duration of this long-term leaching procedure. An alternative to the use of 2 liters of leaching solution involves the use of 225-mL polysulfone bottles. To each bottle, 10 grams (dry weight) of ash is added along with 200 mL of leaching solution. Multiple bottles prepared in this

manner provide at least 150 mL of leachate and allow for the simultaneous extraction of a large number of samples with minimal space and equipment. It has been found that the standard equipment used for TCLP leaching will generally hold four of the polysulfone containers in the same position usually reserved for one 2-liter container.

9.4 Preparation of Leaching Solution: Leaching solution shall be prepared as recommended by an evaluation of field conditions. Where material disposed in a monofill is above the water table, the leaching solution shall be Type IV water (D1193 Specification for Reagent Water). Where the disposed material will likely be contacted by groundwater, either a sample of groundwater from the site or a synthetic groundwater shall be used for leaching. The synthetic groundwater if prepared in the lab shall contain all of the primary mineralization parameters as determined from an analysis of groundwater from the site or from an evaluation of data from analysis reports of water representative of the area of disposal.

9.5 Long-Term Leaching Sampling – Long-term samples are taken from containers prepared for the shake test in an identical manner to the specimen for the 18-hour sampling period. These containers are sampled at the end of 1 week, 1 month, and 2 months. Longer sampling intervals can be added as required. A convenient method for doing this procedure is to prepare the samples at time intervals so that all of the samples are finished at the same time. For example, one sample is prepared, a second is prepared 1 month later, a third sample 1 month later, and a final sample 18 hours before the other samples are due to be terminated. This saves considerable lab time and expedites the entire procedure.

9.6 Sampling of Leachate – Leachate is sampled for analysis as specified in D3987 Standard Test Method for Shake Extraction of Solid Waste with Water, Section 9.8.

9.7 Analysis

9.7.1 Selection of Analytes to Be Included in the Report. Analytes include all elements present in the ash in high enough concentrations to be problematic in disposal. These can be determined through screening procedures such as proton-induced x-ray emission (PIXE), instrumental neutron activation analysis (INAA), or plasma emission such as inductively coupled argon plasma (ICAP) spectroscopy or ICAP–mass spectrometry. Analytes for ash screening generally include the eight Resource Conservation and Recovery Act (RCRA) elements for regulatory purposes.

9.7.2 Determination of Total Concentration of Select Analytes. Analytes selected on the basis of screening (9.6.1) are determined on a bulk sample prepared by digestion of sample in a microwave heated-sealed Teflon bomb. Analyses can be performed according to methods for trace analyses in SW846.

9.7.3 Determination of Analyte Concentrations in Leachates. Concentrations of analytes in leachates shall be determined using methods as described in SW846 or by approved analytical techniques using EPA or other approved techniques.

All data shall be validated using good laboratory practice and approved quality assurance/quality control (QA/QC) procedures.

10. Calculation

10.1 Calculate the solids content as specified in D3987 Standard Test Method for Shake Extraction of Solid Waste with Water, Section 10.1.

10.2 Calculation of maximum analyte concentration is determined by dividing the total mass of analyte in a sample by the volume of liquid used for leaching. C = M/V where
C = Concentration of analyte
M = Mass of sample leached
V = Volume of leaching solution used

For this procedure the M:V ratio should be 1:20 as specified in the leaching protocol.

11. Report

11.1 The report shall include the following:

11.1.1 Source of CCSR, date of sampling, and preservation method used for leachates.
11.1.2 Description of CCSR including coal source, combustion technique, and method of sample collection (electrostatic precipitator, baghouse, etc.)
11.1.3 Solids content (see Method D2216)
11.1.4 A table of maximum analyte concentrations as determined by the method described in Section 10.2. (bulk chemical analysis)
11.1.5 A table of analyte concentrations as determined from analysis of 18-hour, 1-week, 1-month, 2-month, and any additional extended time intervals selected.

12. Precision and Bias

12.1 No information is presently available on the precision and accuracy or bias of this standard practice. It is recommended that standard QA/QC procedures such as analysis of duplicate samples and spiking of analyte be used for verification.

12.2 The precision of this test will vary depending on the material being leached.

APPENDIX E

SAMPLE PRIORITIZATION

Mercury and Air Toxic Element Impacts of Coal Combustion Byproduct Disposal and Utilization

Sample Selection Criteria	EERC Priority (H=high; M=medium; L=low)	Justification
FUEL TYPES		
• Bituminous	H	commonly used
• Subbituminous	H	commonly used
• Lignite	H	commonly used but generally higher mercury content
• Oil	H	Industry sponsor priority
• Bituminous–Subbituminous Blends	~~H~~ M	limited use
• Subbituminous–Lignite Blends	L	Only very limited use
BURNER TYPES		
• pc fired	H	Most common
• Cyclone	M	Limited installations
• Stoker	L	Limited installations
• FBC	L	Limited utility installations
PARTICULATE COLLECTION		
• Fabric Filter	H	commonly used
• ESP Cold Side	H	Most common
• ESP Hot Side	M	Less common
• ESP/Mechanical	L	Limited installations
• FF/Mechanical	L	Limited installations
SO_2 CONTROL		
• None	H	Most common
• Wet FGD (calcium based) (include lime & limestone sorbents; forced oxidation & natural or in situ oxidation systems.)	H	Commonly used
• Dry FGD (calcium based)	M	Less common
• Spray Dryer Atomizer (SDA)	H	Commonly used with potential for additional installations
• Wet FGD (alkali based)	L	Limited installations
• Dry FGD (alkali based)	L	Limited installations
AMMONIA-BASED SYSTEMS		
• None	H	Most common
• Ammonia Injection	H	Commonly used
• SCR	H	Commonly used
• SNCR	~~H~~ L	Limited installations

Mercury and Air Toxic Element Impacts of Coal Combustion Byproduct Disposal and Utilization (continued)

Sample Selection Criteria	EERC Priority (H=high; M=medium; L=low)	Justification
PROPOSED Hg CONTROL		
• Carbon Injection	H	Predicted for high use
• Noncarbon Sorbent Injection	H	Good potential for limited impact to ash quality
• Modified FGD	H	Expected to concentrate mercury on FGD material and limit impact to fly ash quality
• Fine Particulate Control	H	Good potential for limited impact to ash quality
• Fly ash from carbon removal technologies	H	High interest to sponsors

APPENDIX F

SAMPLE IDENTIFICATION NUMBER AND DESCRIPTIONS

ID No.	Collection Date	Sample Type	Sample Type Notes	Sample Treatment	Coal Type	Coal Notes	Burner Type	Particulate Collection	Particulate Collection Description	Collection Point
99-188	2/9/1999	FGD-SDA			PRB Subbituminous		pc-fired	FF		Silo
00-048	10/12/2000	FGD-SDA			Fort Union Lignite		Cyclone	FF		
01-002	2/26/2001	Fly Ash			Eastern Bituminous		pc-fired	ESP	Cold-side	
01-008	4/5/2001	Fly Ash			PRB Subbituminous		pc-fired	ESP	Hot-side	
01-011	5/9/2001	FGD-SDA			Fort Union Lignite		Cyclone	FF		
02-002	4/25/2001	Fly Ash + Activated Carbon			Eastern Bituminous	Low S washed	pc-fired	COHPAC	ESP-HS & COHPAC FF	FF
02-003	4/26/2001	Fly Ash + Activated Carbon			Eastern Bituminous	Low S washed	pc-fired	COHPAC	ESP-HS & COHPAC FF	FF
02-004	11/14/2001	Fly Ash + Activated Carbon			PRB Subbituminous		pc-fired	ESP	Cold-side	ESP Field
02-005	11/14/2001	Fly Ash + Activated Carbon			PRB Subbituminous		pc-fired	ESP	Cold-side	ESP Field
02-006	11/14/2001	Fly Ash + Activated Carbon			PRB Subbituminous		pc-fired	ESP	Cold-side	ESP Field
02-007	4/25/2001	Fly Ash + Activated Carbon			Eastern Bituminous	Low S washed	pc-fired	COHPAC	ESP-HS & COHPAC FF	FF
02-069	7/18/2002	Fly Ash + Activated Carbon			Eastern Bituminous	Low S	pc-fired	ESP	Cold-side	ESP Row
02-070	7/18/2002	Fly Ash			Eastern Bituminous	Low S	pc-fired	ESP	Cold-side	ESP Field
02-071	7/22/2002	Fly Ash + Activated Carbon			Eastern Bituminous	Low S	pc-fired	ESP	Cold-side	ESP Field
02-072	7/22/2002	Fly Ash			Eastern Bituminous	Low S	pc-fired	ESP	Cold-side	ESP Field
02-073	7/6/2002	Fly Ash			Eastern Bituminous	Low S	pc-fired	ESP	Cold-side	ESP Field
02-074	7/6/2002	Fly Ash			Eastern Bituminous	Low S	pc-fired	ESP	Cold-side	ESP Field
02-076	9/24/2002	Fly Ash			South American Bituminous	Low S	pc-fired	ESP	Cold-side	ESP Row
03-004		Fly Ash			Eastern Bituminous	KY & WV; Low S	pc-fired	ESP	Cold-side	ESP Field
03-005		Fly Ash			Eastern Bituminous	KY & WV; Low S	pc-fired	ESP	Cold-side	ESP Field
03-006		Fly Ash			Eastern Bituminous	KY & WV; Low S	pc-fired	ESP	Cold-side	ESP Field
03-007		Fly Ash			Eastern Bituminous	KY & WV; Low S	pc-fired	ESP	Cold-side	ESP Field
03-008	11/19/2002	Fly Ash			South American Bituminous	Low S	pc-fired	ESP	Cold-side	ESP Row
03-009	11/20/2002	Fly Ash + Activated Carbon			South American Bituminous	Low S	pc-fired	ESP	Cold-side	ESP Row
03-010	11/22/2002	Fly Ash + Activated Carbon			South American Bituminous	Low S	pc-fired	ESP	Cold-side	ESP Row
03-016	6/10/2003	Fly Ash			Fort Union Lignite		pc-fired	ESP	Cold-side	ESP Field
03-017	6/10/2003	Fly Ash + Activated Carbon			Fort Union Lignite		pc-fired	ESP	Cold-side	ESP Field
03-018	6/10/2003	Fly Ash + Activated Carbon			Fort Union Lignite		pc-fired	ESP	Cold-side	ESP Field
03-019	6/10/2003	Fly Ash + Activated Carbon			Fort Union Lignite		pc-fired	ESP	Cold-side	ESP Field
03-060	5/21/2003	Fly Ash + Activated Carbon			PRB Subbituminous	Belle Ayr coal; 6109 tons/day coal + 94 tons/day waste seed corn: 98.5% coal/1.5% biomass	Cyclone	Advanced Hybrid		Advanced Hybrid
03-061	5/10/2003	Fly Ash			PRB Subbituminous	6400 tons/day coal	Cyclone	Advanced Hybrid		Advanced Hybrid
03-062	6/10/2003	Fly Ash + Activated Carbon		lab composite of 03-017 – 03-019 (80/10/10 wt%)	Fort Union Lignite		pc-fired	ESP	Cold-side	ESP Field

ID No.	Mercury Control	Mercury Control Configuration	Paired Mercury Control Sample	Low NOx Burner (LNB)	SO_2 Control	SO_2 Control Description	Ammonia-Based System
99-188	No			No	FGD-dry calcium	Lime spray dryer	No
00-048	No			No	FGD-dry	Spray dryer	Unknown
01-002	No			LNB	No		Unknown
01-008	No			LNB	No		Unknown
01-011	No			No	FGD-dry	Spray dryer	Unknown
02-002	Activated Carbon Injection	Post-Primary PCD		LNB	No		No
02-003	Activated Carbon Injection	Post-Primary PCD		LNB	No		No
02-004	Activated Carbon Injection	Pre-Primary PCD		No	No		No
02-005	Activated Carbon Injection	Pre-Primary PCD		No	No		No
02-006	Activated Carbon Injection	Pre-Primary PCD		No	No		No
02-007	Activated Carbon Injection	Post-Primary PCD		LNB	No		No
02-069	Activated Carbon Injection	Post-Primary PCD	Hg control test sample of 02-070	LNB w/ overfire air	No		No
02-070	No		Baseline of 02-069	LNB w/ overfire air	No		No
02-071	Activated Carbon Injection	Post-Primary PCD	Hg control test sample of 02-072	LNB w/ overfire air	No		No
02-072	No		Baseline of 02-071	LNB w/ overfire air	No		No
02-073	No			LNB w/ overfire air	No		No
02-074	No			LNB w/ overfire air	No		No
02-076	No		Baseline of 03-009, 03-010	LNB	No		SNCR
03-004	No			LNB	No		SCR
03-005	No			LNB	No		SCR
03-006	No			LNB	No		SCR
03-007	No			LNB	No		SCR
03-008	No			LNB	No		SNCR: Urea-based
03-009	Activated Carbon Injection	Pre-Primary PCD	Hg control test sample of 02-076	LNB	No		SNCR: Urea-based
03-010	Activated Carbon Injection	Pre-Primary PCD	Hg control test sample of 02-076	LNB	No		SNCR: Urea-based
03-016	No			No	No		No
03-017	Activated Carbon Injection			No	No		No
03-018	Activated Carbon Injection			No	No		No
03-019	Activated Carbon Injection			No	No		No
03-060	Fine Particulate Control + Activated Carbon Injection		Hg control test sample of 03-061	No	No		No
03-061	Fine Particulate Control		Baseline of 03-060	No	No		No
03-062	Activated Carbon Injection			No	No		No

ID No.	Collection Date	Sample Type	Sample Type Notes	Sample Treatment	Coal Type	Coal Notes	Burner Type	Particulate Collection	Particulate Collection Description	Collection Point
03-063	10/2/2003	Fly Ash			Eastern Bituminous	High S OH	pc-fired	ESP	Cold-side	Silo
03-065	10/2/2003	FGD Gypsum			Eastern Bituminous	High S OH	pc-fired	ESP	Cold-side	Stacker pad
03-067	10/2/2003	FGD Slurry		dewatered with Büchner funnel 05/03/05 – resulting liquid saved as 03-103	Eastern Bituminous	High S OH	pc-fired	ESP	Cold-side	Before oxidizer
03-078	10/30/2002	Fly Ash			Fort Union Lignite		Cyclone	ESP	Cold-side	ESP Field
03-079	10/30/2002	Fly Ash			Fort Union Lignite		Cyclone	ESP	Cold-side	ESP Field
03-080	10/30/2002	Fly Ash			Fort Union Lignite		Cyclone	ESP	Cold-side	ESP Field
03-081	10/30/2002	Fly Ash			Fort Union Lignite		Cyclone	ESP	Cold-side	ESP Field
03-082	11/18/2003	FGD Filtercake		dewatered – resulting liquid saved as 03-104	Eastern Bituminous		pc-fired	ESP	Cold-side	
03-083	11/18/2003	Fly Ash			Eastern Bituminous		pc-fired	ESP	Cold-side	
03-084	11/18/2003	Fixated FGD		portion ground & dried at <40°C for microbiological experiment	Eastern Bituminous		pc-fired	ESP	Cold-side	
03-085	11/18/2003	Fly Ash			Eastern Bituminous		pc-fired	ESP	Cold-side	Silo
03-086	11/18/2003	FGD Filtercake		water poured off 1/18/06 – resulting liquid saved as 03-114	Eastern Bituminous		pc-fired	ESP	Cold-side	Vacuum filter discharge
03-087	11/18/2003	Fixated FGD			Eastern Bituminous		pc-fired	ESP	Cold-side	Stockpile
03-088		Fly Ash			Eastern Bituminous		pc-fired	ESP	Cold-side	Silo
03-089		FGD Gypsum			Eastern Bituminous		pc-fired	ESP	Cold-side	Solids from FGD gypsum filter plant
03-103	10/2/2003	Lab dewatered FGD liquor	lab dewatered 03-067: FGD slurry		Eastern Bituminous	High S OH	pc-fired	ESP	Cold-side	Lab generated
03-104	11/18/2003	Lab dewatered FGD liquor	lab dewatered 03-082: FGD filtercake		Eastern Bituminous		pc-fired	ESP	Cold-side	Lab generated
03-114		Lab dewatered FGD liquor	lab dewatered 03-086: FGD filtercake		Eastern Bituminous		pc-fired	ESP	Cold-side	Lab generated
04-003	6/28/2002	Fly Ash			Eastern Bituminous	WV, KY, & PA; Low S	pc-fired	FF		FF
04-004	6/28/2002	Fly Ash			Eastern Bituminous	WV, KY, & PA; Low S	pc-fired	ESP	Cold-side	ESP Field
04-006	11/1/1999	Fly Ash			Western Bituminous	CO	pc-fired	FF		FF
04-007	5/22/2003	Fly Ash			Western Bituminous	UT	pc-fired	FF		FF
04-029		Fly Ash			PRB Subbituminous		pc-fired	COHPAC	ESP-CS & COHPAC FF/Mechanical	ESP Field
04-030	11/17/2003	Fly Ash + Activated Carbon			Fort Union Lignite		pc-fired	ESP	Cold-side	ESP Hopper
04-031	11/18/2003	Fly Ash + Activated Carbon			Fort Union Lignite		pc-fired	ESP	Cold-side	ESP Hopper
04-032	11/20/2003	Fly Ash + Activated Carbon			Fort Union Lignite		pc-fired	ESP	Cold-side	ESP Hopper

ID No.	Mercury Control	Mercury Control Configuration	Paired Mercury Control Sample	Low NOx Burner (LNB)	SO_2 Control	SO_2 Control Description	Ammonia-Based System
03-063	No			No	FGD-wet calcium	Mg-enhanced lime	No
03-065	No			No	FGD-wet calcium	Mg-enhanced lime	No
03-067	No			No	FGD-wet calcium	Mg-enhanced lime	No
03-078	No			No	FGD-wet calcium	Lime with fly ash recycle	No
03-079	No			No	FGD-wet calcium	Lime with fly ash recycle	No
03-080	No			No	FGD-wet calcium	Lime with fly ash recycle	No
03-081	No			No	FGD-wet calcium	Lime with fly ash recycle	No
03-082	No			No	FGD-wet calcium	Limestone sorbents	SCR
03-083	No			No	FGD-wet calcium	Limestone sorbents	SCR
03-084	No			No	FGD-wet calcium	Limestone sorbents	SCR
03-085	No			LNB	FGD-wet calcium	Limestone sorbents	SCR & Ammonia Injection
03-086	No			LNB	FGD-wet calcium	Limestone sorbents	SCR & Ammonia Injection
03-087	No			LNB	FGD-wet calcium	Limestone sorbents	SCR & Ammonia Injection
03-088	No			LNB	FGD-wet calcium	Limestone-forced oxidation	SCR & Ammonia Injection
03-089	No			LNB	FGD-wet calcium	Limestone-forced oxidation	SCR & Ammonia Injection
03-103	No			No	FGD-wet calcium	Mg-enhanced lime	No
03-104	No			No	FGD-wet calcium	Limestone sorbents	SCR
03-114	No			LNB	FGD-wet calcium	Limestone sorbents	SCR & Ammonia Injection
04-003	No			No	No		No
04-004	No			No	No		No
04-006	No			No	No		No
04-007	No			LNB w/ overfire air	FGD-wet calcium	Limestone sorbents	No
04-029	No			LNB	No		Ammonia Injection
04-030	Activated Carbon Injection	Post-Primary PCD		LNB	FGD-wet calcium	Lime-natural or in situ oxidation	No
04-031	Activated Carbon Injection	Post-Primary PCD		LNB	FGD-wet calcium	Lime-natural or in situ oxidation	No
04-032	Activated Carbon Injection	Post-Primary PCD		LNB	FGD-wet calcium	Lime-natural or in situ oxidation	No

ID No.	Collection Date	Sample Type	Sample Type Notes	Sample Treatment	Coal Type	Coal Notes	Burner Type	Particulate Collection	Particulate Collection Description	Collection Point
04-033	11/20/2003	Fly Ash + Activated Carbon			Fort Union Lignite		pc-fired	ESP	Cold-side	ESP Hopper
04-035	3/24/2004	Fly Ash			Fort Union Lignite		pc-fired	ESP	Cold-side	ESP Hopper
04-036	4/27/2004	Fly Ash + Enhancing Agent + Activated Carbon			Fort Union Lignite		pc-fired	ESP	Cold-side	ESP Hopper
04-042	5/11/2004	Fly Ash			Gulf Coast Lignite		Unknown	ESP	Cold-side	ESP Field
04-043	5/11/2004	Fly Ash			Gulf Coast Lignite		Unknown	ESP	Cold-side	ESP Field
04-044	5/11/2004	Fly Ash			Gulf Coast Lignite		Unknown	ESP	Cold-side	ESP Field
04-045	5/11/2004	Fly Ash			Gulf Coast Lignite		Unknown	ESP	Cold-side	ESP Field
04-054	11/18/2003	Fly Ash + Activated Carbon			Eastern Bituminous	Low S washed	pc-fired	COHPAC	ESP-HS & COHPAC FF	FF
04-067	5/21/2004	Fly Ash + Enhancing Agent + Activated Carbon			Fort Union Lignite		pc-fired	ESP	Cold-side	ESP Field
04-082	8/19/2004	FGD Gypsum			Eastern Bituminous		pc-fired	ESP	Cold-side	Vacuum drying belt at gypsum processing facility after drying
04-083	11/8/2004	FGD Gypsum			Eastern Bituminous		pc-fired	ESP	Cold-side	Vacuum drying belt at gypsum processing facility after drying
05-001	2/2/2005	Fly Ash			Fort Union Lignite		pc-fired	FF		FF
05-002	2/2/2005	FGD-SDA			Fort Union Lignite		pc-fired	FF		SDA Hopper
05-003	2/24/2005	Fly Ash + Enhancing Agent + Activated Carbon			Fort Union Lignite		pc-fired	FF		FF
05-004	2/24/2005	FGD-SDA + Enhancing Agent + Activated Carbon			Fort Union Lignite		pc-fired	FF		SDA Hopper
05-005	3/17/2005	Fly Ash			Fort Union Lignite		Cyclone	ESP	Cold-side	ESP Hopper
05-009	7/19/2005	FGD Gypsum			Eastern Bituminous	High S Ohio	pc-fired	ESP	Cold-side	Stockpile
05-010	7/19/2005	Fly Ash			Eastern Bituminous	High S Ohio	pc-fired	ESP	Cold-side	ESP Hopper
05-011	7/19/2005	FGD Gypsum Filtrate			Eastern Bituminous	High S Ohio	pc-fired	ESP	Cold-side	Filtrate pumps
05-013	4/16/2005	Fly Ash + Activated Carbon			Fort Union Lignite		pc-fired	FF		FF
05-017	4/13/2005	Fly Ash + Enhancing Agent			Fort Union Lignite		Cyclone	ESP	Cold-side	ESP Hopper
05-018	8/17/2005	Fly Ash			Eastern Bituminous		pc-fired	ESP	Cold-side	Silo
05-019	8/17/2005	FGD Filtercake		water poured off 9/21/05 & solid pressed – resulting liquid saved as 05-032	Eastern Bituminous		pc-fired	ESP	Cold-side	Vacuum filter discharge
05-020	8/17/2005	Fixated FGD			Eastern Bituminous		pc-fired	ESP	Cold-side	Stockpile
05-022	8/17/2005	FGD Filtrate			Eastern Bituminous		pc-fired	ESP	Cold-side	Filtrate pumps
05-023	5/14/2005	Fly Ash + Activated Carbon			Fort Union Lignite		pc-fired	FF		FF

ID No.	Mercury Control	Mercury Control Configuration	Paired Mercury Control Sample	Low NOx Burner (LNB)	SO_2 Control	SO_2 Control Description	Ammonia-Based System
04-033	Activated Carbon Injection	Post-Primary PCD		LNB	FGD-wet calcium	Lime-natural or in situ oxidation	No
04-035	No		Baseline of 04-036	LNB w/ overfire air	No		No
04-036	Activated Carbon Injection + Enhancing Agent Injection	Pre-Primary PCD	Hg control test sample of 04-035	LNB w/ overfire air	No		No
04-042	No			LNB	FGD-wet calcium	Limestone sorbents	No
04-043	No			LNB	FGD-wet calcium	Limestone sorbents	No
04-044	No			LNB	FGD-wet calcium	Limestone sorbents	No
04-045	No			LNB	FGD-wet calcium	Limestone sorbents	No
04-054	Activated Carbon Injection	Post-Primary PCD		LNB	No		No
04-067	Activated Carbon Injection + Enhancing Agent Injection	Enhancing Agent on Coal, ACI Pre-Primary PCD		LNB w/ overfire air	No		No
04-082	No			No	FGD-wet calcium	Limestone-forced oxidation	SCR
04-083	No			No	FGD-wet calcium	Limestone-forced oxidation	No
05-001	No		Baseline of 05-003	No	FGD-dry	Spray dryer	No
05-002	No		Baseline of 05-004	No	FGD-dry	Spray dryer	No
05-003	Activated Carbon Injection + Enhancing Agent Injection	Enhancing Agent on Coal, ACI before SDA	Hg control test sample of 05-001	No	FGD-dry	Spray dryer	No
05-004	Activated Carbon Injection + Enhancing Agent Injection	Enhancing Agent on Coal, ACI before SDA	Hg control test sample of 05-002	No	FGD-dry	Spray dryer	No
05-005	No		Baseline of 05-017	No	FGD-wet calcium	Lime with fly ash recycle	No
05-009	No			No	FGD-wet calcium	Mg-enhanced lime	No
05-010	No			No	FGD-wet calcium	Mg-enhanced lime	No
05-011	No			No	FGD-wet calcium	Mg-enhanced lime	No
05-013	Activated Carbon Injection	Post-Primary PCD	Hg control test sample of 05-038	No	No		No
05-017	Enhancing Agent Injection	Enhancing Agent on Coal	Hg control test sample of 05-005	No	FGD-wet calcium	Lime with fly ash recycle	No
05-018	No			LNB	FGD-wet calcium	Limestone sorbents	SCR & Ammonia Injection
05-019	No			LNB	FGD-wet calcium	Limestone sorbents	SCR & Ammonia Injection
05-020	No			LNB	FGD-wet calcium	Limestone sorbents	SCR & Ammonia Injection
05-022	No			LNB	FGD-wet calcium	Limestone sorbents	SCR & Ammonia Injection
05-023	Activated Carbon Injection	Post-Primary PCD: High fly ash content	Hg control test sample of 05-038	No	No		No

ID No.	Collection Date	Sample Type	Sample Type Notes	Sample Treatment	Coal Type	Coal Notes	Burner Type	Particulate Collection	Particulate Collection Description	Collection Point
05-024	5/29/2005	Fly Ash + Activated Carbon			Fort Union Lignite		pc-fired	FF		FF
05-025	8/23/2005	Fly Ash + Activated Carbon			Fort Union Lignite		pc-fired	FF		FF
05-032		Lab dewatered FGD liquor	lab filtered 05-019: FGD filtercake		Eastern Bituminous		pc-fired	ESP	Cold-side	Lab generated
05-038	10/18/2005	Fly Ash			Fort Union Lignite		pc-fired	FF		FF
05-040	11/1/2005	Fly Ash + Activated Carbon			Fort Union Lignite		pc-fired	FF		FF
06-001	11/17/2005	Fly Ash + Activated Carbon			Fort Union Lignite		pc-fired	FF		FF

ID No.	Mercury Control	Mercury Control Configuration	Paired Mercury Control Sample	Low NOx Burner (LNB)	SO_2 Control	SO_2 Control Description	Ammonia-Based System
05-024	Activated Carbon Injection	Post-Primary PCD	Hg control test sample of 05-038	No	No		No
05-025	Activated Carbon Injection	Post-Primary PCD: High fly ash content	Hg control test sample of 05-038	No	No		No
05-032	No			LNB	FGD-wet calcium	Limestone sorbents	SCR & Ammonia Injection
05-038	No		Baseline of 05-013, 05-023, 05-024, 05-025, 05-040, 06-001	No	No		No
05-040	Activated Carbon Injection	Post-Primary PCD	Hg control test sample of 05-038	No	No		No
06-001	Activated Carbon Injection	Post-Primary PCD	Hg control test sample of 05-038	No	No		No

APPENDIX G

TOTAL TRACE ELEMENTAL DATA

ID No.	Sample Type	Mercury Control Configuration	Coal Type	As (µg/g)	Cd (µg/g)	Cr (µg/g)	Pb (µg/g)	Hg (µg/g)	Ni (µg/g)	Se (µg/g)	Total Trace Elemental Comments
99-188	FGD-SDA		PRB Subbituminous	14.7	<1	26.3	37	0.112	12.9	9.92	
02-002	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous					55.6			
02-003	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous					32.0			
02-004	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous					1.09			
02-005	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous					5.00			
02-006	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous	37.4	1.97	111	60.2	5.81	50.6	69.4	
02-007	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous					60.5			
02-007	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous					120			
02-069	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous					0.742			
02-070	Fly Ash		Eastern Bituminous					0.190			
02-070	Fly Ash		Eastern Bituminous					0.197			
02-071	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous					0.975			
02-072	Fly Ash		Eastern Bituminous					0.163			
02-073	Fly Ash		Eastern Bituminous					0.234			
02-074	Fly Ash		Eastern Bituminous					0.613			
02-076	Fly Ash		South American Bituminous					0.607			
03-004	Fly Ash		Eastern Bituminous	72.2	<1	142	65.4	0.097	68.3	7.93	
03-005	Fly Ash		Eastern Bituminous	71.4	<1	148	72.6	0.084	85.7	8.54	
03-006	Fly Ash		Eastern Bituminous	78.0	1.36	135	94.3	0.194	60.4	13.6	
03-007	Fly Ash		Eastern Bituminous	68.6	1.13	138	89.0	0.141	55.2	11.4	
03-007	Fly Ash		Eastern Bituminous	72.1	<1	135	72.4		87.4	12.2	
03-008	Fly Ash		South American Bituminous					0.151			
03-016	Fly Ash		Fort Union Lignite	33.7	<1	59.6	25.6	0.016	59.5	13.0	
03-017	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite	40.1	<1	57.7	30.4	0.225	56.5	13.5	
03-018	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite	54.7	<1	61.5	40.4	0.289	54.0	14.8	
03-019	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite	73.9	<1	64.8	47.4	2.22	51.4	21.7	
03-060	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous	19.4	1.87	76.7	82.2	1.86	67.6	34.2	
03-061	Fly Ash		PRB Subbituminous	37.8	1.78	44.2	58.1	0.578	79.0	44.3	
03-061	Fly Ash		PRB Subbituminous	49.2	1.52	76.1	62.1		107		
03-061	Fly Ash		PRB Subbituminous	43.4	1.86	82.4	58.4		95.8	44.7	
03-062	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite	43.3	<1	54.4	30.3	0.490	57.6	13.4	
03-063	Fly Ash		Eastern Bituminous	45.5	<1	128	37.1	<0.1	23.3	4.94	
03-065	FGD Gypsum		Eastern Bituminous	<1	<1	2.90	<3	<0.1	<1	<2	
03-067	FGD Slurry		Eastern Bituminous					0.120			
03-067	FGD Slurry		Eastern Bituminous					0.196		3.01	Dewatered sample
03-067	FGD Slurry		Eastern Bituminous	<1	<1	6.61	<3	<0.1	2.87		
03-078	Fly Ash		Fort Union Lignite					0.662			
03-079	Fly Ash		Fort Union Lignite	351	2.1	83.2	68.3	0.785	40.9	14.7	
03-080	Fly Ash		Fort Union Lignite	157	1.06	66.1	39.9	0.440	63.5	11.9	
03-081	Fly Ash		Fort Union Lignite	492	3.60	85.2	124	0.459	68.4	18.1	
03-082	FGD Filtercake		Eastern Bituminous	<1	<1	10.4	<3	0.218	3.50	<2	
03-082	FGD Filtercake		Eastern Bituminous					0.248		<2	Dewatered sample
03-083	Fly Ash		Eastern Bituminous	163	3.48	134	258		252	4.78	
03-083	Fly Ash		Eastern Bituminous	169	3.66	139	272	0.017	266	3.97	
03-084	Fixated FGD		Eastern Bituminous	53.4	1.24	53.6	80.3	0.180	87.2	4.46	
03-085	Fly Ash		Eastern Bituminous	145	2.55	124	247	0.034	277	4.04	
03-086	FGD Filtercake		Eastern Bituminous	<1	<1	10.2	4.40	0.162	3.98	2.64	
03-087	Fixated FGD		Eastern Bituminous	53.8	1.08	51.6	86.7	0.136	98.7	3.71	
03-088	Fly Ash		Eastern Bituminous	44	8.59	160	249	0.010	74.5	7.42	

ID No.	Sample Type	Mercury Control Configuration	Coal Type	As (µg/g)	Cd (µg/g)	Cr (µg/g)	Pb (µg/g)	Hg (µg/g)	Ni (µg/g)	Se (µg/g)	Total Trace Elemental Comments
03-089	FGD Gypsum		Eastern Bituminous	<1	1.89	4.13	<3	<0.1	<1	<2	
03-089	FGD Gypsum		Eastern Bituminous					0.096			
04-003	Fly Ash		Eastern Bituminous	49.8	<1	138	60.4		77.2	19.3	
04-003	Fly Ash		Eastern Bituminous	42.2	<1	132	60.5	0.685	75.9	19.1	
04-004	Fly Ash		Eastern Bituminous	31.5	<1	144	55.7	0.041	81.6	5.77	
04-006	Fly Ash		Western Bituminous	5.90	<1	43.8	38.8	0.144	26.1	10.2	
04-007	Fly Ash		Western Bituminous	7.09	<1	64.9	29.1	0.521	22.0	13.5	
04-029	Fly Ash		PRB Subbituminous	31.1	1.07	63.7	38.6	0.261	39.9	15.7	
04-030	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	136	3.34	92.8	85.3	0.147	24.2	28.1	
04-031	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	134	3.24	91.8	83.4	0.174	28.2	31.2	
04-032	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	161	3.38	94.8	74.9	0.470	40.0	19.6	
04-033	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	148	2.91	86.5	74.9	1.43	29.1	23.2	
04-035	Fly Ash		Fort Union Lignite	36.0	<1	55.4	21.9	0.159	17.2	9.78	
04-036	Fly Ash + Activated Carbon + Enhancing Agent	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite	43.4	<1	48.4	18.3	0.287	23.1	11.0	
04-036	Fly Ash + Activated Carbon + Enhancing Agent	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite	46.3	<1	49.1	19.1		23.8	9.86	
04-042	Fly Ash		Gulf Coast Lignite					0.371			
04-043	Fly Ash		Gulf Coast Lignite					0.689			
04-044	Fly Ash		Gulf Coast Lignite					0.878			
04-045	Fly Ash		Gulf Coast Lignite					0.849			
04-054	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous	444	1.16	115	49.0	17.7	94.5	457	
04-067	Fly Ash + Activated Carbon + Enhancing Agent	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite	26.8	<1	44.8	25.9	0.640	41.5	18.3	
04-082	FGD Gypsum		Eastern Bituminous	1.65	<1	3.39	<3	0.043	6.83	2.56	
04-083	FGD Gypsum		Eastern Bituminous	<2	<1	3.95	<3	0.103	6.81	2.68	
05-001	Fly Ash		Fort Union Lignite	24.4	<1	45.1	17.4	<0.01	30.3	8.84	
05-002	FGD-SDA		Fort Union Lignite	22.6	<1	42.8	18.6	<0.01	29.7	9.15	
05-003	Fly Ash + Activated Carbon + Enhancing Agent	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite	28.6	<1	45.5	21.2	0.565	25.7	11.5	
05-004	FGD-SDA + Activated Carbon + Enhancing Agent	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite	21.8	<1	37.3	20.9	0.332	25.3	9.79	
05-005	Fly Ash		Fort Union Lignite					0.431			
05-009	FGD Gypsum		Eastern Bituminous					0.032			
05-010	Fly Ash		Eastern Bituminous					0.080			
05-013	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	38.6	<1	36.5	73.2	39.0	15.4	60.3	
05-017	Fly Ash + Enhancing Agent	Enhancing Agent on Coal	Fort Union Lignite					0.717			
05-018	Fly Ash		Eastern Bituminous					0.123			
05-019	FGD Filtercake		Eastern Bituminous					0.305			
05-020	Fixated FGD		Eastern Bituminous					0.249			
05-023	Fly Ash + Activated Carbon	Post-Primary PCD: High fly ash content	Fort Union Lignite	48.3	<1	42.6	87.1	12.7	18.6	22.5	
05-024	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	42.5	<1	35.5	82.2	35.9	17.6	87.3	
05-025	Fly Ash + Activated Carbon	Post-Primary PCD: High fly ash content	Fort Union Lignite	46.8	<1	39.1	84.7	12.6	20.4	30.1	
05-038	Fly Ash		Fort Union Lignite	43.4	<1	43.4	90.1	0.104	21.1	23.4	
05-040	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	38.4	<1	42.2	74.5	44.5	22.0	42.2	
06-001	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	35.3	<1	40.5	71.2	64.5	20.6	38.9	
06-001	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	35.6	<1	39.0	72.7		20.5	38.8	

APPENDIX H

FGD LIQUOR TOTAL TRACE ELEMENTAL CONCENTRATION AND pH DATA

ID No.	Sample Type	Sample Type Notes	Coal Type	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Pb (µg/L)	Hg (µg/L)	Ni (µg/L)	Se (µg/L)	pH
03-103	Lab dewatered FGD liquor	lab dewatered 03-067: FGD slurry	Eastern Bituminous	114	0.79	10.1	<2	<0.15	258	1140	6.75
03-104	Lab dewatered FGD liquor	lab dewatered 03-082: FGD filtercake	Eastern Bituminous	54.4	2.89	2.9	<2	<0.15	333	154	6.73
03-114	Lab dewatered FGD liquor	lab dewatered 03-086: FGD filtercake	Eastern Bituminous	121	4.34	4.3	<2	NT	123	759	7.56
05-011	FGD Gypsum Filtrate		Eastern Bituminous	82.8	4.79	9.9	<2	<0.01	338	684	5.20
05-032	Lab dewatered FGD liquor	lab filtered 05-019: FGD filtercake	Eastern Bituminous	33.1	2.09	5.7	<2	NT	88.8	305	5.92

ID No.	Sample Type	Sample Type Notes	Coal Type	Sample Prep	10–15-Min pH	10–15-Min pH Date	24-Hr pH	24-Hr pH Date
03-103	Lab dewatered FGD liquor	lab dewatered 03-067: FGD slurry	Eastern Bituminous		6.73	5/3/2005		
03-103	Lab dewatered FGD liquor	lab dewatered 03-067: FGD slurry	Eastern Bituminous	filtered	6.75	5/3/2005		
03-103	Lab dewatered FGD liquor	lab dewatered 03-067: FGD slurry	Eastern Bituminous		6.78	6/21/2006	7.38	6/22/2006
03-104	Lab dewatered FGD liquor	lab dewatered 03-082: FGD filtercake	Eastern Bituminous		6.53	5/3/2005		
03-104	Lab dewatered FGD liquor	lab dewatered 03-082: FGD filtercake	Eastern Bituminous	filtered	6.73	5/3/2005		
03-114	Lab dewatered FGD liquor	lab dewatered 03-086: FGD filtercake	Eastern Bituminous		6.99	6/15/2006	7.51	6/16/2006
03-114	Lab dewatered FGD liquor	lab dewatered 03-086: FGD filtercake	Eastern Bituminous		7.36	8/1/2006	7.56	8/2/2006
05-011	FGD Gypsum Filtrate		Eastern Bituminous		5.44	5/8/2006	5.25	5/9/2006
05-011	FGD Gypsum Filtrate		Eastern Bituminous		5.40	8/1/2006	5.20	8/2/2006
05-022	FGD Filtrate		Eastern Bituminous		7.26	5/8/2006	8.13	5/9/2006
05-022	FGD Filtrate		Eastern Bituminous		7.20	8/1/2006	8.17	8/2/2006
05-032	Lab dewatered FGD liquor	lab filtered 05-019: FGD filtercake	Eastern Bituminous		6.75	6/13/2006	7.47	6/14/2006
05-032	Lab dewatered FGD liquor	lab filtered 05-019: FGD filtercake	Eastern Bituminous		6.63	8/1/2006	5.92	8/2/2006

APPENDIX I

TOTAL BULK CHEMICAL COMPOSITION DATA, REPORTED AS OXIDES

ID No.	Sample Type	Mercury Control Configuration	Coal Type	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	Na_2O (%)	K_2O (%)	TiO_2 (%)	MnO_2 (%)	P_2O_5 (%)	SrO (%)	BaO (%)	SO_3 (%)	LOI (%)	Moisture, as Received (%)
99-188	FGD-SDA		PRB Subbituminous	30.79	17.69	3.54	25.68	2.93	1.65	0.48	0.59	0.09	0.63	0.45	0.37	13.60	1.49	1.01
03-004	Fly Ash		Eastern Bituminous	55.23	27.48	6.37	1.44	0.78	0.37	2.47	1.62	0.02	0.40	0.11	0.14	0.12	3.46	0.12
03-005	Fly Ash		Eastern Bituminous	55.29	27.51	5.84	1.54	0.91	0.41	2.59	1.64	0.04	0.36	0.11	0.14	0.06	3.56	0.12
03-006	Fly Ash		Eastern Bituminous	55.83	27.51	6.65	1.34	0.96	0.41	2.57	1.66	0.03	0.35	0.11	0.13	0.07	2.40	0.14
03-007	Fly Ash		Eastern Bituminous	54.88	27.62	5.77	1.32	0.90	0.33	2.60	1.64	0.02	0.35	0.10	0.13	0.08	4.25	0.12
03-016	Fly Ash		Fort Union Lignite	44.19	15.87	7.34	17.67	5.56	4.39	1.61	0.60	0.05	0.13	0.42	0.73	1.13	0.32	0.01
03-017	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite	40.46	15.24	7.59	19.38	6.62	4.79	1.33	0.58	0.08	0.20	0.45	0.81	1.43	1.04	0.09
03-018	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite	38.71	15.64	6.54	19.95	6.80	5.02	1.37	0.60	0.07	0.19	0.48	0.98	2.74	0.91	0.05
03-019	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite	35.23	14.87	5.63	18.86	6.38	5.12	1.31	0.57	0.07	0.20	0.49	1.16	5.89	4.22	0.23
03-060	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous	30.07	17.63	5.87	27.50	6.11	2.42	0.68	1.35	0.02	2.32	0.44	0.84	2.54	2.22	0.09
03-061	Fly Ash		PRB Subbituminous	22.64	17.25	6.87	31.56	8.48	2.99	0.49	1.21	0.03	1.24	0.49	0.87	4.73	1.15	0.11
03-062	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite	40.30	15.61	7.31	19.37	5.95	4.91	1.32	0.58	0.08	0.20	0.46	0.87	1.86	1.17	0.05
03-063	Fly Ash		Eastern Bituminous	41.01	18.78	32.46	2.88	0.72	0.41	1.58	0.96	0.05	0.20	0.04	0.06	0.34	0.52	0.02
03-065	FGD Gypsum		Eastern Bituminous	0.39	0.05	0.03	34.69	0.91	0.00	0.01	0.02	0.01	0.03	0.01	0.03	51.14	12.68	17.37

APPENDIX J

MOISTURE CONTENT AND LOI DATA

ID No.	Sample Type	Hg Control Configuration	Coal Type	Moisture Content, %	LOI, %
99-188	FGD-SDA		PRB Subbituminous	1.18%	2.07%
02-002	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous	5.56%	22.2%
02-002	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous	4.07%	24.2%
02-003	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous	2.92%	19.4%
02-003	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous	2.59%	19.3%
02-004	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous	0.53%	2.84%
02-005	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous	0.72%	4.14%
02-006	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous	1.07%	3.88%
02-007	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous	4.63%	23.9%
02-007	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous	3.99%	24.3%
02-069	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous	0.86%	12.6%
02-069	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous	0.69%	12.6%
02-070	Fly Ash		Eastern Bituminous	0.24%	5.88%
02-070	Fly Ash		Eastern Bituminous	0.15%	5.85%
02-071	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous	1.18%	17.2%
02-072	Fly Ash		Eastern Bituminous	0.13%	5.18%
02-072	Fly Ash		Eastern Bituminous	0.21%	5.39%
02-073	Fly Ash		Eastern Bituminous	0.14%	5.00%
02-074	Fly Ash		Eastern Bituminous	0.36%	6.27%
02-074	Fly Ash		Eastern Bituminous	0.22%	6.09%
02-076	Fly Ash		South American Bituminous	0.60%	21.1%
02-076	Fly Ash		South American Bituminous	0.44%	21.0%
03-004	Fly Ash		Eastern Bituminous	0.12%	3.48%
03-004	Fly Ash		Eastern Bituminous	0.15%	3.20%
03-005	Fly Ash		Eastern Bituminous	0.17%	3.59%
03-005	Fly Ash		Eastern Bituminous	0.18%	3.60%
03-006	Fly Ash		Eastern Bituminous	0.18%	5.28%
03-006	Fly Ash		Eastern Bituminous	0.21%	5.19%
03-006	Fly Ash		Eastern Bituminous	0.12%	5.24%
03-007	Fly Ash		Eastern Bituminous	0.15%	4.54%
03-007	Fly Ash		Eastern Bituminous	0.19%	4.41%
03-008	Fly Ash		South American Bituminous	0.15%	12.7%
03-009	Fly Ash + Activated Carbon	Pre-Primary PCD	South American Bituminous	NT	NT
03-010	Fly Ash + Activated Carbon	Pre-Primary PCD	South American Bituminous	NT	NT
03-016	Fly Ash		Fort Union Lignite	0.05%	0.34%
03-016	Fly Ash		Fort Union Lignite	0.04%	0.24%
03-017	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite	0.06%	0.96%
03-017	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite	0.10%	1.23%
03-018	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite	0.12%	1.17%
03-018	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite	0.09%	0.97%
03-019	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite	0.61%	4.21%
03-060	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous	0.18%	2.47%
03-060	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous	0.15%	2.28%
03-061	Fly Ash		PRB Subbituminous	0.19%	1.00%
03-061	Fly Ash		PRB Subbituminous	0.14%	1.08%

ID No.	Sample Type	Hg Control Configuration	Coal Type	Moisture Content, %	LOI, %
03-062	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite	0.10%	1.29%
03-062	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite	0.02%	1.26%
03-063	Fly Ash		Eastern Bituminous	0.06%	0.47%
03-065	FGD Gypsum		Eastern Bituminous	25.7%	1.22%
03-067	FGD Slurry		Eastern Bituminous	56.8%	4.37%
03-067	FGD Slurry		Eastern Bituminous	65.7%	6.38%
03-078	Fly Ash		Fort Union Lignite	0.48%	1.47%
03-079	Fly Ash		Fort Union Lignite	0.28%	2.54%
03-080	Fly Ash		Fort Union Lignite	0.45%	7.48%
03-081	Fly Ash		Fort Union Lignite	0.68%	1.15%
03-082	FGD Filtercake		Eastern Bituminous	28.9%	5.04%
03-082	FGD Filtercake		Eastern Bituminous	40.0%	4.20%
03-082	FGD Filtercake		Eastern Bituminous	28.6%	4.86%
03-083	Fly Ash		Eastern Bituminous	0.15%	1.20%
03-084	Fixated FGD		Eastern Bituminous	26.6%	3.17%
03-084	Fixated FGD		Eastern Bituminous	27.1%	3.11%
03-085	Fly Ash		Eastern Bituminous	0.16%	2.10%
03-086	FGD Filtercake		Eastern Bituminous	43.3%	5.87%
03-087	Fixated FGD		Eastern Bituminous	31.3%	3.80%
03-087	Fixated FGD		Eastern Bituminous	31.9%	4.17%
03-088	Fly Ash		Eastern Bituminous	0.17%	1.07%
03-089	FGD Gypsum		Eastern Bituminous	21.6%	1.94%
04-003	Fly Ash		Eastern Bituminous	0.16%	8.46%
04-003	Fly Ash		Eastern Bituminous	0.24%	8.44%
04-004	Fly Ash		Eastern Bituminous	0.13%	1.38%
04-004	Fly Ash		Eastern Bituminous	0.11%	1.38%
04-006	Fly Ash		Western Bituminous	0.17%	1.42%
04-007	Fly Ash		Western Bituminous	0.08%	2.56%
04-007	Fly Ash		Western Bituminous	0.05%	2.46%
04-029	Fly Ash		PRB Subbituminous	0.14%	0.48%
04-030	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	0.14%	0.76%
04-030	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	0.13%	0.62%
04-031	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	0.11%	0.67%
04-031	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	0.18%	0.59%
04-032	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	0.11%	1.09%
04-032	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	0.40%	0.93%
04-033	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	0.43%	1.39%
04-033	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	0.22%	1.27%
04-035	Fly Ash		Fort Union Lignite	0.19%	2.45%
04-035	Fly Ash		Fort Union Lignite	0.16%	2.68%
04-035	Fly Ash		Fort Union Lignite	0.06%	2.24%
04-036	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite	0.05%	2.49%
04-036	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite	0.07%	2.16%
04-054	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous	0.60%	18.6%

ID No.	Sample Type	Hg Control Configuration	Coal Type	Moisture Content, %	LOI, %
04-067	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite	0.06%	2.11%
04-082	FGD Gypsum		Eastern Bituminous	26.5%	1.60%
04-083	FGD Gypsum		Eastern Bituminous	26.6%	2.26%
05-001	Fly Ash		Fort Union Lignite	1.00%	0.90%
05-002	FGD-SDA		Fort Union Lignite	1.08%	0.95%
05-003	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite	0.85%	1.04%
05-004	FGD-SDA + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite	0.75%	1.12%
05-005	Fly Ash		Fort Union Lignite	0.02%	1.29%
05-009	FGD Gypsum		Eastern Bituminous	26.1%	1.92%
05-010	Fly Ash		Eastern Bituminous	0.33%	2.05%
05-013	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	0.29%	13.2%
05-017	Fly Ash + Enhancing Agent	Enhancing Agent on Coal	Fort Union Lignite	0.05%	1.70%
05-018	Fly Ash		Eastern Bituminous	0.04%	3.01%
05-019	FGD Filtercake		Eastern Bituminous	33.3%	6.19%
05-020	Fixated FGD		Eastern Bituminous	31.1%	3.65%
05-023	Fly Ash + Activated Carbon	Post-Primary PCD: High Ash	Fort Union Lignite	0.13%	3.84%
05-024	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	0.23%	9.45%
05-025	Fly Ash + Activated Carbon	Post-Primary PCD: High Ash	Fort Union Lignite	0.13%	3.20%
05-025	Fly Ash + Activated Carbon	Post-Primary PCD: High Ash	Fort Union Lignite	0.00%	3.18%
05-038	Fly Ash		Fort Union Lignite	0.04%	0.22%
05-040	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	0.10%	9.68%
06-001	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	0.39%	11.6%

APPENDIX K

pH DATA

ID No.	Sample Type	Mercury Control Configuration	Coal Type	Sample Prep	10–15-Min pH	10–15-Min pH Date	24-Hr pH	24-Hr pH Date	Overnight pH	Overnight pH Date	1 M KCl pH	1 M KCl pH Date
99-188	FGD-SDA		PRB Subbituminous		12.41	5/2/2006	12.22	5/3/2006			12.53	9/1/2004
99-188	FGD-SDA		PRB Subbituminous		12.34	1/17/2002					12.53	9/10/2004
02-002	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous		3.62	7/27/2004					3.51	9/15/2004
02-003	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous		4.19	5/24/2006	4.76	5/25/2006			3.98	9/15/2004
02-003	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous		3.91	7/27/2004						
02-004	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous		11.47	7/27/2004						
02-005	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous		10.65	7/27/2004						
02-006	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous		10.99	5/24/2006	10.95	5/25/2006			10.48	8/31/2004
02-006	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous		10.86	4/8/2004						
02-007	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous		3.47	5/24/2006	3.99	5/25/2006			3.52	9/15/2004
02-007	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous		3.54	7/27/2004						
02-069	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous		8.85	5/24/2006	8.43	5/25/2006				
02-069	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous		8.94	7/27/2004						
02-069	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous		9.00	9/26/2002						
02-070	Fly Ash		Eastern Bituminous		9.98	5/24/2006	8.50	5/25/2006			10.11	9/13/2004
02-070	Fly Ash		Eastern Bituminous		10.25	9/26/2002						
02-071	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous		9.26	5/24/2006	8.63	5/25/2006			9.38	9/13/2004
02-071	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous		9.59	9/26/2002						
02-072	Fly Ash		Eastern Bituminous		10.09	5/24/2006	8.83	5/25/2006				
02-072	Fly Ash		Eastern Bituminous		10.35	9/26/2002					10.16	9/1/2004
02-073	Fly Ash		Eastern Bituminous		12.18	5/24/2006	12.44	5/25/2006			12.72	9/13/2004
02-073	Fly Ash		Eastern Bituminous		12.56	9/26/2002						
02-074	Fly Ash		Eastern Bituminous		12.00	5/30/2006	11.80	5/31/2006			12.69	9/13/2004
02-074	Fly Ash		Eastern Bituminous		12.18	9/26/2002						
02-076	Fly Ash		South American Bituminous		10.38	5/30/2006	9.13	5/31/2006			10.66	9/10/2004
02-076	Fly Ash		South American Bituminous		9.93	10/19/2004						
03-004	Fly Ash		Eastern Bituminous		4.54	5/30/2006	7.08	5/31/2006			4.69	9/15/2004
03-004	Fly Ash		Eastern Bituminous		4.26	9/29/2003						
03-005	Fly Ash		Eastern Bituminous		4.45	5/30/2006	5.88	5/31/2006			4.48	9/15/2004
03-005	Fly Ash		Eastern Bituminous		4.26	9/29/2003						
03-006	Fly Ash		Eastern Bituminous		4.82	4/26/2006	6.78	4/27/2006			4.72	9/15/2004
03-006	Fly Ash		Eastern Bituminous		4.60	9/29/2003						
03-007	Fly Ash		Eastern Bituminous		4.38	4/26/2006	5.52	4/27/2006			4.42	9/15/2004
03-007	Fly Ash		Eastern Bituminous		4.15	9/29/2003						
03-008	Fly Ash		South American Bituminous		11.72	3/14/2003						
03-009	Fly Ash + Activated Carbon	Pre-Primary PCD	South American Bituminous		11.79	3/14/2003						
03-010	Fly Ash + Activated Carbon	Pre-Primary PCD	South American Bituminous		10.34	3/14/2003						
03-016	Fly Ash		Fort Union Lignite		12.63	5/30/2006	12.54	5/31/2006			12.82	9/1/2004
03-016	Fly Ash		Fort Union Lignite		12.60	9/29/2003					12.84	9/10/2004
03-017	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite		12.69	6/1/2006	12.61	6/2/2006				
03-017	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite		12.57	9/29/2003					12.84	8/31/2004
03-018	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite		12.58	6/1/2006	12.38	6/2/2006			12.76	8/31/2004
03-018	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite		12.57	9/29/2003						
03-019	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite		11.92	6/1/2006	11.86	6/2/2006			12.38	9/1/2004
03-019	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite		11.74	10/9/2003					12.46	9/10/2004

ID No.	Sample Type	Mercury Control Configuration	Coal Type	Sample Prep	10–15-Min pH	10–15-Min pH Date	24-Hr pH	24-Hr pH Date	Overnight pH	Overnight pH Date	1 M KCl pH	1 M KCl pH Date
03-060	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous		11.31	6/1/2006	11.90	6/2/2006			10.95	9/1/2004
03-060	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous		11.32	10/9/2003					11.16	9/10/2004
03-061	Fly Ash		PRB Subbituminous		11.91	6/1/2006	12.56	6/2/2006			11.96	8/31/2004
03-061	Fly Ash		PRB Subbituminous		12.02	10/10/2003						
03-062	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite		12.67	6/1/2006	12.60	6/2/2006			12.81	8/30/2004
03-062	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite		12.57	10/10/2003						
03-063	Fly Ash		Eastern Bituminous		10.98	6/1/2006	11.00	6/2/2006			11.62	9/10/2004
03-063	Fly Ash		Eastern Bituminous		11.30	12/3/2003						
03-065	FGD Gypsum		Eastern Bituminous		8.07	5/2/2006	7.75	5/3/2006				
03-065	FGD Gypsum		Eastern Bituminous		8.59	12/3/2003						
03-067	FGD Slurry		Eastern Bituminous	dewatered	8.95	6/21/2006	8.75	6/22/2006				
03-067	FGD Slurry		Eastern Bituminous	dewatered	7.84	8/25/2005						
03-067	FGD Slurry		Eastern Bituminous		8.05	6/9/2004						
03-078	Fly Ash		Fort Union Lignite		11.59	12/3/2003						
03-079	Fly Ash		Fort Union Lignite		11.81	6/1/2006	11.62	6/2/2006			11.63	9/13/2004
03-079	Fly Ash		Fort Union Lignite		11.72	12/3/2003						
03-080	Fly Ash		Fort Union Lignite		11.72	6/13/2006	11.68	6/14/2006				
03-080	Fly Ash		Fort Union Lignite		11.64	12/3/2003					11.84	8/30/2004
03-081	Fly Ash		Fort Union Lignite		11.20	6/13/2006	10.50	6/14/2006			11.05	8/30/2004
03-081	Fly Ash		Fort Union Lignite		11.26	12/3/2003						
03-082	FGD Filtercake		Eastern Bituminous		8.18	5/8/2006	7.85	5/9/2006				
03-082	FGD Filtercake		Eastern Bituminous		7.47	6/9/2004						
03-083	Fly Ash		Eastern Bituminous		4.75	6/13/2006	9.00	6/14/2006			4.59	9/15/2004
03-083	Fly Ash		Eastern Bituminous		4.28	12/3/2003						
03-084	Fixated FGD		Eastern Bituminous		11.57	6/13/2006	11.03	6/14/2006			12.30	9/13/2004
03-084	Fixated FGD		Eastern Bituminous		12.52	12/3/2003						
03-085	Fly Ash		Eastern Bituminous		9.54	5/8/2006	8.79	5/9/2006				
03-085	Fly Ash		Eastern Bituminous		7.06	12/3/2003						
03-086	FGD Filtercake		Eastern Bituminous		7.81	6/13/2006	7.70	6/14/2006				
03-086	FGD Filtercake		Eastern Bituminous		7.70	6/9/2004						
03-087	Fixated FGD		Eastern Bituminous		10.87	6/13/2006	10.50	6/14/2006			11.75	9/13/2004
03-087	Fixated FGD		Eastern Bituminous		12.51	12/3/2003						
03-088	Fly Ash		Eastern Bituminous		10.72	5/2/2006	11.15	5/3/2006				
03-088	Fly Ash		Eastern Bituminous		5.02	2/12/2004						
03-088	Fly Ash		Eastern Bituminous		7.50	4/8/2004						
03-089	FGD Gypsum		Eastern Bituminous		8.13	5/2/2006	7.95	5/3/2006				
03-089	FGD Gypsum		Eastern Bituminous		8.22	4/15/2004						
04-003	Fly Ash		Eastern Bituminous		9.36	4/26/2006	8.54	4/27/2006			9.42	9/1/2004
04-003	Fly Ash		Eastern Bituminous		9.34	2/12/2004						
04-004	Fly Ash		Eastern Bituminous		9.89	4/26/2006	8.92	4/27/2006			10.10	9/1/2004
04-004	Fly Ash		Eastern Bituminous		4.47	2/12/2004						
04-004	Fly Ash		Eastern Bituminous		10.29	4/8/2004						
04-006	Fly Ash		Western Bituminous		11.56	6/13/2006	10.38	6/14/2006			11.76	9/1/2004
04-006	Fly Ash		Western Bituminous		11.52	3/4/2004					11.73	9/1/2004
04-006	Fly Ash		Western Bituminous								11.40	9/10/2004
04-007	Fly Ash		Western Bituminous		12.74	6/13/2006	12.65	6/14/2006			12.82	9/1/2004
04-007	Fly Ash		Western Bituminous		13.00	4/8/2004					12.80	9/1/2004
04-007	Fly Ash		Western Bituminous								12.83	9/10/2004
04-029	Fly Ash		PRB Subbituminous		12.56	6/15/2006	12.27	6/16/2006			12.62	9/1/2004
04-029	Fly Ash		PRB Subbituminous		12.37	4/8/2004					12.61	9/10/2004

ID No.	Sample Type	Mercury Control Configuration	Coal Type	Sample Prep	10–15-Min pH	10–15-Min pH Date	24-Hr pH	24-Hr pH Date	Overnight pH	Overnight pH Date	1 M KCl pH	1 M KCl pH Date
04-030	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite		11.56	6/15/2006	11.30	6/16/2006				
04-030	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite		11.51	4/15/2004					11.54	8/31/2004
04-031	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite		11.64	6/21/2006	11.25	6/22/2006			11.73	8/31/2004
04-031	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite		11.60	4/15/2004						
04-032	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite		9.54	6/15/2006	10.52	6/16/2006			9.42	8/31/2004
04-032	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite		9.67	4/15/2004						
04-033	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite		10.70	4/15/2004					10.98	8/31/2004
04-035	Fly Ash		Fort Union Lignite		12.77	6/15/2006	12.74	6/16/2006			12.83	8/30/2004
04-035	Fly Ash		Fort Union Lignite		12.68	6/9/2004						
04-036	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite		12.79	6/15/2006	12.77	6/16/2006			12.82	8/30/2004
04-036	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite		12.64	6/9/2004						
04-042	Fly Ash		Gulf Coast Lignite		11.87	6/21/2006	11.31	6/22/2006				
04-042	Fly Ash		Gulf Coast Lignite		11.77	10/19/2004						
04-043	Fly Ash		Gulf Coast Lignite		11.82	6/21/2006	11.28	6/22/2006				
04-043	Fly Ash		Gulf Coast Lignite		11.48	6/9/2004						
04-044	Fly Ash		Gulf Coast Lignite		11.76	6/21/2006	11.27	6/22/2006				
04-044	Fly Ash		Gulf Coast Lignite		11.52	10/19/2004						
04-054	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous		8.48	4/20/2006	9.20	4/21/2006			9.43	8/30/2004
04-054	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous		9.10	12/12/2005			9.59	12/13/2005		
04-054	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous		6.40	10/19/2004						
04-067	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite		12.70	6/21/2006	12.60	6/22/2006				
04-067	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite		12.80	11/5/2004						
04-082	FGD Gypsum		Eastern Bituminous		8.19	5/8/2006	7.72	5/9/2006				
04-082	FGD Gypsum		Eastern Bituminous		8.10	2/17/2005						
04-083	FGD Gypsum		Eastern Bituminous		8.19	5/8/2006	7.80	5/9/2006				
04-083	FGD Gypsum		Eastern Bituminous		8.10	2/17/2005						
05-001	Fly Ash		Fort Union Lignite		12.50	5/2/2006	12.51	5/3/2006				
05-001	Fly Ash		Fort Union Lignite		12.84	2/22/2005						
05-002	FGD-SDA		Fort Union Lignite		12.55	5/2/2006	12.50	5/3/2006				
05-002	FGD-SDA		Fort Union Lignite		12.85	2/22/2005						
05-003	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite		12.39	5/2/2006	12.29	5/3/2006				
05-003	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite		12.85	3/7/2005						
05-004	FGD-SDA + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite		12.51	5/2/2006	12.54	5/3/2006				
05-004	FGD-SDA + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite		13.06	3/7/2005						
05-005	Fly Ash		Fort Union Lignite		11.77	4/26/2006	11.57	4/27/2006				
05-005	Fly Ash		Fort Union Lignite		11.95	5/17/2005						
05-009	FGD Gypsum		Eastern Bituminous		8.68	5/8/2006	7.88	5/9/2006				
05-009	FGD Gypsum		Eastern Bituminous		8.83	8/25/2005						
05-010	Fly Ash		Eastern Bituminous		11.91	6/15/2006	11.72	6/16/2006				
05-010	Fly Ash		Eastern Bituminous		12.11	8/25/2005						
05-013	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite		9.00	4/20/2006	11.33	4/21/2006				
05-013	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite		9.05	11/3/2005						

ID No.	Sample Type	Mercury Control Configuration	Coal Type	Sample Prep	10–15-Min pH	10–15-Min pH Date	24-Hr pH	24-Hr pH Date	Overnight pH	Overnight pH Date	1 M KCl pH	1 M KCl pH Date
05-017	Fly Ash + Enhancing Agent	Enhancing Agent on Coal	Fort Union Lignite		12.04	4/26/2006	11.77	4/27/2006				
05-017	Fly Ash + Enhancing Agent	Enhancing Agent on Coal	Fort Union Lignite		12.19	8/25/2005						
05-018	Fly Ash		Eastern Bituminous		7.42	4/26/2006	8.49	4/27/2006				
05-018	Fly Ash		Eastern Bituminous		7.56	8/25/2005						
05-019	FGD Filtercake		Eastern Bituminous		7.90	5/8/2006	7.88	5/9/2006				
05-019	FGD Filtercake		Eastern Bituminous		8.07	11/3/2005						
05-020	Fixated FGD		Eastern Bituminous		12.10	5/8/2006	12.43	5/9/2006				
05-020	Fixated FGD		Eastern Bituminous		12.75	8/25/2005						
05-023	Fly Ash + Activated Carbon	Post-Primary PCD: High Fly Ash Content	Fort Union Lignite		11.35	4/20/2006	12.00	4/21/2006				
05-023	Fly Ash + Activated Carbon	Post-Primary PCD: High Fly Ash Content	Fort Union Lignite		11.65	11/3/2005						
05-024	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite		7.43	4/20/2006	11.41	4/21/2006				
05-024	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite		8.93	11/3/2005						
05-025	Fly Ash + Activated Carbon	Post-Primary PCD: High Fly Ash Content	Fort Union Lignite		11.53	4/20/2006	11.99	4/21/2006				
05-025	Fly Ash + Activated Carbon	Post-Primary PCD: High Fly Ash Content	Fort Union Lignite		11.67	11/3/2005						
05-038	Fly Ash		Fort Union Lignite		11.67	4/20/2006	11.73	4/21/2006				
05-038	Fly Ash		Fort Union Lignite		12.03	12/7/2005						
05-040	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite		7.03	4/20/2006	11.36	4/21/2006				
05-040	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite		6.80	12/8/2005			11.74	12/9/2005		
06-001	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite		6.69	4/4/2006			11.44	4/5/2006		
06-001	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite		7.20	4/20/2006	11.37	4/21/2006				

APPENDIX L

CARBON FORMS DATA

ID No.	Sample Type	Mercury Control Configuration	Coal Type	Dominant Carbon Form
02-002	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous	Anisotropic Coke
02-004	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous	Isotropic Coke
02-007	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous	Anisotropic Coke
02-070	Fly Ash		Eastern Bituminous	Unburned Coal
02-076	Fly Ash		South American Bituminous	Anisotropic Coke
03-004	Fly Ash		Eastern Bituminous	Inertinite
03-005	Fly Ash		Eastern Bituminous	Unburned Coal
03-006	Fly Ash		Eastern Bituminous	Unburned Coal
03-007	Fly Ash		Eastern Bituminous	Vitrinite
03-008	Fly Ash		South American Bituminous	Unburned Coal
03-016	Fly Ash		Fort Union Lignite	Vitrinite
03-017	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite	Inertinite
03-018	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite	Anisotropic Coke
03-019	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite	Inertinite
03-060	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous	Anisotropic Coke
03-061	Fly Ash		PRB Subbituminous	Isotropic Coke
03-062	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite	Unburned Coal
03-063	Fly Ash		Eastern Bituminous	Vitrinite
03-078	Fly Ash		Fort Union Lignite	Vitrinite
03-079	Fly Ash		Fort Union Lignite	Anisotropic Coke
03-080	Fly Ash		Fort Union Lignite	Isotropic Coke
03-083	Fly Ash		Eastern Bituminous	Unburned Coal

APPENDIX M

LEACHATE DATA

ID No.	Sample Type	Hg Control Configuration	Coal Type	Leachate Test	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Pb (µg/L)	Hg (µg/L)	Ni (µg/L)	Se (µg/L)	Leachate pH
99-188	FGD-SDA		PRB Subbituminous	18-Hour SGLP	3.5	0.37	116	<2	<0.01	27.0	65.8	12.14
99-188	FGD-SDA		PRB Subbituminous	18-Hour SGLP	<10	<10	105	<10		16.4	29.9	12.33
99-188	FGD-SDA		PRB Subbituminous	30-Day LTL	2.6	0.58	215	<2	<0.01	<2	53.5	11.41
99-188	FGD-SDA		PRB Subbituminous	60-Day LTL	2.2	0.59	223	<2	0.043	<2	53.1	11.43
02-002	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous	18-Hour SGLP					<0.01			4.00
02-002	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous	TCLP #1					0.01			4.54
02-003	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous	18-Hour SGLP					<0.01			4.53
02-003	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous	TCLP #1					<0.01			4.76
02-004	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous	18-Hour SGLP					<0.01			12.00
02-004	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous	30-Day LTL					<0.01			11.95
02-004	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous	60-Day LTL					<0.01			11.90
02-004	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous	TCLP #2					<0.01			5.51
02-005	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous	18-Hour SGLP					<0.01			11.08
02-005	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous	30-Day LTL					<0.01			11.84
02-005	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous	60-Day LTL					0.01			11.85
02-005	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous	TCLP #2					<0.01			6.53
02-006	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous	18-Hour SGLP	3.5	<0.2	560	<2	0.064	<2	57.1	11.57

ID No.	Sample Type	Hg Control Configuration	Coal Type	Leachate Test	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Pb (µg/L)	Hg (µg/L)	Ni (µg/L)	Se (µg/L)	Leachate pH
02-006	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous	TCLP #2					<0.01			6.56
02-007	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous	18-Hour SGLP					<0.01			4.06
02-069	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous	18-Hour SGLP					0.03			9.48
02-069	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous	TCLP #2					0.07			3.79
02-070	Fly Ash		Eastern Bituminous	18-Hour SGLP					0.01			10.55
02-070	Fly Ash		Eastern Bituminous	TCLP #2					0.03			3.56
02-071	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous	18-Hour SGLP					0.01			9.89
02-071	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous	TCLP #2					<0.01			4.06
02-072	Fly Ash		Eastern Bituminous	18-Hour SGLP					0.02			10.81
02-072	Fly Ash		Eastern Bituminous	TCLP #2					0.02			3.54
02-073	Fly Ash		Eastern Bituminous	18-Hour SGLP					0.05			12.67
02-073	Fly Ash		Eastern Bituminous	TCLP #2					0.02			4.97
02-074	Fly Ash		Eastern Bituminous	18-Hour SGLP					0.01			12.40
02-074	Fly Ash		Eastern Bituminous	TCLP #2					0.01			4.88
02-076	Fly Ash		South American Bituminous	18-Hour SGLP					0.016			11.18
02-076	Fly Ash		South American Bituminous	TCLP #2					<0.01			3.89
03-004	Fly Ash		Eastern Bituminous	18-Hour SGLP	7.7	6.27		<2	<0.01	50.0	16.7	5.54

ID No.	Sample Type	Hg Control Configuration	Coal Type	Leachate Test	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Pb (µg/L)	Hg (µg/L)	Ni (µg/L)	Se (µg/L)	Leachate pH
03-004	Fly Ash		Eastern Bituminous	18-Hour SGLP	9.3	1.10	9.8	<0.001		31.0	26.0	6.30
03-004	Fly Ash		Eastern Bituminous	18-Hour SGLP	10.5	1.81	11	<2	0.019	80.6	31.8	6.30
03-004	Fly Ash		Eastern Bituminous	60-Day LTL	118	1.11	10.1	<2	0.012	8.1	125	7.29
03-005	Fly Ash		Eastern Bituminous	18-Hour SGLP	5.9	8.08		<2	<0.01	60.0	13.2	4.98
03-005	Fly Ash		Eastern Bituminous	18-Hour SGLP					<0.01			5.00
03-005	Fly Ash		Eastern Bituminous	18-Hour SGLP	2.9	7.36	<2	<2	0.019	66.4	16.1	5.00
03-005	Fly Ash		Eastern Bituminous	60-Day LTL	6.5	7.22	<2	<2	0.239	70.0	48.9	5.59
03-006	Fly Ash		Eastern Bituminous	18-Hour SGLP	12.5	3.58	8.8	<2	<0.01	58.0	49.6	6.22
03-006	Fly Ash		Eastern Bituminous	18-Hour SGLP	10.0	3.00	7.4	<0.001		50.0	49.0	6.22
03-006	Fly Ash		Eastern Bituminous	18-Hour SGLP	19.2	4.31		<2	<0.01	40.0	48.5	6.41
03-006	Fly Ash		Eastern Bituminous	60-Day LTL	110	1.37	7.5	<2	0.06	18.2	212	7.20
03-007	Fly Ash		Eastern Bituminous	18-Hour SGLP	20.0	7.83		<2	<0.01	50.0	36.6	4.71
03-007	Fly Ash		Eastern Bituminous	18-Hour SGLP	16.2	7.58	2.0	<2	<0.01	73.5	36.0	4.97
03-007	Fly Ash		Eastern Bituminous	18-Hour SGLP	15.0	7.30	1.4	<0.001		75.0	29.0	4.97
03-007	Fly Ash		Eastern Bituminous	60-Day LTL	10.6	6.70	<2	<2	<0.01	70.0	86.9	5.55
03-008	Fly Ash		South American Bituminous	18-Hour SGLP					<0.01			11.68
03-008	Fly Ash		South American Bituminous	TCLP #2					0.034			4.11

ID No.	Sample Type	Hg Control Configuration	Coal Type	Leachate Test	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Pb (µg/L)	Hg (µg/L)	Ni (µg/L)	Se (µg/L)	Leachate pH
03-009	Fly Ash + Activated Carbon	Pre-Primary PCD	South American Bituminous	18-Hour SGLP					<0.01			11.71
03-009	Fly Ash + Activated Carbon	Pre-Primary PCD	South American Bituminous	TCLP #2					<0.01			4.20
03-010	Fly Ash + Activated Carbon	Pre-Primary PCD	South American Bituminous	18-Hour SGLP					<0.01			10.71
03-010	Fly Ash + Activated Carbon	Pre-Primary PCD	South American Bituminous	TCLP #2					<0.01			3.80
03-060	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous	18-Hour SGLP	2.7	<0.2	<50	<2	<0.01		8.4	12.15
03-060	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous	18-Hour SGLP	<2	0.22	54.1	<2	0.025	23.1	16.5	12.21
03-060	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous	30-Day LTL	<2	<0.2	6.3	3.0	<0.01	4.5	8.5	12.46
03-060	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous	60-Day LTL					<0.01			12.38
03-060	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous	60-Day LTL	<2	<0.2	10.7	2.4	0.068	<2	11.4	12.38
03-061	Fly Ash		PRB Subbituminous	18-Hour SGLP	2.0	<2		<2	<0.01		5.4	12.40
03-061	Fly Ash		PRB Subbituminous	18-Hour SGLP	<2	<0.2	15.5	<2	0.018	2.5	14.2	12.49
03-061	Fly Ash		PRB Subbituminous	30-Day LTL	<2	<0.2	3.0	3.6	<0.01	4.1	9.8	12.63
03-061	Fly Ash		PRB Subbituminous	60-Day LTL	<2	<0.2	3.2	8.5	0.325	<2	13.9	12.58
03-062	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite	18-Hour SGLP	6.6	0.34	80.0	<2	<0.01		68.0	12.59
03-062	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite	18-Hour SGLP	6.0	0.45	103	<2	<0.01	10.7	81.1	12.60
03-062	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite	18-Hour SGLP	<4	<0.3	99.0	<0.001		<4	68.0	12.60
03-062	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite	30-Day LTL	<2	<0.2	3.6	<2	<0.01	<2	<2	12.34

ID No.	Sample Type	Hg Control Configuration	Coal Type	Leachate Test	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Pb (µg/L)	Hg (µg/L)	Ni (µg/L)	Se (µg/L)	Leachate pH
03-062	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite	60-Day LTL	5.2	<0.2	5.2	<2	<0.01	<2	3.8	12.40
03-063	Fly Ash		Eastern Bituminous	18-Hour SGLP	67.8	<0.2		<2	<0.01		29.1	11.61
03-063	Fly Ash		Eastern Bituminous	18-Hour SGLP	52.0	<0.3	38.8	<0.001		<4	29.0	11.70
03-063	Fly Ash		Eastern Bituminous	18-Hour SGLP	60.2	0.57	43.5	<2	<0.01	3	31.6	11.70
03-063	Fly Ash		Eastern Bituminous	30-Day LTL	37.7	0.64	38.6	<2	<0.01	<2	42.6	11.49
03-063	Fly Ash		Eastern Bituminous	60-Day LTL	36.1	0.61	38.8	<2	0.038	<2	37.4	11.36
03-065	FGD Gypsum		Eastern Bituminous	18-Hour SGLP	<2	<0.2	<2	<2	<0.01	<2	3.3	7.80
03-065	FGD Gypsum		Eastern Bituminous	60-Day LTL	<2	<0.2	<2	<2	<0.01	10.1	2.7	7.99
03-067	FGD Slurry		Eastern Bituminous	18-Hour SGLP	<4	<0.3	<1	<0.001	0.047	15.0	65.0	8.02
03-078	Fly Ash		Fort Union Lignite	18-Hour SGLP	95.1	0.43	150	<2	<0.01		151	11.32
03-078	Fly Ash		Fort Union Lignite	18-Hour SGLP	90.5	4.47	166	<2	<0.01	11.1	149	NT
03-079	Fly Ash		Fort Union Lignite	18-Hour SGLP	75.7	0.37	150	<2	<0.01		60.4	11.82
03-079	Fly Ash		Fort Union Lignite	18-Hour SGLP	74.8	3.71	174	<2	<0.01	7.4	89.4	11.91
03-079	Fly Ash		Fort Union Lignite	30-Day LTL	45.3	4.23	265	<2	<0.01	<2	40.1	11.60
03-079	Fly Ash		Fort Union Lignite	60-Day LTL	59.8	3.96	250	<2	0.049	<2	38.9	11.56
03-079	Fly Ash		Fort Union Lignite	60-Day LTL	49.3	4.40	277	<2	<0.01	<2	37.7	11.60
03-079	Fly Ash		Fort Union Lignite	60-Day LTL					<0.01			11.60
03-080	Fly Ash		Fort Union Lignite	18-Hour SGLP	44.6	1.57	90.0	<2	0.011	<2	75.1	12.04
03-080	Fly Ash		Fort Union Lignite	30-Day LTL	35.2	1.97	134	<2	0.113	<2	23.8	11.78
03-080	Fly Ash		Fort Union Lignite	60-Day LTL	29.2	2.06	110	<2	0.041	<2	22.7	11.80
03-080	Fly Ash		Fort Union Lignite	60-Day LTL	28.7	2.14	135	<2	<0.01	<2	24.1	11.84

ID No.	Sample Type	Hg Control Configuration	Coal Type	Leachate Test	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Pb (µg/L)	Hg (µg/L)	Ni (µg/L)	Se (µg/L)	Leachate pH
03-081	Fly Ash		Fort Union Lignite	18-Hour SGLP	140	3.75	120	<2	0.083	<2	240	10.95
03-081	Fly Ash		Fort Union Lignite	30-Day LTL	232	6.02	264	<2	0.013	<2	112	11.34
03-081	Fly Ash		Fort Union Lignite	60-Day LTL	226	5.38	230	<2	0.019	<2	98.2	11.25
03-081	Fly Ash		Fort Union Lignite	60-Day LTL					0.017			11.31
03-081	Fly Ash		Fort Union Lignite	60-Day LTL	223	5.60	273	<2	0.124	<2	91.6	11.31
03-082	FGD Filtercake		Eastern Bituminous	18-Hour SGLP	3.7	<0.2	<2	<2	0.404	7.4	71.2	8.39
03-082	FGD Filtercake		Eastern Bituminous	30-Day LTL					<0.01			7.69
03-082	FGD Filtercake		Eastern Bituminous	30-Day LTL	3.5	0.83	<2	<2	<0.01	32.1	55.2	7.69
03-082	FGD Filtercake		Eastern Bituminous	60-Day LTL	<2	0.47	<2	<2	<0.01	25.4	45.3	7.57
03-083	Fly Ash		Eastern Bituminous	18-Hour SGLP	48.0	<0.3	9.1	<0.001		<4	46.0	9.21
03-083	Fly Ash		Eastern Bituminous	18-Hour SGLP	54.3	2.92	10.7	<2	<0.01	4.4	49.9	9.21
03-083	Fly Ash		Eastern Bituminous	18-Hour SGLP	97.3	<0.2		<2	<0.01		44.1	9.40
03-084	Fixated FGD		Eastern Bituminous	18-Hour SGLP	4.9	0.44	4.7	14.3	0.289	<2	2.7	12.34
03-084	Fixated FGD		Eastern Bituminous	30-Day LTL					<0.01			11.87
03-084	Fixated FGD		Eastern Bituminous	30-Day LTL	5.2	0.66	3.1	<2	<0.01	4.0	2.4	11.87
03-084	Fixated FGD		Eastern Bituminous	60-Day LTL	<2	0.48	2.4	<2	<0.01	3.5	2.0	11.94
03-084	Fixated FGD		Eastern Bituminous	60-Day LTL	<2	0.50	2.5	<2	<0.01	3.7	<2	11.94
03-085	Fly Ash		Eastern Bituminous	18-Hour SGLP					<0.01			10.75
03-085	Fly Ash		Eastern Bituminous	18-Hour SGLP	250	2.57	21.3	<2	<0.01	3.2	90.2	10.87

ID No.	Sample Type	Hg Control Configuration	Coal Type	Leachate Test	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Pb (µg/L)	Hg (µg/L)	Ni (µg/L)	Se (µg/L)	Leachate pH
03-085	Fly Ash		Eastern Bituminous	18-Hour SGLP	250	<0.3	19.5	<0.001		<4	75.0	10.87
03-085	Fly Ash		Eastern Bituminous	18-Hour SGLP	266	0.28		<2	<0.01		77.6	10.91
03-087	Fixated FGD		Eastern Bituminous	18-Hour SGLP	7.0	0.43	3.0	6.6	0.237	<2	2.1	12.07
03-087	Fixated FGD		Eastern Bituminous	30-Day LTL	24.0	0.30	2.2	<2	<0.01	<2	3.4	11.31
03-087	Fixated FGD		Eastern Bituminous	60-Day LTL	19.1	0.37	3.3	<2	<0.01	2.1	<2	11.50
03-088	Fly Ash		Eastern Bituminous	18-Hour SGLP	18.4	4.93	110	<2	0.029	<2	76.4	11.77
03-088	Fly Ash		Eastern Bituminous	30-Day LTL	23.0	7.64	160	<2	<0.01	5.4	15.5	11.21
03-088	Fly Ash		Eastern Bituminous	60-Day LTL	23.4	8.30	180	<2	<0.01	5.6	19.0	11.03
03-089	FGD Gypsum		Eastern Bituminous	18-Hour SGLP	<2	0.46	<2	<2	<0.01	<2	9.4	7.62
03-089	FGD Gypsum		Eastern Bituminous	60-Day LTL	<2	<0.2	<2	<2	<0.01	12.6	8.2	7.85
04-003	Fly Ash		Eastern Bituminous	18-Hour SGLP	188	0.56	48.8	<2	<0.01	<2	412	9.67
04-003	Fly Ash		Eastern Bituminous	30-Day LTL	305	0.88	69.3	<2	0.104	<2	489	9.38
04-003	Fly Ash		Eastern Bituminous	60-Day LTL	282	0.71	70.6	<2	<0.01	<2	492	9.08
04-003	Fly Ash		Eastern Bituminous	60-Day LTL	336	0.77	70.0	<2	<0.01	<2	514	9.13
04-004	Fly Ash		Eastern Bituminous	18-Hour SGLP	136	0.70	70.0	<2	<0.01	<2	166	10.75
04-004	Fly Ash		Eastern Bituminous	30-Day LTL	135	1.02	98.1	<2	<0.01	<2	186	10.57
04-004	Fly Ash		Eastern Bituminous	60-Day LTL	140	0.84	100	<2	0.077	<2	180	10.69

ID No.	Sample Type	Hg Control Configuration	Coal Type	Leachate Test	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Pb (µg/L)	Hg (µg/L)	Ni (µg/L)	Se (µg/L)	Leachate pH
04-006	Fly Ash		Western Bituminous	18-Hour SGLP					<0.01			11.57
04-006	Fly Ash		Western Bituminous	18-Hour SGLP	12.3	0.28	34.6	<2	<0.01	<2	160	11.61
04-006	Fly Ash		Western Bituminous	30-Day LTL	3.4	0.36	49.2	<2	0.076	<2	111	11.37
04-006	Fly Ash		Western Bituminous	60-Day LTL	7.3	0.33	52.8	<2	0.087	<2	76.2	11.31
04-007	Fly Ash		Western Bituminous	18-Hour SGLP	10.7	<2	120	<2	0.021	<2	265	12.81
04-007	Fly Ash		Western Bituminous	30-Day LTL	<2	<0.2	7.3	2.2	0.035	10.6	26.7	12.54
04-007	Fly Ash		Western Bituminous	60-Day LTL	<2	<0.2	6.7	<2	<0.01	10.0	17.4	12.52
04-029	Fly Ash		PRB Subbituminous	18-Hour SGLP	<2	<0.2	24.1	<2	0.023	<2	2.1	12.09
04-029	Fly Ash		PRB Subbituminous	30-Day LTL	<2	<0.2	5.1	<2	<0.01	4.0	<2	12.36
04-029	Fly Ash		PRB Subbituminous	60-Day LTL	<2	<0.2	2.3	<2	<0.01	4.8	<2	12.45
04-030	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	18-Hour SGLP	26.9	1.40	399	<2	<0.01	<2	222	11.65
04-030	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	30-Day LTL	8.1	1.86	640	<2	<0.01	5.6	53.2	11.78
04-030	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	60-Day LTL	10.6	2.35	670	<2	<0.01	3.3	63.4	11.64
04-031	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	18-Hour SGLP	23.2	1.49	410	<2	0.012	<2	177	11.70
04-031	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	30-Day LTL	9.6	1.95	650	<2	<0.01	4.4	54.4	11.82
04-031	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	60-Day LTL	11.5	2.34	680	<2	0.028	2.9	60.3	11.71
04-032	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	18-Hour SGLP	28.0	1.24	333	<2	<0.01	<2	215	11.00

ID No.	Sample Type	Hg Control Configuration	Coal Type	Leachate Test	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Pb (µg/L)	Hg (µg/L)	Ni (µg/L)	Se (µg/L)	Leachate pH
04-033	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	18-Hour SGLP	31.1	1.32	351	<2	<0.01	<2	156	11.41
04-033	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	30-Day LTL	10.1	1.99	580	<2	<0.01	5.8	64.8	11.55
04-033	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	60-Day LTL	10.4	2.46	620	<2	<0.01	4.7	71.0	11.43
04-035	Fly Ash		Fort Union Lignite	18-Hour SGLP	<2	<0.2	55.8	<2	0.081	<2	17.8	12.60
04-035	Fly Ash		Fort Union Lignite	30-Day LTL	<2	<0.2	<2	<2	0.02	9.6	<2	12.65
04-035	Fly Ash		Fort Union Lignite	60-Day LTL	<2	<0.2	2.1	<2	<0.01	6.2	<2	12.54
04-036	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite	18-Hour SGLP	<2	0.27	67.6	3.0	0.016	<2	19.9	12.54
04-036	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite	18-Hour SGLP					<0.01			12.57
04-036	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite	30-Day LTL	<2	<0.2	<2	<2	<0.01	8.2	<2	12.61
04-036	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite	60-Day LTL	<2	<0.2	2.1	<2	<0.01	5.4	<2	12.59
04-054	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous	18-Hour SGLP	842	1.87	17.3	<2	<0.01	5.6	8620	NT
04-067	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite	18-Hour SGLP	15.2	0.39	<2	2.2	<0.01	21.0	47.2	12.50
04-082	FGD Gypsum		Eastern Bituminous	18-Hour SGLP	<2	0.33	<2	<2	<0.01	28.4	12.5	7.42
04-082	FGD Gypsum		Eastern Bituminous	18-Hour SGLP					<0.01			8.17
04-083	FGD Gypsum		Eastern Bituminous	18-Hour SGLP	<2	0.25	<2	<2	<0.01	23.3	18.7	8.02
05-001	Fly Ash		Fort Union Lignite	18-Hour SGLP	3.0	0.24	45.3	<2	<0.01	43.6	12.9	12.42

ID No.	Sample Type	Hg Control Configuration	Coal Type	Leachate Test	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Pb (µg/L)	Hg (µg/L)	Ni (µg/L)	Se (µg/L)	Leachate pH
05-001	Fly Ash		Fort Union Lignite	30-Day LTL	<4	<0.3	153	<0.001	<0.01	<4	14.0	12.11
05-001	Fly Ash		Fort Union Lignite	30-Day LTL	2.1	0.26	132	<2	0.016	<2	15.6	12.32
05-001	Fly Ash		Fort Union Lignite	60-Day LTL	2.5	0.22	152	<2	0.011	<2	18.0	12.39
05-002	FGD-SDA		Fort Union Lignite	18-Hour SGLP	2.1	0.22	34.6	<2	<0.01	39.1	11.3	12.40
05-002	FGD-SDA		Fort Union Lignite	30-Day LTL	<4	<0.3	126	<0.001	<0.01	<4	12.0	12.23
05-002	FGD-SDA		Fort Union Lignite	30-Day LTL	3.3	<0.2	113	<2	0.095	<2	65.2	12.41
05-002	FGD-SDA		Fort Union Lignite	60-Day LTL	2.3	0.20	132	<2	0.013	<2	14.4	12.47
05-003	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite	18-Hour SGLP	7.2	0.30	49.9	<2	<0.01	25.2	34.2	12.34
05-003	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite	30-Day LTL	<4	<0.3	133	<0.001	<0.05	<4	25.0	12.21
05-003	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite	30-Day LTL	6.4	<0.2	123	<2	0.061	<2	27.2	12.39
05-003	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite	60-Day LTL	7.5	<0.2	133	<2	0.016	<2	30.3	12.48
05-003	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite	60-Day LTL	6.9	<0.2	134	<2	0.013	<2	29.8	12.49
05-004	FGD-SDA + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite	18-Hour SGLP	4.3	0.20	21.8	<2	<0.01	29.3	24.3	12.43
05-004	FGD-SDA + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite	30-Day LTL	<4	<0.3	78.0	<0.001	<0.02	<4	12.0	12.41
05-004	FGD-SDA + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite	30-Day LTL	3.6	<0.2	67.7	<2	<0.01	<2	13.2	12.55
05-004	FGD-SDA + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite	60-Day LTL	3.8	<0.2	87.7	<2	0.012	<2	17.0	12.60

ID No.	Sample Type	Hg Control Configuration	Coal Type	Leachate Test	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Pb (µg/L)	Hg (µg/L)	Ni (µg/L)	Se (µg/L)	Leachate pH
05-005	Fly Ash		Fort Union Lignite	18-Hour SGLP	134	2.79	137	<2	<0.01	15.5	123	11.65
05-005	Fly Ash		Fort Union Lignite	18-Hour SGLP					<0.01			11.73
05-005	Fly Ash		Fort Union Lignite	30-Day LTL					<0.01			11.61
05-005	Fly Ash		Fort Union Lignite	30-Day LTL	101	2.48	179	<2	<0.01	<2	51.6	11.86
05-005	Fly Ash		Fort Union Lignite	60-Day LTL	140	<0.3	166	<0.001		<4	15.0	11.82
05-005	Fly Ash		Fort Union Lignite	60-Day LTL	160	2.65	183	<2	<0.01	<2	38.5	11.82
05-005	Fly Ash		Fort Union Lignite	60-Day LTL					<0.01			11.83
05-005	Fly Ash		Fort Union Lignite	60-Day LTL					<0.01			11.84
05-009	FGD Gypsum		Eastern Bituminous	18-Hour SGLP	<4	<0.3	<1	<0.001	<0.01	<4	<4	7.83
05-010	Fly Ash		Eastern Bituminous	18-Hour SGLP	41.0	<0.3	19.4	<0.001	<0.01	<4	160	11.79
05-013	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	18-Hour SGLP	30.4	1.29	112	<2	<0.01	15.8	498	11.45
05-013	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	30-Day LTL	30.4	1.08	159	<2	<0.01	5.9	312	11.66
05-013	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	60-Day LTL	27.3	1.14	156	<2	<0.01	4.1	199	11.61
05-017	Fly Ash + Enhancing Agent	Enhancing Agent on Coal	Fort Union Lignite	18-Hour SGLP					<0.01			11.94
05-017	Fly Ash + Enhancing Agent	Enhancing Agent on Coal	Fort Union Lignite	30-Day LTL					<0.01			11.69
05-017	Fly Ash + Enhancing Agent	Enhancing Agent on Coal	Fort Union Lignite	30-Day LTL	46.3	2.40	203	<2	<0.01	2.8	97.0	11.89
05-017	Fly Ash + Enhancing Agent	Enhancing Agent on Coal	Fort Union Lignite	60-Day LTL					<0.01			11.99
05-017	Fly Ash + Enhancing Agent	Enhancing Agent on Coal	Fort Union Lignite	60-Day LTL	73.0	<0.3	182	<0.001		<4	<4	12.00
05-017	Fly Ash + Enhancing Agent	Enhancing Agent on Coal	Fort Union Lignite	60-Day LTL	95.3	2.55	206	<2	0.02	<2	50.9	12.00
05-017	Fly Ash + Enhancing Agent	Enhancing Agent on Coal	Fort Union Lignite	60-Day LTL	95.9	2.68	211	<2	0.012	<2	49.2	12.01

ID No.	Sample Type	Hg Control Configuration	Coal Type	Leachate Test	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Pb (µg/L)	Hg (µg/L)	Ni (µg/L)	Se (µg/L)	Leachate pH
05-017	Fly Ash + Enhancing Agent	Enhancing Agent on Coal	Fort Union Lignite	60-Day LTL					<0.01			12.01
05-018	Fly Ash		Eastern Bituminous	18-Hour SGLP	150	<0.3	11.1	<0.001	0.022	<4	280	8.96
05-019	FGD Filtercake		Eastern Bituminous	18-Hour SGLP	<4	<0.3	<1	<0.001	0.476	6.1	41.0	8.10
05-023	Fly Ash + Activated Carbon	Post-Primary PCD: High Fly Ash Content	Fort Union Lignite	18-Hour SGLP	14.5	1.01	168	<2	<0.01	11.8	145	11.85
05-023	Fly Ash + Activated Carbon	Post-Primary PCD: High Fly Ash Content	Fort Union Lignite	30-Day LTL	8.1	0.75	134	<2	<0.01	4.9	65.1	12.05
05-023	Fly Ash + Activated Carbon	Post-Primary PCD: High Fly Ash Content	Fort Union Lignite	60-Day LTL	9.1	0.72	138	<2	<0.01	5.0	72.2	12.09
05-024	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	18-Hour SGLP	24.6	1.50	141	<2	<0.01	20.3	343	11.51
05-024	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	30-Day LTL	17.9	1.13	173	<2	<0.01	5.2	75.9	11.67
05-024	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	60-Day LTL	14.0	1.16	167	<2	<0.01	4.0	73.2	11.68
05-025	Fly Ash + Activated Carbon	Post-Primary PCD: High Fly Ash Content	Fort Union Lignite	18-Hour SGLP	16.3	1.49	153	<2	<0.01	12.2	147	11.88
05-025	Fly Ash + Activated Carbon	Post-Primary PCD: High Fly Ash Content	Fort Union Lignite	30-Day LTL	9.9	1.06	147	<2	<0.01	5.4	100	12.04
05-025	Fly Ash + Activated Carbon	Post-Primary PCD: High Fly Ash Content	Fort Union Lignite	60-Day LTL	11.7	0.90	133	<2	<0.01	5.3	114	12.07
05-038	Fly Ash		Fort Union Lignite	18-Hour SGLP	8.1	1.10	169	<2	<0.01	18.9	60.5	11.85
05-038	Fly Ash		Fort Union Lignite	30-Day LTL	2.4	0.58	92.0	<2	<0.01	5.3	20.1	12.00
05-038	Fly Ash		Fort Union Lignite	60-Day LTL	<2	0.67	88.6	<2	<0.01	5.2	26.8	12.09

ID No.	Sample Type	Hg Control Configuration	Coal Type	Leachate Test	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Pb (µg/L)	Hg (µg/L)	Ni (µg/L)	Se (µg/L)	Leachate pH
05-040	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	18-Hour SGLP	20.9	1.35	112	<2	<0.01	19.4	161	11.47
05-040	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	30-Day LTL	17.0	0.96	152	<2	<0.01	5.6	47.7	11.55
05-040	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	60-Day LTL	15.6	1.08	155	<2	<0.01	3.9	45.2	11.54
06-001	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	18-Hour SGLP	20.2	0.99	119	<2	<0.01	23.4	99.3	11.38
06-001	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	18-Hour SGLP	21.3	1.01	120	<2	<0.01	22.8	101	11.39
06-001	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	30-Day LTL	18.6	0.85	166	<2	<0.01	7.1	66.4	11.52
06-001	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	60-Day LTL	17.5	0.89	160	<2	<0.01	5.1	46.1	11.45
06-001	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite	60-Day LTL	17.7	0.85	157	<2	<0.01	4.9	49.9	11.49

APPENDIX N

MERCURY AND AIR TOXIC ELEMENT LEACHING FROM COAL COMBUSTION BY-PRODUCTS

MERCURY AND AIR TOXIC ELEMENT LEACHING FROM COAL COMBUSTION BY-PRODUCTS

Topical Report

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MERCURY AND AIR TOXIC ELEMENT LEACHING FROM COAL COMBUSTION BY-PRODUCTS

EXECUTIVE SUMMARY

Under this 3-year project, funded by the U.S. Department of Energy and industry, the Energy & Environmental Research Center (EERC) is evaluating the impact of mercury and other air toxic elements on the management of coal combustion by-products (CCBs). The EERC is measuring the release of mercury and other air toxic elements from fly ash and flue gas desulfurization (FGD) material under different controlled laboratory conditions. One key release mechanism is being investigated in the laboratory is that of mercury and other air toxic element releases by direct leaching. The goal of the leaching task was to develop a broad set of mercury and air toxic element leaching data on CCBs in order to determine the leachability of these elements from CCBs generated at existing systems and mercury emission control test systems. Tests of direct leachability have long been used to assess the environmental performance of CCBs, and the EERC has elected to apply short- and long-term batch leaching procedures to samples of fly ash and FGD material that have been assembled for this project. The project sample set includes samples of fly ash and FGD material that were obtained from full-scale coal-fired power plants operating under typical conditions and with no mercury control technologies being used. The sample set also includes fly ash samples and one FGD sample that were collected at pilot- and full-scale facilities while mercury control technologies were being tested.

Leaching data were assembled and presented in two formats: 1) a comparison of total elemental concentration with leachate concentrations for all samples *without* and ***with*** mercury controls for fly ash and separately for FGD materials and 2) a comparison of "paired" fly ash samples with a true baseline fly ash sample *without* mercury control and a test fly ash sample ***with*** mercury control. Key conclusions drawn from the mercury leaching data are as follows:

- Total mercury content of samples generated both *without* and ***with*** mercury emission controls present and mercury leachate concentrations did not correlate.

- Leachate mercury concentrations were independent of short-term leaching procedures used.

- Leachate mercury concentrations have been found to be extremely low regardless of the total mercury content of the sample.

- Total mercury content of paired test fly ash samples ***with*** mercury control was consistently higher than the paired baseline fly ash sample *without* mercury control.

Leaching data for other air toxic elements did not indicate any consistent increase in total elemental content where mercury control was in place. Leaching profiles tended to be sample-dependent. Additional leaching work is planned to increase the data set for the other air toxic elements and specifically for FGD materials.

MERCURY AND AIR TOXIC ELEMENT LEACHING FROM COAL COMBUSTION BY-PRODUCTS

INTRODUCTION

The stability of mercury associated with coal combustion by-products (CCBs) has become a prominent question as the coal-fired utility industry works to develop and test mercury emission controls that may consequently increase the mercury associated with CCBs. The reasons for evaluating the release of mercury from CCBs are 1) to determine if mercury captured on CCBs is stable or if it will be released, thus negating the purpose of the removal of the mercury from the emissions, and 2) to aid utilities in determining and understanding potential changes in CCBs associated with mercury control and associated CCB management.

Under this 3-year project, funded by the U.S. Department of Energy (DOE) and industry, the Energy & Environmental Research Center (EERC) is evaluating the impact of mercury and other air toxic elements on the management of CCBs. The EERC is measuring the release of mercury and other air toxic elements under different controlled laboratory conditions and investigating the release of these same air toxic elements in select field settings. Results will be used to determine if mercury release from CCBs, both as currently produced and as produced with mercury and other emission controls in place, will potentially impact CCB management practices.

Laboratory tasks were designed to address three primary potential release mechanisms for mercury over the life cycle of CCBs in a variety of management scenarios. These release mechanisms are:

1. Direct leachability of air toxic constituents from CCBs.
2. Vapor release of mercury from CCBs at ambient and elevated temperatures.
3. Biologically mediated leachability and vapor release of mercury and other air toxic elements from CCBs.

This report focuses on the results generated from the assessment of the direct leachability of mercury and other air toxic elements from CCBs. Tests of direct leachability have long been used to assess the environmental performance of CCBs as well as other materials, by-products, and wastes for both organic and inorganic constituents. In this project, inorganic constituents, and especially air toxic elements were the focus. The air toxic elements included in the evaluations were mercury, arsenic, cadmium, chromium, lead, nickel, and selenium. All of these elements have been found to be present on CCBs and to exhibit leachability under various conditions. This report is a preliminary summary of leaching results for the overall project entitled “Mercury and Air Toxic Element Impacts of Coal Combustion By-Product Disposal and Utilization.”

BACKGROUND

Leaching tests have been applied to CCBs as the primary means of assessing the potential for constituents present in CCBs to be released to the environment when these materials are placed in the environment. Over the last nearly 28 years, researchers at the EERC have leached a very large number of various CCBs. Many groups have worked to develop appropriate leaching tests for a variety of materials including CCBs, understand leaching mechanisms of various materials, and assemble leachate data sets. Kim (1) and Sorini (2) published summaries of available leaching methods, and Kim (3) published results of extensive leaching studies of CCBs. Even though a broad variety of leaching tests of varying types (batch, serial batch, flow-around, flow-through, etc. [1, 2]) are published, the EERC has concluded that an appropriate leaching test for the assessment of the potential for environmental impact of CCBs must meet the following criteria if it is to stand up to legal and scientific scrutiny:

- The test must take into account any reactivity or unusual properties of the material being leached.

- The test must as closely as possible utilize a leaching solution that mimics the leaching solution most likely to contact the material in its use or disposal setting.

- If the ash is reactive with water, the test must take this into account by allowing the hydration reactions to occur during the course of the leaching test. This necessitates the use of long-term leaching (LTL).

The EERC developed a test that meets these criteria (4). The test is referred to as the synthetic groundwater leaching procedure (SGLP) and generally includes an 18-hour batch leaching test and two longer-term leaching tests. 30- and 60-day leaching times are recommended for the long-term tests.

OBJECTIVES

The goal of the leaching task was to develop a broad set of mercury and air toxic element leaching data on CCBs in order to determine the leachability of these elements from CCBs generated at existing systems and mercury emission control test systems. Supporting objectives were to:

- Select and apply one or more appropriate laboratory leaching methods to evaluate the potential for release of mercury and other air toxic elements from CCBs under conditions that are relevant to management options applied to CCBs.

- Develop leaching data on “paired” samples from systems where baseline and test samples were available.

- Draw conclusions about the mobility of these elements, especially mercury, that may impact choices for CCB management options.

METHODS

A report entitled "Laboratory Methods for the Evaluation of Potential Release of Mercury from Coal Utilization By-Products" was published in April 2005 under separate cover for this project. A discussion of methods available and the justification for method selection is included in detail in that report and is not replicated in this report. The leaching tests performed on the samples in this project were the toxicity characteristic leaching procedure (TCLP) (5), SGLP, and LTL with 30- and 60-day equilibration periods.

Under this project, the EERC is participating in an interlaboratory comparative study of leaching procedures and has provided a sample of regional fly ash for inclusion in the comparative study. Participants in that study are the DOE National Energy Technology Laboratory (NETL), the EERC, the University of the Western Cape Department of Chemistry, the Virginia Tech Department of Crop and Soil Environmental Sciences, and the West Virginia Water Research Institute National Mine Land Reclamation Center (WVWRI). The methods being compared are those developed at NETL, WVWRI, the EERC, and the 3-tier procedure published by Kosson and others (6). The EERC results of this interlaboratory study were not yet available at the writing of this report but will be included in future project reports.

LEACHING RESULTS AND DISCUSSION

Sample descriptions for samples included in this study are shown in Appendix A. All leaching data are included in tabular form in Appendix B. As can be noted in Appendix B, not all leaching procedures were applied to all samples. Where TCLP was included as one of the procedures applied, it was generally included because of specific requests from the sample submitter. SGLP was generally applied to all submitted samples, and as noted in the report entitled "Laboratory Methods for the Evaluation of Potential Release of Mercury from Coal Utilization Byproducts," SGLP applied using distilled deionized water is equivalent to ASTM International D3987 Standard Test Method for Shake Extraction of Solid Waste with Water (7). For samples with a pH >10, the LTL procedure was also applied in order to assess the impact of reactivity of the material on the leaching profile of the sample.

Fly ash samples evaluated in this study for leachability of mercury and other air toxic elements were from several sources and are delineated in the graphics in this report as noted in Table 1.

Similarly, a variety of flue gas desulfurization (FGD) material samples were evaluated for leachability of mercury and other air toxic elements. Table 2 details the types and descriptions used for the FGD materials included in the study.

Table 1. Fly Ash Sample Types and Descriptions

Types of Fly Ash	Sample Description Used in Report Figures
Currently generated fly ash from existing coal-fired system	Fly ash – *without* mercury control
Fly ash collected from coal-fired system with mercury emission control installed (usually as a demonstration)	Fly ash – ***with*** mercury control*
Fly ash collected at true baseline conditions in a system preparing to run a mercury emission control technology test	Baseline fly ash (a subset of "Fly ash – *without* mercury control")
Fly ash collected during a mercury emission control technology test where a baseline fly ash sample was also collected	Paired fly ash – ***with*** mercury control* (a subset of "Fly ash –***with*** mercury control")

* Note: "***with*** mercury control" indicates the presence of activated carbon.

Table 2. FGD Material Types and Descriptions

Types of FGD Materials	Sample Description Used in Report Figures
Currently generated FGD material from existing coal-fired system	FGD material – *without* mercury control
FGD material collected from system with mercury emission control installed (usually as a demonstration)	FGD material –***with*** mercury control
FGD material collected at true baseline conditions in a system preparing to run a mercury emission control technology test	Baseline FGD material (a subset of "FGD material – *without* mercury control")
FGD material collected during a mercury emission control technology test where a baseline FGD material was also collected	Paired FGD material –***with*** mercury control (a subset of "FGD material – ***with*** mercury control")

In the text of this report, multiple figures are included for mercury and each of the air toxic elements of interest, as follows:

1. A figure comparing the total elemental concentration to all short- and long-term leachate concentrations generated in the project for all samples of fly ash *without* and ***with*** mercury control. Blue is used to represent concentrations of samples *without* mercury control and red represents samples ***with*** mercury control.

2. A figure showing the SGLP leaching results for the paired fly ash samples, where paired samples are represented with one color with open points for fly ash *without* mercury control and solid points for the paired fly ash ***with*** mercury control.

3. A figure showing all leachate results for all FGD materials evaluated including the only FGD material paired sample set, which are noted in each of these figures. Blue points represent results of samples *without* mercury control and a red point is used to

represent the one sample generated ***with*** mercury control. In addition, samples of FGD gypsum collected at a single bituminous-fired facility with selective catalytic reduction (SCR) on and off are called out; however, these samples are not "paired" samples because they were collected several months apart.

Appendix C includes figures showing the short- and long-term leaching data for individual paired fly ash samples. The SGLP-only graphs were used in the text to allow ease of viewing the data, and the graphs of individual paired fly ash sample sets provide more detail and allow comparison of the short- and long-term leaching results.

Several samples had total elemental or leachate concentrations below the lower limit of quantitation (LLQ). The LLQs were variable throughout the project, with some reported values below the LLQ of other samples. Therefore, these values are represented as one-half the LLQ graphically, and a red dashed line represents the highest LLQ.

Mercury Leaching Results

Mercury was the element of greatest interest for this project, and significant data were produced through Year 2 of the project on the leaching profiles of mercury associated with fly ash. Additional figures are presented in the text for mercury leaching results. Figure 1 shows all short- and long-term leaching data for mercury for fly ash samples both *without* and ***with*** mercury control.

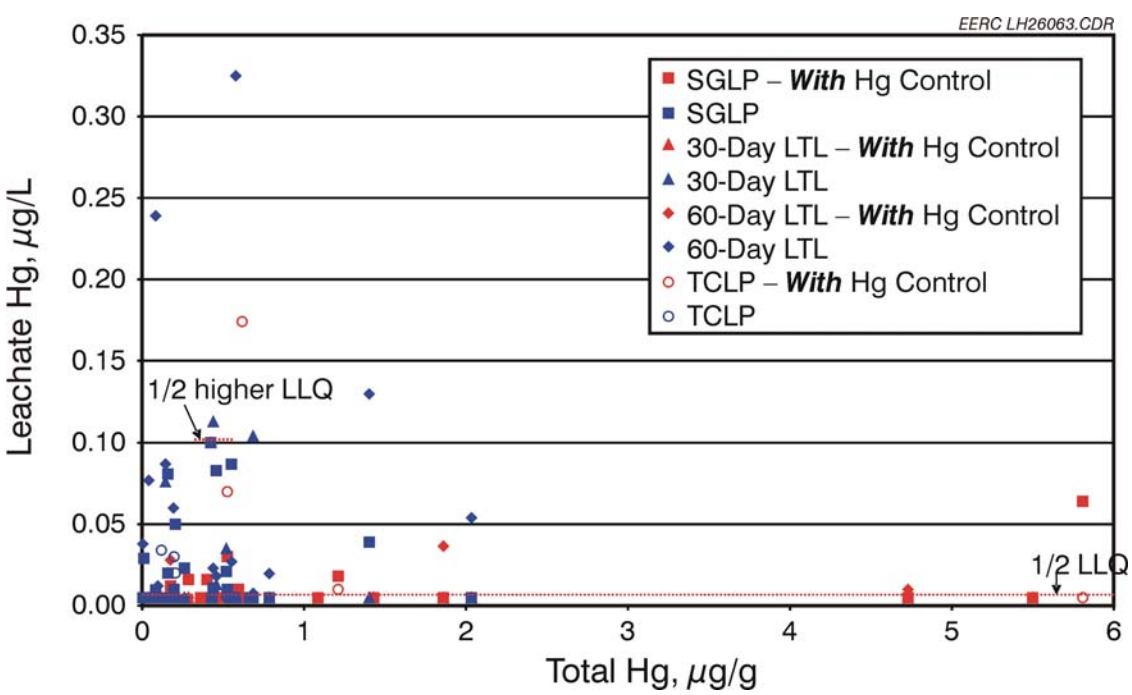

Figure 1. Total mercury vs. short- and long-term leachable mercury: all fly ash – *without* mercury control and fly ash – ***with*** mercury control samples. The x-axis is reduced from 120 µg/g.

Figure 2 shows all short- and long-term mercury leaching data for baseline fly ash *without* mercury control and the paired fly ash ***with*** mercury control in addition to Figure 3, which shows only the SGLP mercury leaching data for this same sample set. In Figures 2 and 3, the baseline fly ash results are noted as open points and the paired fly ash ***with*** mercury control is noted as solid points. Paired samples are denoted by the same color points.

A comparison of short-term leaching results from SGLP and TCLP is shown in Figure 4. Results presented in Figure 4 show that neither of these short-term leaching tests resulted in a consistently higher or lower leachate concentration, indicating that neither test should be considered a more aggressive test.

Figure 5 summarizes all available mercury leaching data for FGD materials. As noted, only a single sample with baseline FGD material and paired FGD material ***with*** mercury control is represented. In addition, samples of FGD gypsum collected at a single bituminous-fired facility with SCR on and off are also called out in Figure 5. Studies have shown that the speciation of mercury in the flue gas can be impacted by SCR systems, but as can be noted by the sample descriptions in Appendix A, these samples are not "paired" samples because they were collected several months apart. The variability of mercury in coal over time has been noted in other studies and may be an explanation for the lower total mercury in the sample with SCR on as compared to the one with SCR off. These samples are interesting in that they point out the potential for erroneous conclusions if samples *without* mercury control are compared one-to-one with samples

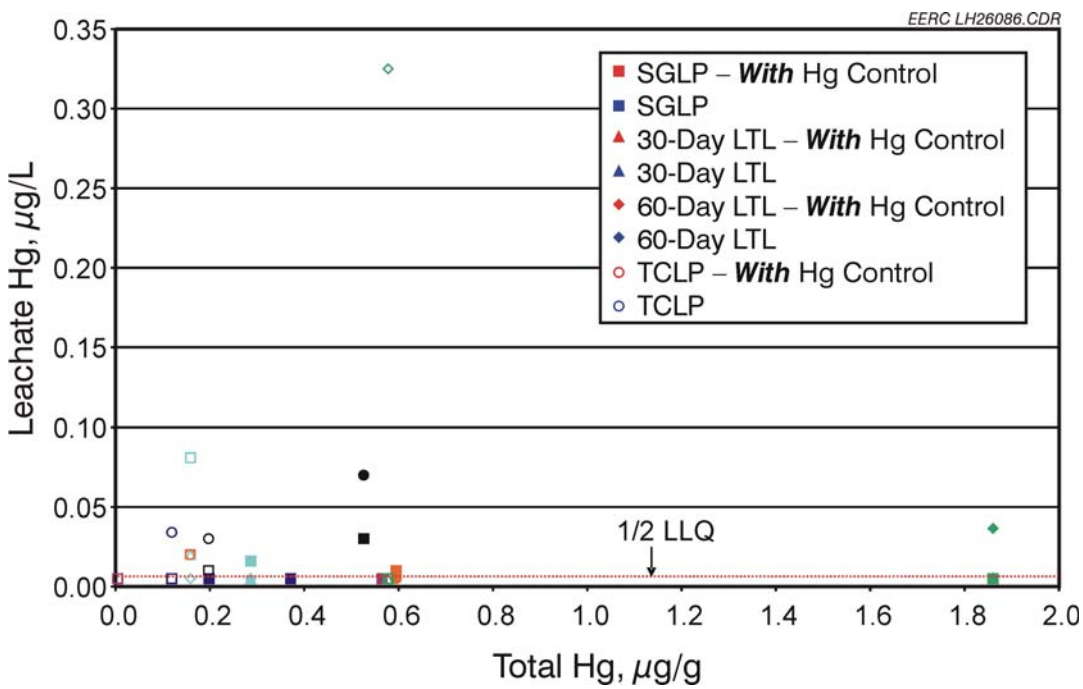

Figure 2. Total mercury vs. short- and long-term leachable mercury: all available paired fly ash samples. One paired sample set has two fly ash – ***with*** mercury control samples.

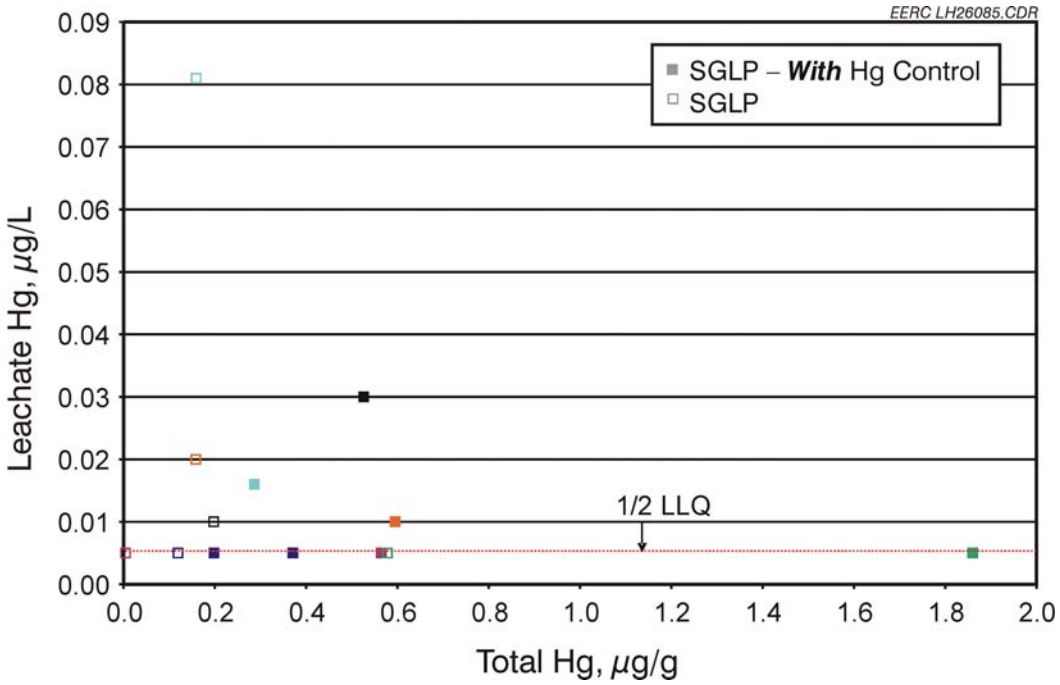

Figure 3. Total mercury vs. SGLP leachable mercury: all available paired fly ash samples. One paired sample set has two fly ash – ***with*** mercury control samples.

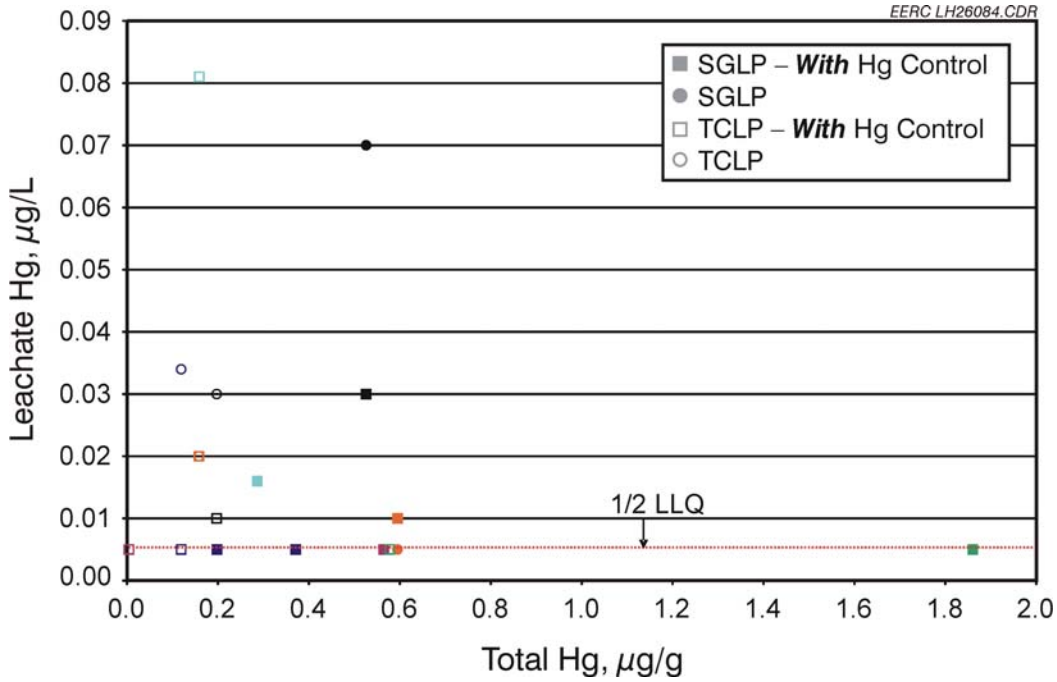

Figure 4. Total mercury vs. SGLP and TCLP leachable mercury: all available paired fly ash samples. One paired sample set has two fly ash – ***with*** mercury control samples.

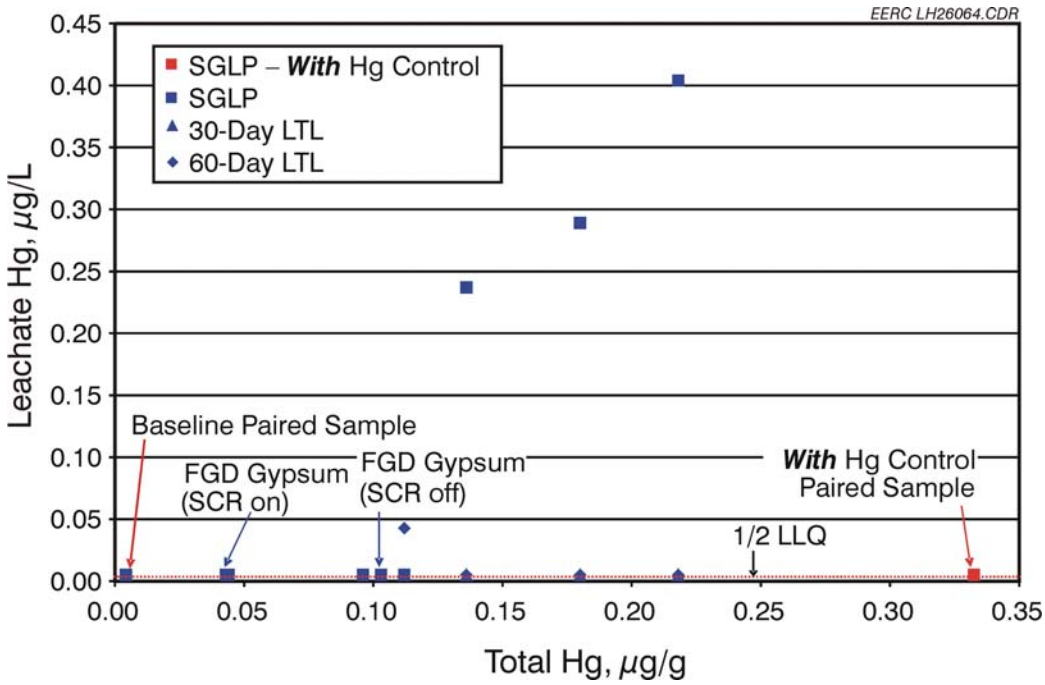

Figure 5. Total mercury vs. short- and long-term leachable mercury: all FGD material samples.

with mercury control, unless these samples are a true baseline sample and a paired sample ***with*** mercury control. Since many FGD materials exhibit a near-neutral pH, only a few FGD materials tested included LTL data points.

Based on the mercury leaching data currently available from this project, the following preliminary observations were made:

- Total mercury content of samples generated both ***with*** and *without* mercury emission controls present and leachate concentrations did not correlate.

- Leachate concentrations were independent of short-term leaching procedures used.

- Leachate mercury concentrations have been found to be extremely low regardless of the total mercury content of the sample. Most leachates exhibited mercury concentrations less than the reporting limit of 0.01 µg/L. All leachate concentrations fell well below the primary drinking water (PDW) limit of 2.0 µg/L for mercury as well as the limit at 30 × PDW (60 µg/L) and 100 × PDW (200 µg/L).

- Total mercury content of paired test fly ash samples ***with*** mercury control was consistently higher than the paired baseline fly ash sample *without* mercury control.

Other Air Toxic Element Leaching Results

The other air toxic elements of interest for this project were arsenic, cadmium, chromium, lead, nickel, and selenium. SGLP and LTL only were evaluated for these elements because, as already noted, TCLP was only done on submitter request.

Arsenic

Figure 6 shows a comparison of the total arsenic concentrations versus the leachate arsenic concentrations for all fly ash samples *without* and ***with*** mercury control. The fly ash samples *without* and ***with*** mercury control contained similar concentrations of total arsenic and generally leached similar levels of arsenic. Leaching results from baseline fly ash and paired fly ash ***with*** mercury control are shown in Figure 7. The presence of activated carbon in the samples designated as ***with*** mercury control does not correlate with a higher total arsenic concentration for this limited sample set. The FGD material data shown in Figure 8 may indicate that FGD materials with higher total arsenic concentrations may leach higher levels of arsenic; however, the sample set is too small to draw a firm conclusion. Data on the paired sample set are very similar and within the error of the experiments and analytical procedures, so no conclusions can be drawn based on those data points. Figure C-3 shows that the long-term leachates exhibited lower arsenic concentrations than the SGLP, and this trend can also be seen in Figure C-4.

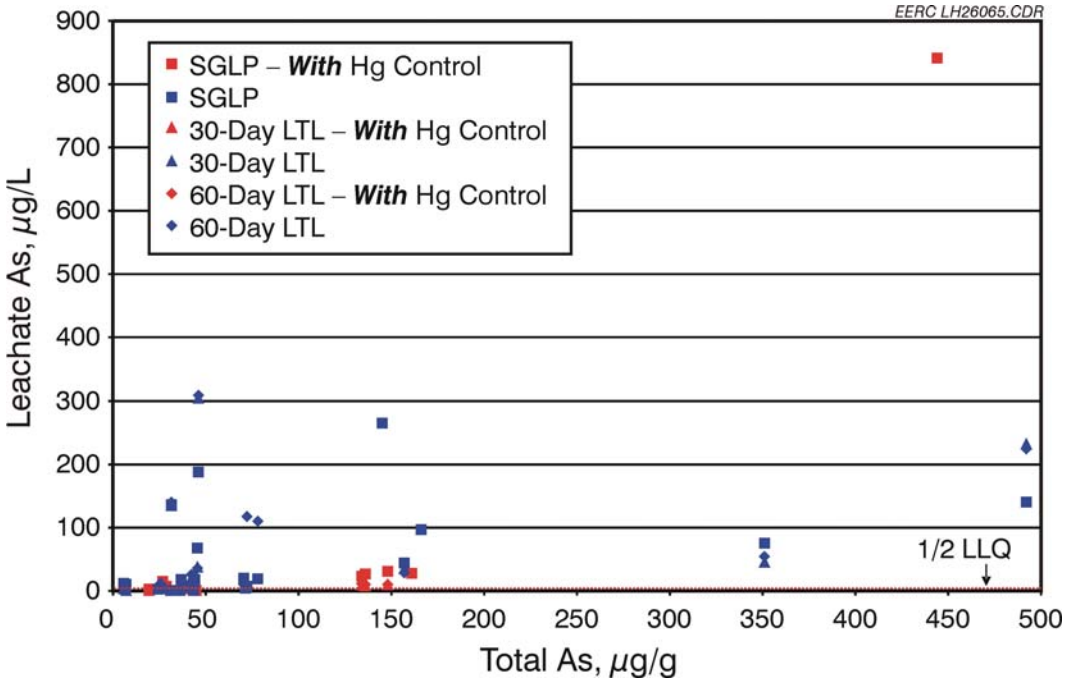

Figure 6. Total arsenic vs. short- and long-term leachable arsenic: all fly ash – *without* mercury control and fly ash – ***with*** mercury control samples.

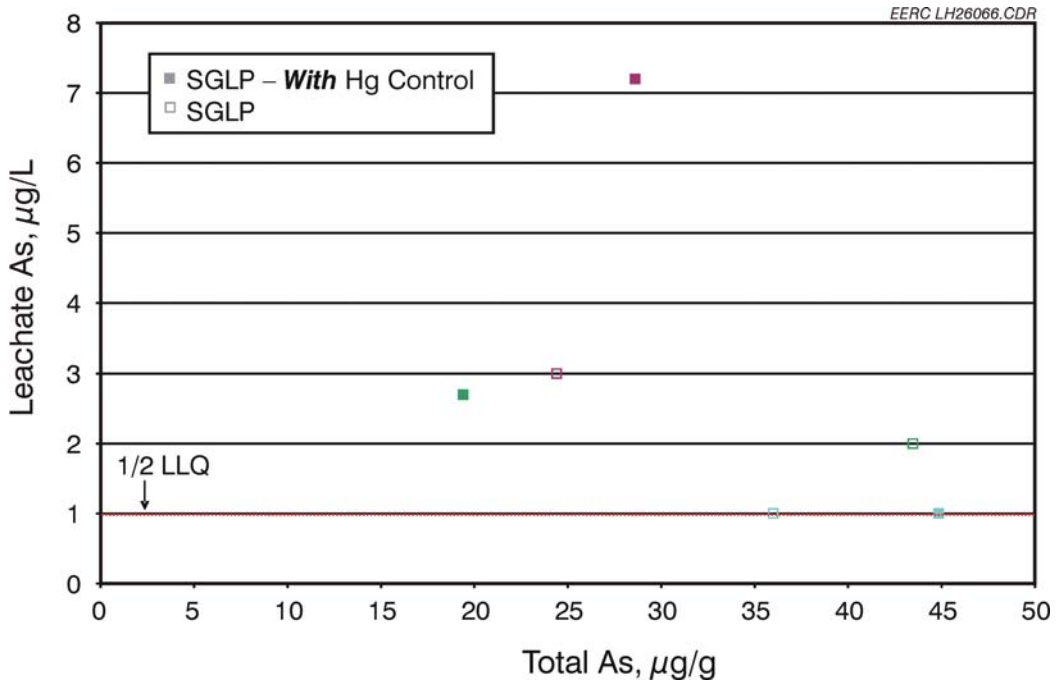

Figure 7. Total arsenic vs. SGLP leachable arsenic: all available paired fly ash samples.

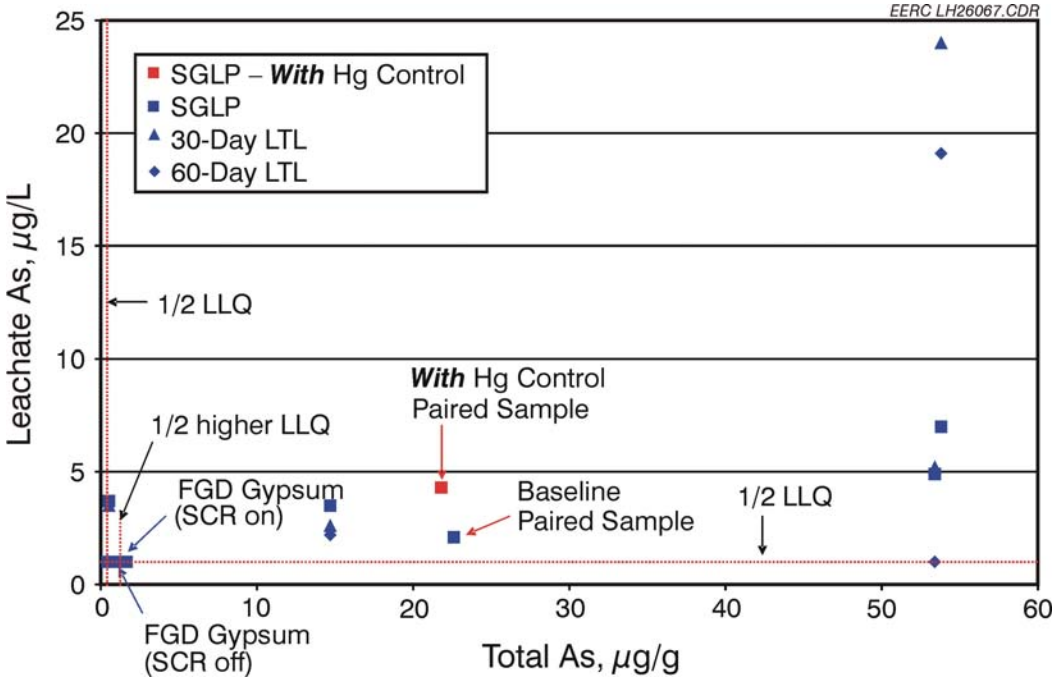

Figure 8. Total arsenic vs. short- and long-term leachable arsenic: all FGD material samples. One sample had a total arsenic LLQ higher than the reported value of another sample.

Cadmium

Figures 9–11 are results of cadmium leaching, with Figure 9 including all samples of fly ash *without* and ***with*** mercury control and Figure 10 comparing the baseline fly ash with the paired fly ash ***with*** mercury control. Figure 11 shows the data on the FGD materials evaluated. Results are similar to those noted for arsenic, with no indication that higher levels of cadmium are found in samples with activated carbon present and the limited data on the paired sample set varying within the limits of the test and analysis. As can be seen in Figure C-5, the three values reading above the LLQ for cadmium were from the SGLP. Remaining data points were at the LLQ.

Chromium

Figure 12, comparing all fly ash samples for total chromium versus leachate chromium, shows that there appears to be an increased chromium leachate concentration for some fly ash samples ***with*** mercury control. Figure 13, showing the SGLP data for the paired fly ash sample sets, also indicates a small increase in chromium leachate concentrations for two sample sets. The third sample set has an unusually high LLQ and cannot be used to confirm or refute this observation. However, in Figure C-7, it can be noted that the long-term chromium leachate concentrations were significantly lower than those for the SGLP for two samples. The third sample did show a slightly higher total chromium concentration for the paired fly ash ***with*** mercury control and subsequent slightly higher leachate concentrations for the long-term

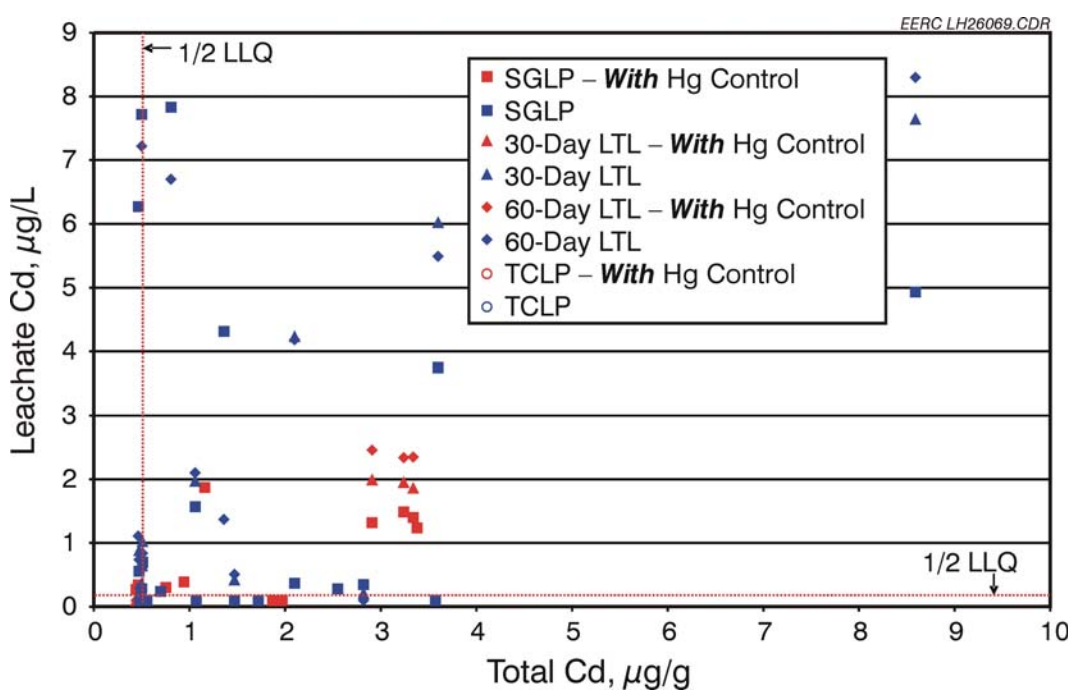

Figure 9. Total cadmium vs. short- and long-term leachable cadmium: all fly ash – *without* mercury control and fly ash – ***with*** mercury control samples.

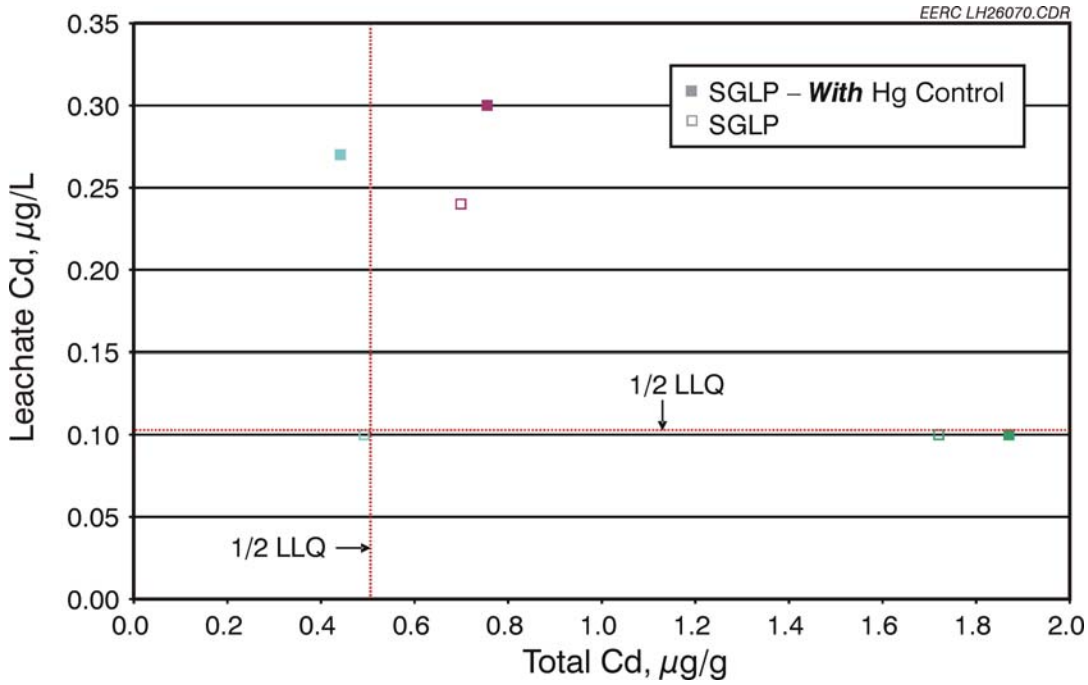

Figure 10. Total cadmium vs. SGLP leachable cadmium: all available paired fly ash samples.

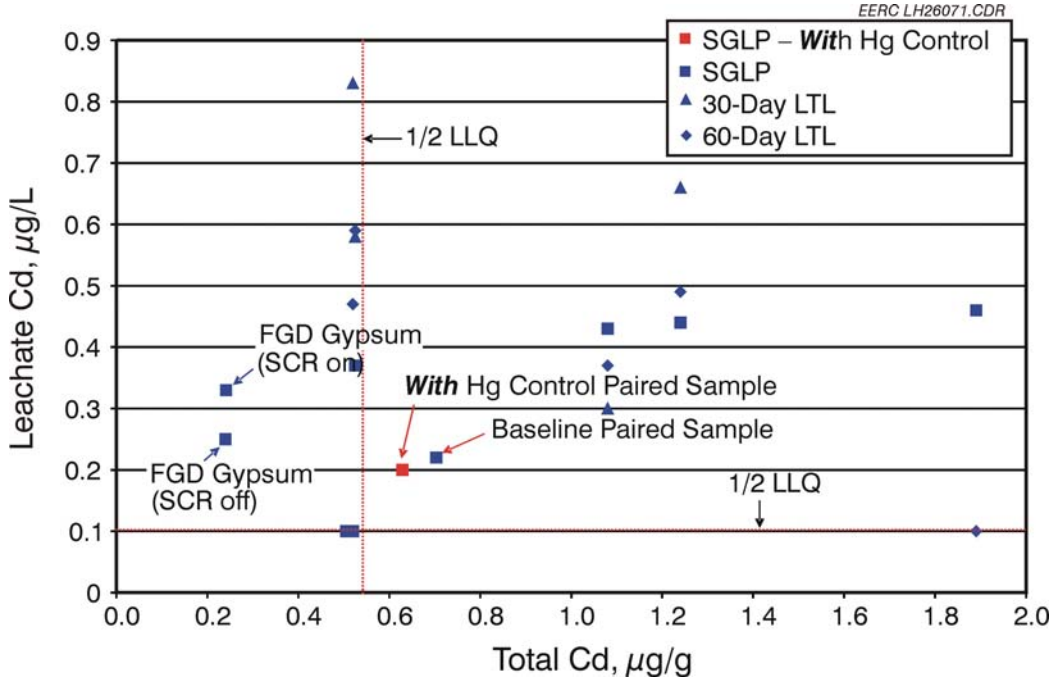

Figure 11. Total cadmium vs. short- and long-term leachable cadmium: all FGD material samples.

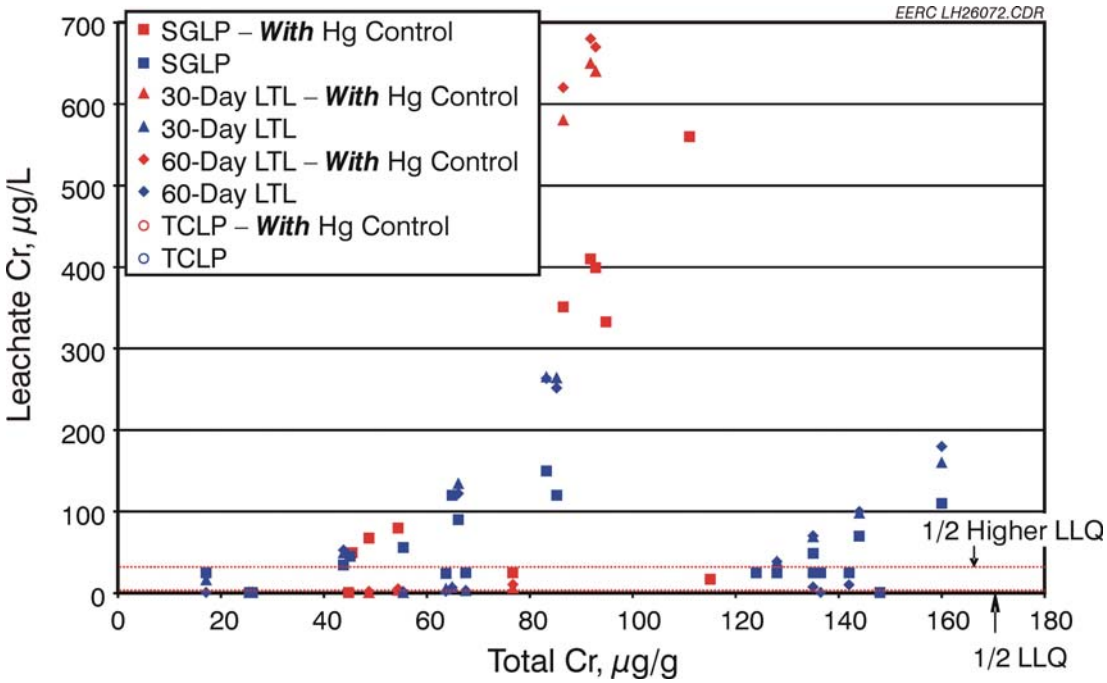

Figure 12. Total chromium vs. short- and long-term leachable chromium: all fly ash – *without* mercury control and fly ash – ***with*** mercury control samples. Several samples had a leachable chromium LLQ higher than the reported values of other samples.

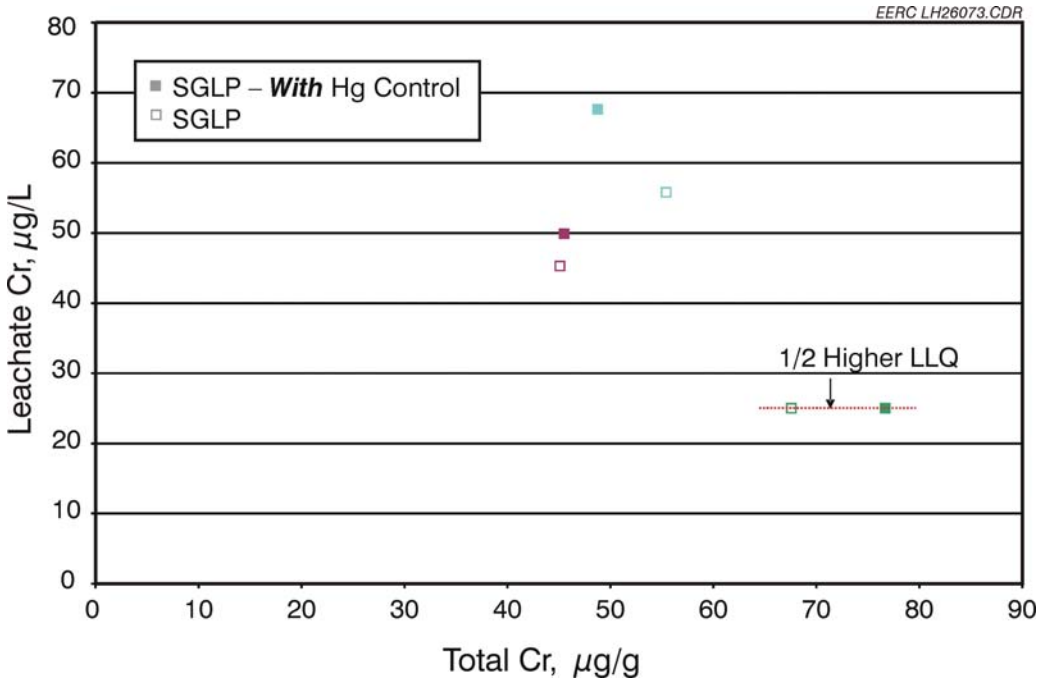

Figure 13. Total chromium vs. SGLP leachable chromium: all available paired fly ash samples. One paired sample set had a leachable chromium LLQ higher than the reported values of other samples.

leaching tests. A reduced y-axis on Figure C-8 shows this in detail; however, the SGLP values cannot be used in this evaluation because they are below the LLQ, as noted in the figure. Figure 14 shows the data on the FGD materials evaluated.

Lead

As shown in Figures 15 through 17, leachate lead concentrations were below the LLQ for most samples evaluated. It can be seen in Figure C-10 and C-11 that for one of the paired fly ash samples, the long-term leachate lead concentrations were well above the LLQ.

Nickel

Data for total nickel content versus leachate nickel content in Figure 18 for all fly ash samples appears to indicate that those samples containing activated carbon (***with*** mercury control) exhibit reduced leaching of nickel, but the data in Figures 19 and C-13 through C-15 showing comparisons of the paired fly ash samples are insufficient to support this observation. Figure 20 shows no correlation between total and leachable nickel for FGD materials.

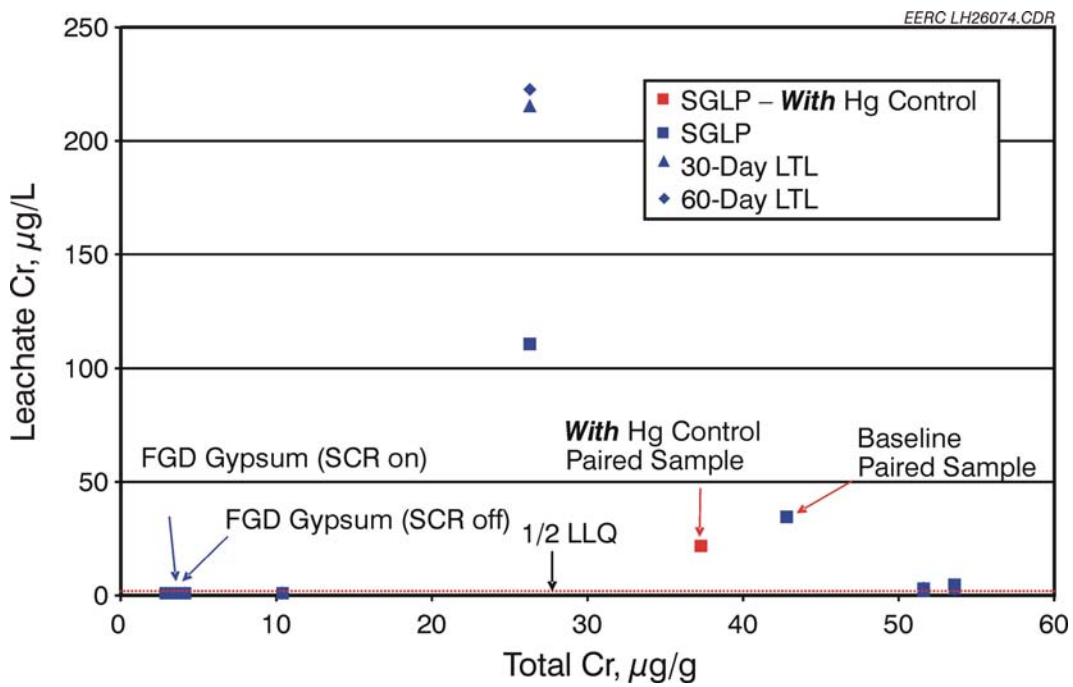

Figure 14. Total chromium vs. short- and long-term leachable chromium: all FGD material samples.

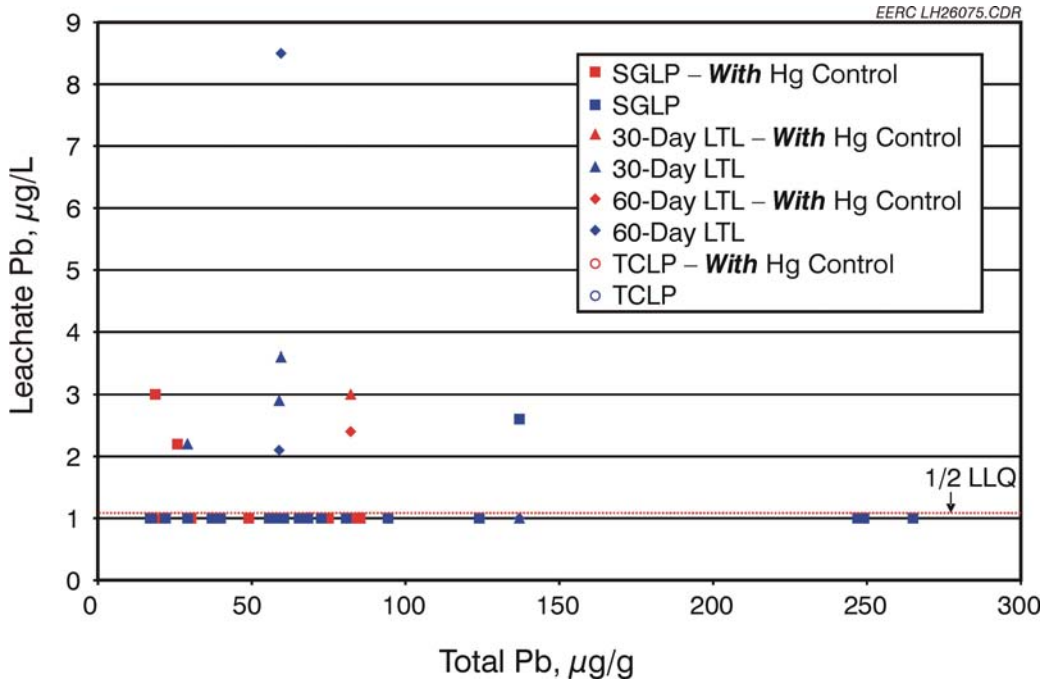

Figure 15. Total lead vs. short- and long-term leachable lead: all fly ash – *without* mercury control and fly ash – ***with*** mercury control samples.

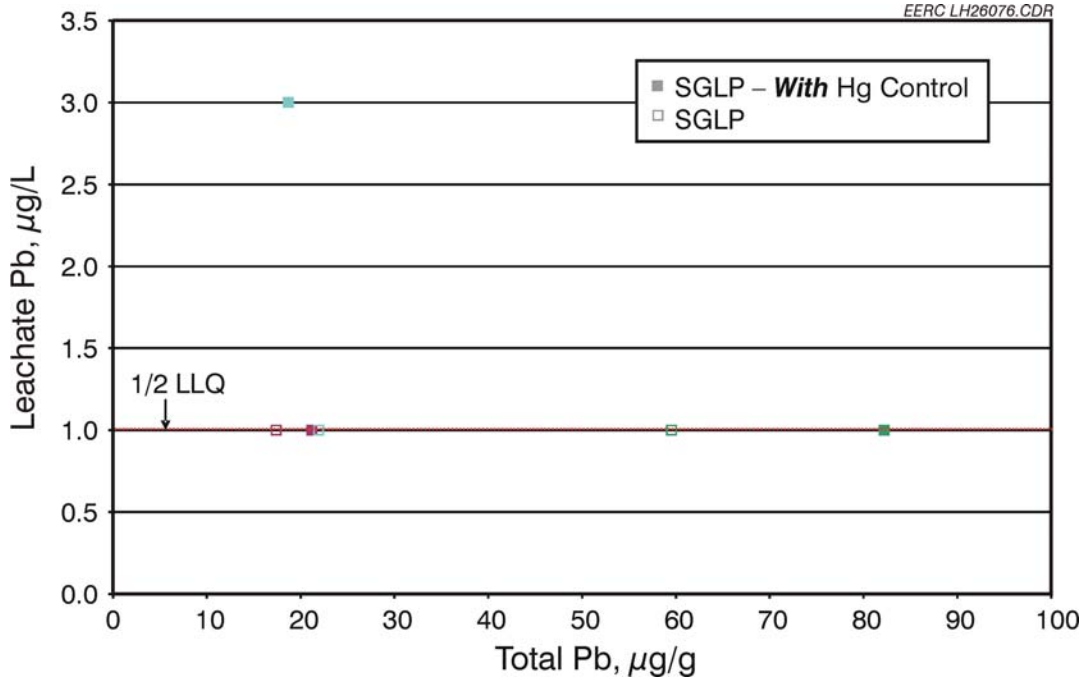

Figure 16. Total lead vs. SGLP leachable lead: all available paired fly ash samples.

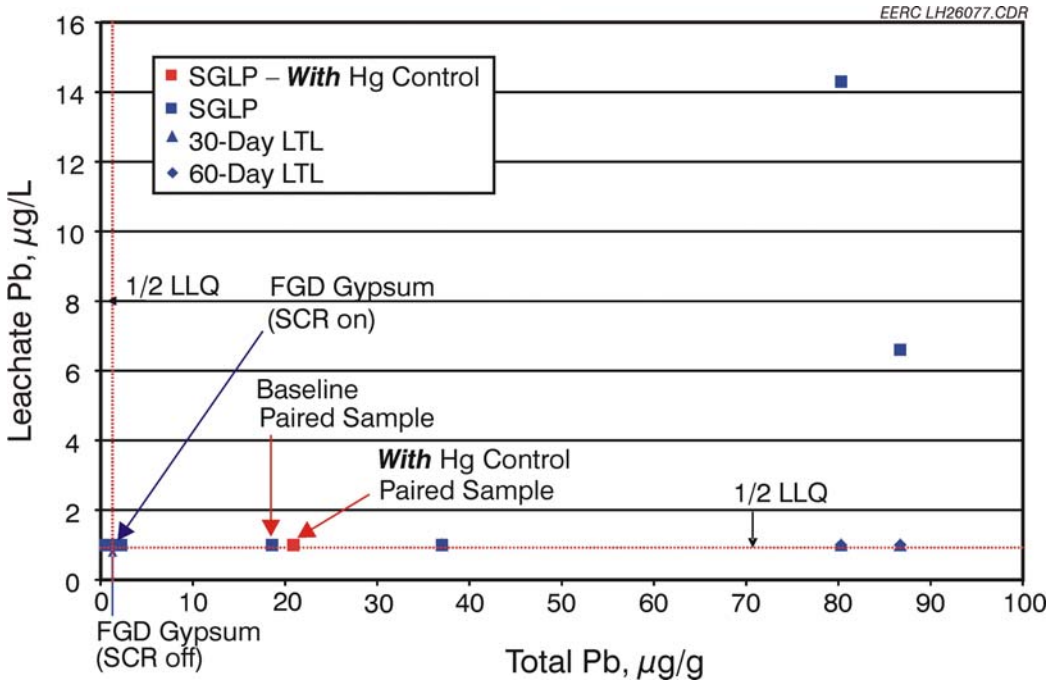

Figure 17. Total lead vs. short- and long-term leachable lead: all FGD material samples.

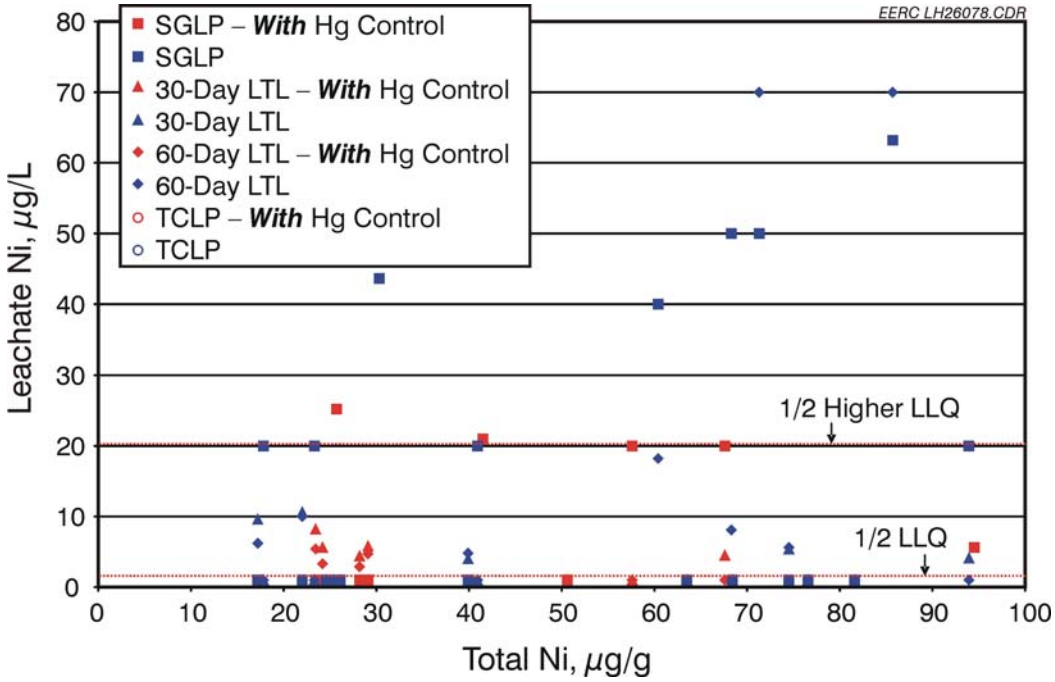

Figure 18. Total nickel vs. short- and long-term leachable nickel: all fly ash – *without* mercury control and fly ash – ***with*** mercury control samples. Several samples had a leachable nickel LLQ higher than the reported values of other samples. The x-axis is reduced from 300 µg/g.

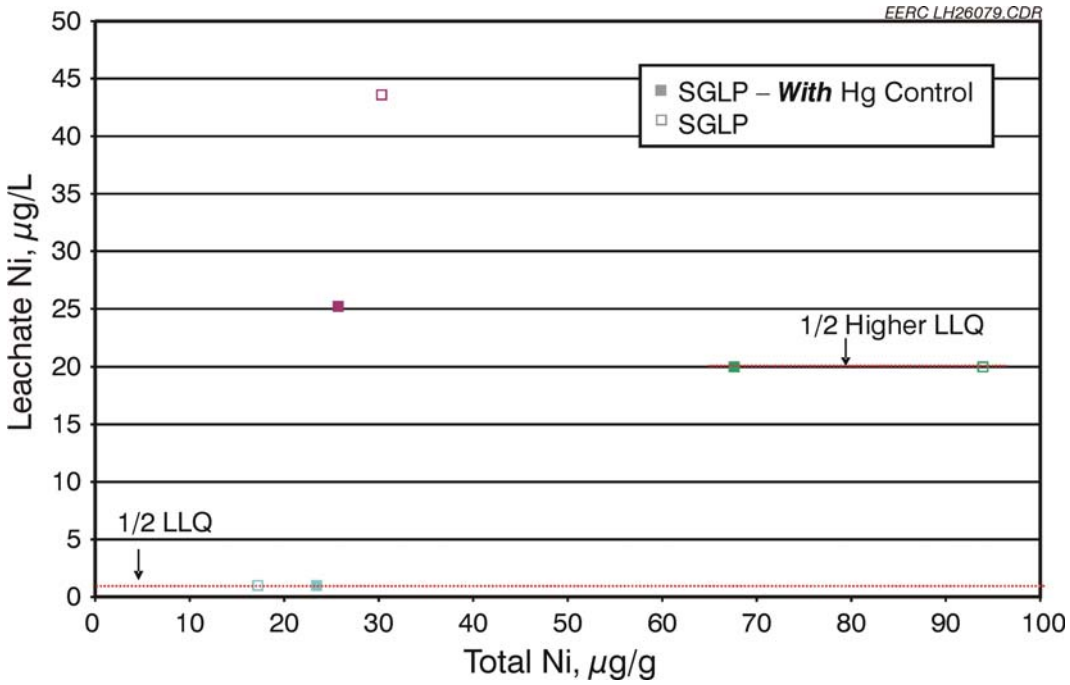

Figure 19. Total nickel vs. SGLP leachable nickel: all available paired fly ash samples. One paired sample set had a leachable nickel LLQ higher than the reported values of other samples.

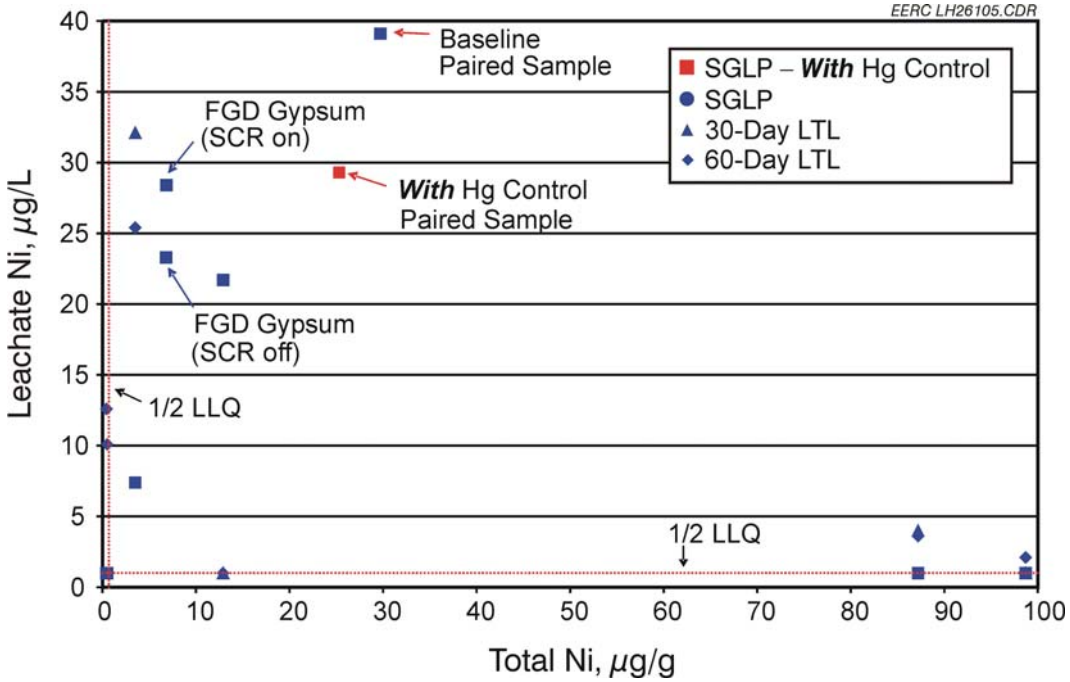

Figure 20. Total nickel vs. short- and long-term leachable nickel: all FGD material samples.

Selenium

Figures 21 and 22 show the comparative concentrations for total selenium and leachate selenium for fly ash samples with Figure 21 showing data points for all fly ash samples and Figure 22 showing SGLP results for the paired fly ash samples. Figure 23 contains data on the FGD materials evaluated including one paired sample. The selenium data are under continuing review, but preliminary interpretive efforts show similar total concentrations and leachate concentrations for fly ash regardless of the origin of the sample. Repeat analyses of selected samples for total selenium and leaching will be performed.

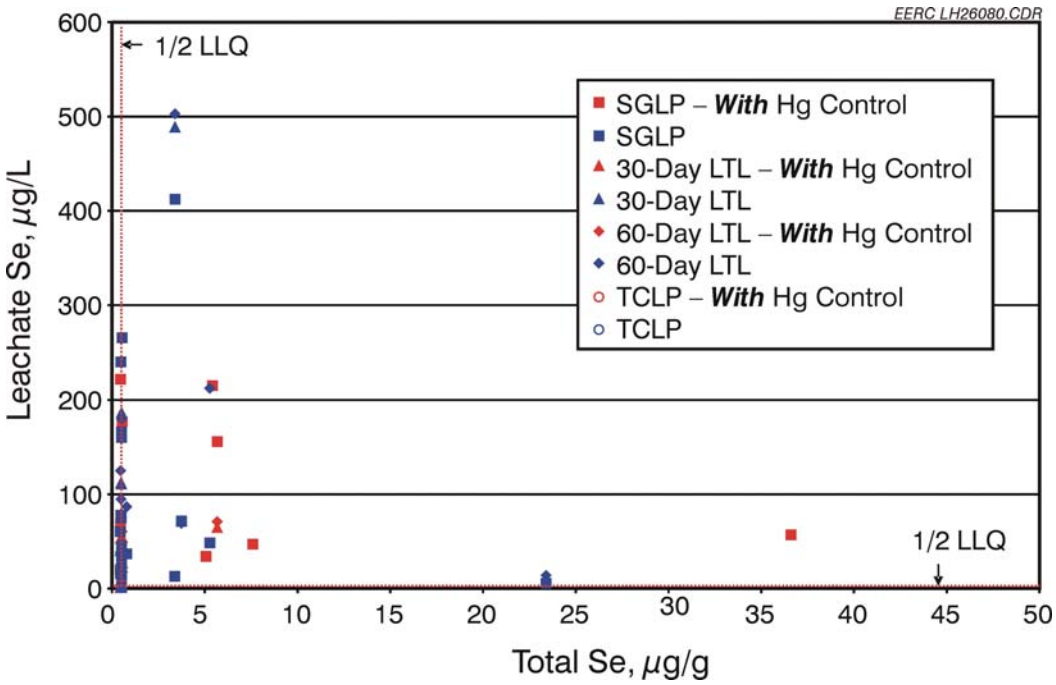

Figure 21. Total selenium vs. short- and long-term leachable selenium: all fly ash – *without* mercury control and fly ash – ***with*** mercury control samples. The x-axis is reduced from 450 µg/g. The y-axis is reduced from 9000 µg/g.

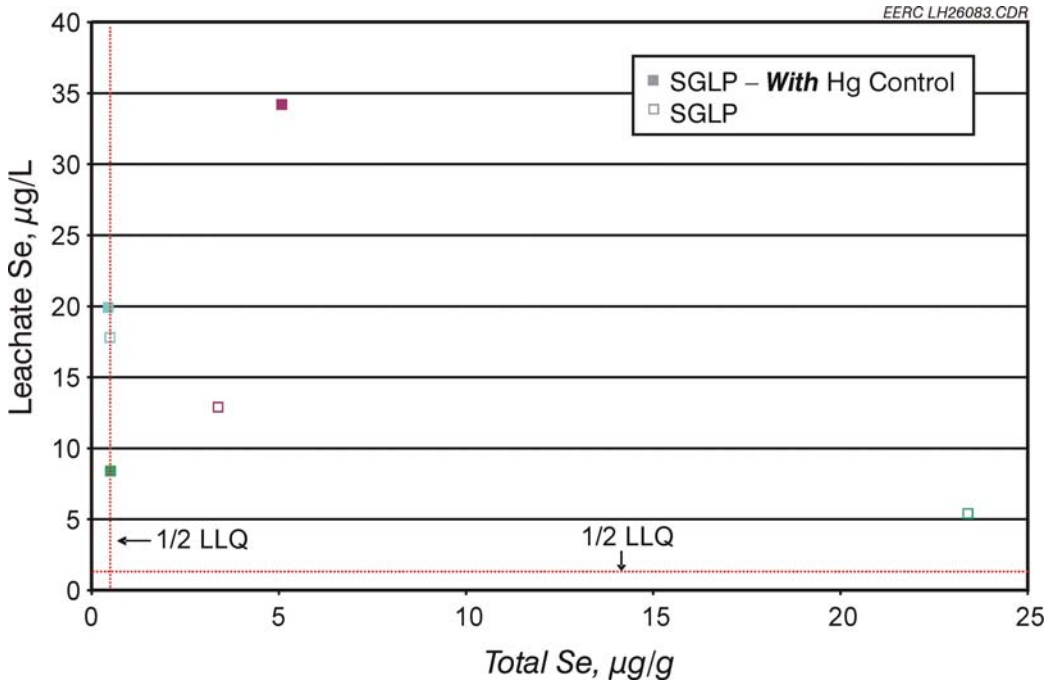

Figure 22. Total selenium vs. SGLP leachable selenium: all available paired fly ash samples.

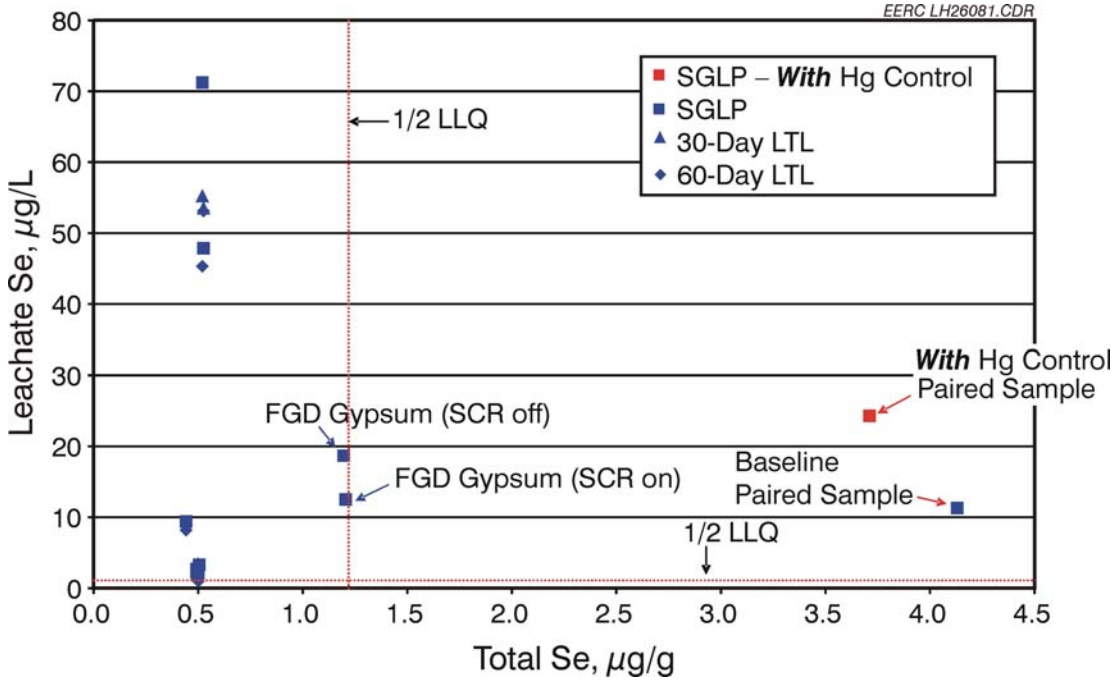

Figure 23. Total selenium vs. short- and long-term leachable selenium: all FGD material samples.

SUMMARY

The data presented in this report include all leaching data for the project entitled "Mercury and Air Toxic Element Impacts of Coal Combustion By-Product Disposal and Utilization." The most complete data set is for the element mercury, and the data presented support the following preliminary conclusions:

- Total mercury content of samples generated both ***with*** and *without* mercury emission controls present and leachate concentrations did not correlate.

- Leachate concentrations were independent of short-term leaching procedures used.

- Leachate mercury concentrations have been found to be extremely low regardless of the total mercury content of the sample. Most leachates exhibited mercury concentrations less than the reporting limit of 0.01 µg/L. All leachate concentrations fell well below the PDW limit of 2.0 µg/L for mercury as well as the limit at 30 × PDW (60 µg/L) and 100 × PDW (200 µg/L).

- Total mercury content of paired test fly ash samples ***with*** mercury control was consistently higher than the paired baseline fly ash sample *without* mercury control.

For the remaining air toxic elements, the following preliminary observations can be made:

- The presence of activated carbon in fly ash samples ***with*** mercury control is not an indicator of increased total concentrations of any of the air toxic elements studied. The data from a limited number of paired fly ash samples support this observation.

- Generally, higher total concentrations of air toxic elements do not correlate to higher leachate concentrations.

- All air toxic elements showed reduced, increased, or variable leachate concentrations with increased time using the SGLP and LTL tests. Based on previous EERC work, these leaching profiles are expected to be sample-dependent.

Continuing work on leaching in this project will focus on adding leaching data from FGD materials and paired samples of both fly ash and FGD materials. Data verification will also be completed for inclusion in the project final report. The results of an interlaboratory comparison of leaching methods will also be completed by the conclusion of this project, and results of that study will be reported in the project final report.

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6. Kosson, D.S.; van der Sloot, H.A.; Sanchez, F.; Garrabrants, A.C. An Integrated Framework for Evaluating Leaching in Waste Management and Utilization of Secondary Materials. *Environmental Engineering Science* **2002**, *19* (3), 159–203.

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APPENDIX A

Hg/ATE PROJECT SAMPLE SET AND ANALYSIS STATUS

Hg/ATE Project Sample Set and Analysis Status

pH = pH too low.
IS = Insufficient sample.
LP/SOW = Low priority, analysis was not part of the proposed statement of work.
LP/ID = Low priority, insufficient sample identification information.
NA = Not applicable.

ID No.	Sample Type	Coal Type	Hg Control	Hg (µg/g)	pH	LOI	Hg Total	Total Trace	SGLP	30-day LTL	60-day LTL	Thermal Curve	Long-Term Ambient	Microbiological	Carbon Forms
02-002	Fly ash	Eastern bituminous	Yes	30.6	3.62	24.2%	Completed	IS	Completed	pH	pH	Under way	IS	IS	Completed
02-003	Fly ash	Eastern bituminous	Yes	21.7	3.91	19.3%	Completed	LP	Completed	pH	pH	Under way	IS	IS	LP/SOW
02-004	Fly ash	Subbituminous	Yes	5.50	11.47	IS	Completed	IS	Completed	Completed	Completed	Under way	IS	IS	Completed
02-005	Fly ash	Subbituminous	Yes	4.73	10.65	IS	Completed	IS	Completed	Completed	Completed	Under way	IS	IS	LP/SOW
02-006	Fly ash	Subbituminous	Yes	5.81	10.86	3.88%	Completed	Completed	Completed	IS	IS	Under way	IS	IS	LP/SOW
02-007	Fly ash	Eastern bituminous	Yes	120	3.54	24.3%	Completed	LP	Completed	pH	pH	Under way	IS	IS	Completed
02-069	Fly ash	Eastern bituminous	Yes	0.526	8.94	12.6%	Completed	Completed	Completed	pH	pH	Under way	IS	IS	LP/SOW
02-070	Fly ash	Eastern bituminous	No	0.197	10.25	5.85%	Completed	Completed	Completed	Pending	Pending	Under way	IS	IS	Completed
02-071	Fly ash	Eastern bituminous	Yes	0.595	9.59	17.2%	Completed	Completed	Completed	pH	pH	Under way	IS	IS	LP/SOW
02-072	Fly ash	Eastern bituminous	No	0.158	10.35	5.18%	Completed	Completed	Completed	Pending	Pending	Under way	IS	IS	LP/SOW
02-073	Fly ash	Eastern bituminous	No	0.205	12.56	5.00%	Completed	Completed	Completed	Pending	Pending	Under way	IS	IS	LP/SOW
02-074	Fly ash	Eastern bituminous	No	0.526	12.18	6.09%	Completed	Completed	Completed	Pending	Pending	Under way	IS	IS	LP/SOW
02-076	Fly ash	Eastern bituminous	Yes	0.400	9.93	21.0%	Completed	LP	Completed	pH	pH	Under way	IS	IS	Completed
03-004	Fly ash	Eastern bituminous	No	0.0973	4.26	3.20%	Completed	Completed	Completed	pH	Completed	Under way	NA – low Hg	NA – low Hg	Completed
03-005	Fly ash	Eastern bituminous	No	0.0842	4.26	3.59%	Completed	Completed	Completed	pH	Completed	Under way	NA – low Hg	NA – low Hg	Completed
03-006	Fly ash	Eastern bituminous	No	0.194	4.60	5.28%	Completed	Completed	Completed	pH	Completed	Under way	Completed	Pending	Completed
03-007	Fly ash	Eastern bituminous	No	0.141	4.15	4.41%	Completed	Completed	Completed	pH	Completed	Under way	Pending	Pending	Completed
03-008	Fly ash	Eastern bituminous	No	0.119	11.72	IS	Completed	IS	Completed	IS	IS	Under way	IS	IS	Completed
03-009	Fly ash	Eastern bituminous	Yes	0.198	11.79	IS	Completed	IS	Completed	IS	IS	IS	IS	IS	NA
03-010	Fly ash	Eastern bituminous	Yes	0.371	10.34	IS	Completed	IS	Completed	IS	IS	IS	IS	IS	NA
03-011	Fly ash	Unknown	Yes	0.618	8.44	10.5%	Completed	LP	Completed	pH	pH	Under way	IS	IS	LP/SOW
03-012	Fly ash	Unknown	Yes	1.09	11.58	12.8%	Completed	IS	Completed	IS	IS	Under way	IS	IS	LP/SOW
03-013	Fly ash	Unknown	Yes	0.362	10.39	10.9%	Completed	LP	Completed	IS	IS	Under way	IS	IS	LP/SOW
03-014	Fly ash	Unknown	Yes	1.21	9.95	10.9%	Completed	LP	Completed	NA	NA	Under way	NA	NA	LP/SOW
03-015	Fly ash	Unknown	Yes	IS	10.52	IS	IS	IS	Completed	NA	NA	NA	NA	NA	NA
03-016	Fly ash	Lignite	No	0.0161	12.60	0.34%	Completed	Completed	Pending	Pending	Pending	Under way	Pending	Pending	Completed
03-017	Fly ash	Lignite	Yes	0.225	12.57	0.96%	Completed	Completed	LP/Composite	LP/Composite	LP/Composite	Under way	Completed	Pending	Completed
03-018	Fly ash	Lignite	Yes	0.289	12.57	0.97%	Completed	Completed	LP/Composite	LP/Composite	LP/Composite	Under way	Completed	Pending	Completed
03-019	Fly ash	Lignite	Yes	2.22	11.74	4.21%	Completed	Completed	LP/Composite	LP/Composite	LP/Composite	Under way	IS	IS	Completed
03-060	Fly ash	Subbituminous	Yes	1.86	11.32	2.28%	Completed	Completed	Completed	Completed	Completed	Under way	Completed	Completed	Completed
03-061	Fly ash	Subbituminous	No	0.578	12.02	1.00%	Completed	Completed	Completed	Completed	Completed	Under way	Completed	Pending	Completed
03-062	Fly ash	Lignite	Yes	0.490	12.57	1.29%	Completed	Completed	Completed	Completed	Completed	Under way	Completed	Pending	Completed
03-063	Fly ash	Eastern bituminous	No	< 0.005	11.30	0.47%	Completed	Completed	Completed	Completed	Completed	Under way	Pending	Pending	Completed
03-065	Gypsum	Eastern bituminous	No	0.0440	8.59	1.22%	Completed	Completed	Completed	pH	Completed	Under way	Pending	Pending	NA
03-067	FGD Slurry	Eastern bituminous	No	< 0.1	8.05	6.38%	Completed	Completed	Pending	pH	pH	Pending	Pending	Pending	NA
03-074	Dust collector ash	Lignite	No	< 0.005	12.63	34.5%	Completed	Completed	Completed	NA – low Hg	Completed	Under way	NA – low Hg	NA – low Hg	Completed
03-075	Fly ash	Lignite	No	1.40	12.70	15.4%	Completed	Completed	Completed	Completed	Completed	Under way	IS	IS	Completed
03-076	Fly ash	Lignite	No	0.553	12.71	21.5%	Completed	Completed	Completed	Completed	Completed	Under way	IS	Pending	Completed
03-077	Fly ash	Lignite	No	2.03	11.85	IS	Completed	Completed	Completed	Completed	Completed	Under way	IS	IS	Completed
03-078	Fly ash	Lignite	No	0.662	11.59	IS	Completed	IS	Completed	IS	IS	Under way	IS	IS	Completed
03-079	Fly ash	Lignite	No	0.785	11.72	2.54%	Completed	Completed	Completed	Completed	Completed	Under way	IS	Completed	Completed
03-080	Fly ash	Lignite	No	0.440	11.64	7.48%	Completed	Completed	Completed	Completed	Completed	Under way	Pending	Pending	Completed
03-081	Fly ash	Lignite	No	0.459	11.26	1.15%	Completed	Completed	Completed	Completed	Completed	Under way	IS	IS	LP/SOW
03-082	FGD filtercake	Eastern bituminous	No	0.218	7.47	4.20%	Completed	Completed	Completed	Completed	Completed	Pending	Underway	Completed	NA
03-083	Fly ash	Eastern bituminous	No	0.0174	4.28	1.20%	Completed	Completed	Completed	pH	pH	Under way	Pending	Pending	Completed
03-084	Fixated FGD	Eastern bituminous	No	0.180	12.52	3.17%	Completed	Completed	Completed	Completed	Completed	Under way	Pending	Pending	LP/SOW
03-085	Fly ash	Eastern bituminous	No	0.0337	7.06	2.10%	Completed	Completed	Completed	pH	pH	Under way	Pending	Pending	LP/SOW
03-086	FGD filtercake	Eastern bituminous	No	0.162	7.70	5.87%	Completed	Completed	Pending	pH	pH	Pending	Pending	Pending	NA
03-087	Fixated FGD	Eastern bituminous	No	0.136	12.51	3.80%	Completed	Completed	Completed	Completed	Completed	Pending	Pending	Pending	LP/SOW
03-088	Fly ash	Eastern bituminous	No	0.0103	7.50	1.07%	Completed	Completed	Completed	Completed	Completed	Under way	Pending	Pending	LP/SOW
03-089	Gypsum	Eastern bituminous	No	0.0960	8.22	1.94%	Completed	Completed	Completed	pH	Completed	Under way	Pending	Pending	NA
03-103	FGD slurry water	Eastern bituminous	No	Pending	6.73	NA – water	Underway	Underway	NA – water	NA – water	NA – water	NA – water	NA – water	NA – water	NA – water
03-104	FGD Filtercake Water	Eastern bituminous	No	Pending	6.53	NA – water	Underway	Underway	NA – water	NA – water	NA – water	NA – water	NA – water	NA – water	NA – water

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LP/ID = Low priority, insufficient sample identification information.
NA = Not applicable.

ID No.	Sample Type	Coal Type	Hg Control	Hg (µg/g)	pH	LOI	Hg Total	Total Trace	SGLP	30-day LTL	60-day LTL	Thermal Curve	Long-Term Ambient	Microbiological	Carbon Forms
04-003	Fly ash	Eastern bituminous	No	0.685	9.34	8.44%	Completed	Completed	Completed	Completed	Completed	Under way	Pending	Pending	LP/SOW
04-004	Fly ash	Eastern bituminous	No	0.0411	10.29	1.38%	Completed	Completed	Completed	Completed	Completed	Under way	Pending	Pending	LP/SOW
04-006	Fly ash	Western bituminous	No	0.144	11.52	1.42%	Completed	Completed	Completed	Completed	Completed	Under way	Underway	Pending	LP/SOW
04-007	Fly ash	Western bituminous	No	0.521	13.00	2.46%	Completed	Completed	Completed	Completed	Completed	Under way	Underway	Pending	LP/SOW
04-029	Fly ash	Subbituminous	No	0.261	12.37	0.48%	Completed	Completed	Completed	Completed	Completed	Under way	Pending	Pending	LP/SOW
04-030	Fly ash	Lignite	Yes	0.147	11.51	0.70%	Completed	Completed	Completed	Completed	Completed	Under way	IS	Pending	LP/SOW
04-031	Fly ash	Lignite	Yes	0.174	11.60	0.64%	Completed	Completed	Completed	Completed	Completed	Under way	IS	IS	LP/SOW
04-032	Fly ash	Lignite	Yes	0.470	9.67	1.09%	Completed	Completed	Completed	pH	pH	Under way	IS	IS	LP/SOW
04-033	Fly ash	Lignite	Yes	1.43	10.70	1.27%	Completed	Completed	Completed	Completed	Completed	Under way	IS	IS	LP/SOW
04-034	Fly ash	Unknown	No	0.424	11.92	29.3%	Completed	Underway	Completed	Completed	Completed	LP/ID	LP/ID	LP/ID	LP/SOW
04-035	Fly ash	Lignite	No	0.159	12.68	2.24%	Completed	Completed	Completed	Completed	Completed	Completed	Under way	Pending	LP/SOW
04-036	Fly ash	Lignite	Yes	0.287	12.64	2.16%	Completed	Completed	Completed	Completed	Completed	Completed	Under way	Pending	LP/SOW
04-037	Fly ash	Lignite/subbituminous	No	0.435	11.80	Pending	Completed	Pending	Pending	Pending	Pending	Pending	Pending	Pending	LP/SOW
04-038	Fly ash	Lignite/subbituminous	No	0.802	11.72	Pending	Completed	Pending	Pending	Pending	Pending	Pending	Pending	Pending	LP/SOW
04-039	Fly ash	Lignite/subbituminous	No	0.767	11.32	Pending	Completed	Pending	Pending	Pending	Pending	Pending	IS	Pending	LP/SOW
04-040	Fly ash	Lignite/subbituminous	No	0.507	9.58	Pending	Completed	Pending	Pending	Pending	Pending	Pending	IS	Pending	LP/SOW
04-041	Fly ash	Lignite/subbituminous	No	0.287	IS	IS	Completed	Pending	IS	IS	IS	IS	IS	IS	IS
04-042	Fly ash	Lignite	No	0.371	11.77	Pending	Completed	Pending	Pending	Pending	Pending	Pending	Pending	Pending	LP/SOW
04-043	Fly ash	Lignite	No	0.689	11.48	Pending	Completed	Pending	Pending	Pending	Pending	Pending	IS	Completed	LP/SOW
04-044	Fly ash	Lignite	No	0.878	11.52	Pending	Completed	Pending	Pending	Pending	Pending	Pending	IS	Pending	LP/SOW
04-045	Fly ash	Lignite	No	0.849	IS	IS	Completed	Pending	Pending	IS	IS	IS	IS	IS	IS
04-054	Fly ash	Eastern bituminous	Yes	17.7	6.40	18.6%	Completed	Completed	Completed	NA	NA	Completed	Under way	Pending	LP/SOW
04-055	Field – fly ash	Lignite	No	0.0070	Pending	5.73%	Completed	Pending	Pending	Pending	Pending	Pending	Pending	Pending	LP/SOW
04-056	Field – wet FGD/Mill Rejects	Lignite	No	0.187	Pending	3.31%	Completed	Pending	Pending	Pending	Pending	Pending	Pending	Pending	LP/SOW
04-057	Field – Wet FGD/mill rejects	Lignite	No	0.207	Pending	2.18%	Completed	Pending	Pending	Pending	Pending	Pending	Pending	Pending	LP/SOW
04-058	Field – soil	Lignite	No	0.0500	Pending	6.88%	Completed	Pending	Pending	Pending	Pending	Pending	Pending	Pending	LP/SOW
04-059	Field – bottom ash	Lignite	No	0.0440	Pending	1.99%	Completed	Pending	Pending	Pending	Pending	Pending	Pending	Pending	LP/SOW
04-060	Field – wet FGD	Lignite	No	0.299	Pending	2.49%	Completed	Pending	Pending	Pending	Pending	Pending	Pending	Pending	LP/SOW
04-061	Field – bottom ash	Lignite	No	< 0.005	Pending	13.0%	Completed	Pending	Pending	Pending	Pending	Pending	Pending	Pending	LP/SOW
04-062	Field – bottom ash	Lignite	No	< 0.005	Pending	7.73%	Completed	Pending	Pending	Pending	Pending	LP/SOW	LP/SOW	LP/SOW	LP/SOW
04-063	Field – FGD/fly ash	Lignite	No	0.0800	Pending	3.40%	Completed	Pending	Pending	Pending	Pending	Pending	Pending	Pending	LP/SOW
04-064	Field – FGD/fly ash	Lignite	No	0.250	Pending	2.68%	Completed	Pending	Pending	Pending	Pending	Pending	Pending	Pending	LP/SOW
04-065	Field – FGD/fly ash	Lignite	No	0.0110	Pending	3.68%	Completed	Pending	Pending	Pending	Pending	Pending	Pending	Pending	LP/SOW
04-067	Fly ash	Subbituminous	Yes	0.640	12.80	2.11%	Completed	Completed	Underway	Pending	Pending	Under way	Under way	Pending	LP/SOW
04-082	FGD gypsum	Eastern bituminous	No	0.0430	8.10	1.60%	Completed	Completed	Underway	pH	pH	Pending	Pending	Pending	LP/SOW
04-083	FGD gypsum	Eastern bituminous	No	0.103	8.10	2.26%	Completed	Completed	Underway	pH	pH	Pending	Pending	Pending	LP/SOW
05-001	Fly ash	Lignite	No	< 0.005	12.84	0.90%	Completed	Completed	Underway	Pending	Pending	Under way	Pending	Pending	LP/SOW
05-002	FGD–SDA	Lignite	No	< 0.005	12.85	0.95%	Completed	Completed	Underway	Pending	Pending	Under way	Pending	Pending	LP/SOW
05-003	Fly ash	Lignite	Yes	0.565	12.85	1.04%	Completed	Completed	Underway	Pending	Pending	Under way	Pending	Pending	LP/SOW
05-004	FGD–SDA	Lignite	Yes	0.332	13.06	1.12%	Completed	Completed	Underway	Pending	Pending	Under way	Pending	Pending	LP/SOW
05-005	Fly ash	Lignite	No	0.431	Pending	Pending	Completed	Pending	Underway	Pending	Pending	Under way	Pending	Pending	LP/SOW
05-006	FGD slurry	Lignite	No	Pending	Pending	Pending	Pending	Pending	Pending	Pending	Pending	Pending	IS	Pending	LP/SOW
05-007	FGD slurry water	Lignite	No	Underway	Pending	NA	Underway	Underway	NA – water	NA – water	NA – water	NA – water	NA – water	NA – water	NA – water
99-188	Fly ash + FGD–SDA	Subbituminous	No	0.112	12.34	2.07%	Completed	Completed	Completed	Completed	Completed	Under way	Completed	Completed	LP/SOW

APPENDIX B

TABLES

Table B-1. Fly Ash Arsenic Data

ID No.	Hg Control	As, µg/g	SGLP	30-Day LTL	60-Day LTL	TCLP
02-006	Yes	37.4	3.5	NT*	NT	NT
03-004	No	72.2	7.7	NT	118	NT
03-005	No	71.4	4.4	NT	6.5	NT
03-006	No	78	19.2	NT	110	NT
03-007	No	70.4	20	NT	10.6	NT
03-011	Yes	NT	NT	NT	NT	1482
03-060	Yes	19.4	2.7	<2	<2	NT
03-061	No	43.5	2	<2	<2	NT
03-062	Yes	43.3	6.6	<2	5.2	NT
03-063	No	45.5	67.8	37.7	36.1	NT
03-075	No	42.2	5.4	20.3	26	NT
03-076	No	25.6	3.3	5.2	12.2	NT
03-077	No	36.8	18.4	7.6	10.8	NT
03-078	No	NT	95.1	NT	NT	NT
03-079	No	351	75.7	45.3	54.6	NT
03-080	No	157	44.6	35.2	29.0	NT
03-081	No	492	140	232	224	NT
03-083	No	166	97.3	NT	NT	NT
03-085	No	145	266	NT	NT	NT
03-088	No	44	18.4	23	23.4	NT
04-003	No	46	188	305	309	NT
04-004	No	31.5	136	135	140	NT
04-006	No	5.9	12.3	3.4	7.3	NT
04-007	No	7.09	10.7	<2	<2	NT
04-029	No	31.1	<2	<2	<2	NT
04-030	Yes	136	26.9	8.1	10.6	NT
04-031	Yes	134	23.2	9.6	11.5	NT
04-032	Yes	161	28	NT	NT	NT
04-033	Yes	148	31.1	10.1	10.4	NT
04-034	No	NT	30.8	15.2	16.0	NT
04-035	No	36	<2	<2	<2	NT
04-036	Yes	44.9	<2	<2	<2	NT
04-054	Yes	444	842	NT	NT	NT
04-067	Yes	26.8	15.2	NT	NT	NT
05-001	No	24.4	3	NT	NT	NT
05-003	Yes	28.6	7.2	NT	NT	NT
05-005	No	NT	134	NT	NT	NT

*=Not tested.

Table B-2. Fly Ash Cadmium Data

ID No.	Hg Control	Cd, µg/g	SGLP	30-Day LTL	60-Day LTL	TCLP
02-006	Yes	1.97	<0.2	NT	NT	NT
03-004	No	<1	6.27	NT	1.11	NT
03-005	No	<1	7.72	NT	7.22	NT
03-006	No	1.36	4.31	NT	1.37	NT
03-007	No	<1	7.83	NT	6.7	NT
03-011	Yes	NT	NT	NT	NT	27.4
03-060	Yes	1.87	<0.2	<0.2	<0.2	NT
03-061	No	1.72	<0.2	<0.2	<0.2	NT
03-062	Yes	<1	0.34	<0.2	<0.2	NT
03-063	No	<1	<0.2	0.64	0.61	NT
03-075	No	1.47	<0.2	0.42	0.51	NT
03-076	No	<1	<0.2	0.25	0.29	NT
03-077	No	2.82	0.35	0.21	<0.2	NT
03-078	No	NT	0.43	NT	NT	NT
03-079	No	2.1	0.37	4.23	4.18	NT
03-080	No	1.06	1.57	1.97	2.10	NT
03-081	No	3.6	3.75	6.02	5.49	NT
03-083	No	3.57	<0.2	NT	NT	NT
03-085	No	2.55	0.28	NT	NT	NT
03-088	No	8.59	4.93	7.64	8.3	NT
04-003	No	<1	0.56	0.88	0.74	NT
04-004	No	<1	0.7	1.02	0.84	NT
04-006	No	<1	0.28	0.36	0.33	NT
04-007	No	<1	<0.2	<0.2	<0.2	NT
04-029	No	1.07	<0.2	<0.2	<0.2	NT
04-030	Yes	3.34	1.4	1.86	2.35	NT
04-031	Yes	3.24	1.49	1.95	2.34	NT
04-032	Yes	3.38	1.24	NT	NT	NT
04-033	Yes	2.91	1.32	1.99	2.46	NT
04-034	No	NT	0.217	0.27	0.5	NT
04-035	No	<1	<0.2	<0.2	<0.2	NT
04-036	Yes	<1	0.27	<0.2	<0.2	NT
04-054	Yes	1.16	1.87	NT	NT	NT
04-067	Yes	0.942	0.39	NT	NT	NT
05-001	No	0.669	0.24	NT	NT	NT
05-003	Yes	0.755	0.3	NT	NT	NT
05-005	No	NT	2.79	NT	NT	NT

Table B-3. Fly Ash Chromium Data

ID No.	Hg Control	Cr, µg/g	SGLP	30-Day LTL	60-Day LTL	TCLP
02-006	Yes	111	560	NT	NT	NT
03-004	No	142	<50	NT	10.1	NT
03-005	No	148	<2	NT	<2	NT
03-006	No	135	<50	NT	7.5	NT
03-007	No	137	<50	NT	<2	NT
03-011	Yes	NT	NT	NT	NT	437
03-060	Yes	76.7	<50	6.3	10.7	NT
03-061	No	67.6	<50	3	3.2	NT
03-062	Yes	54.4	80	3.6	5.2	NT
03-063	No	128	<50	38.6	38.8	NT
03-075	No	26.1	<2	<2	<2	NT
03-076	No	25.5	<2	<2	<2	NT
03-077	No	17.1	<50	16.1	<2	NT
03-078	No	NT	150	NT	NT	NT
03-079	No	83.2	150	265	263	NT
03-080	No	66.1	90	134	122	NT
03-081	No	85.2	120	264	252	NT
03-083	No	137	<50	NT	NT	NT
03-085	No	124	<50	NT	NT	NT
03-088	No	160	110	160	180	NT
04-003	No	135	48.8	69.3	70.3	NT
04-004	No	144	70	98.1	100	NT
04-006	No	43.8	34.6	49.2	52.8	NT
04-007	No	64.9	120	7.3	6.7	NT
04-029	No	63.7	24.1	5.1	2.3	NT
04-030	Yes	92.8	399	640	670	NT
04-031	Yes	91.8	410	650	680	NT
04-032	Yes	94.8	333	NT	NT	NT
04-033	Yes	86.5	351	580	620	NT
04-034	No	NT	29.5	62.5	83.3	NT
04-035	No	55.4	55.8	<2	2.1	NT
04-036	Yes	48.8	67.6	<2	2.1	NT
04-054	Yes	115	17.3	NT	NT	NT
04-067	Yes	44.8	<2	NT	NT	NT
05-001	No	45.1	45.3	NT	NT	NT
05-003	Yes	45.5	49.9	NT	NT	NT
05-005	No	NT	137	NT	NT	NT

Table B-4. Fly Ash Lead Data

ID No.	Hg Control	Pb, µg/g	SGLP	30-Day LTL	60-Day LTL	TCLP
02-006	Yes	60.2	<2	NT	NT	NT
03-004	No	65.4	<2	NT	<2	NT
03-005	No	72.6	<2	NT	<2	NT
03-006	No	94.3	<2	NT	<2	NT
03-007	No	80.7	<2	NT	<2	NT
03-011	Yes	NT	NT	NT	NT	37.4
03-060	Yes	82.2	<2	3	2.4	NT
03-061	No	59.5	<2	3.6	8.5	NT
03-062	Yes	30.3	<2	<2	<2	NT
03-063	No	37.1	<2	<2	<2	NT
03-075	No	58.9	<2	2.9	2.1	NT
03-076	No	17	<2	<2	<2	NT
03-077	No	137	2.6	<2	<2	NT
03-078	No	NT	<2	NT	NT	NT
03-079	No	68.3	<2	<2	<2	NT
03-080	No	39.9	<2	<2	<2	NT
03-081	No	124	<2	<2	<2	NT
03-083	No	265	<2	NT	NT	NT
03-085	No	247	<2	NT	NT	NT
03-088	No	249	<2	<2	<2	NT
04-003	No	60.5	<2	<2	<2	NT
04-004	No	55.7	<2	<2	<2	NT
04-006	No	38.8	<2	<2	<2	NT
04-007	No	29.1	<2	2.2	<2	NT
04-029	No	38.6	<2	<2	<2	NT
04-030	Yes	85.3	<2	<2	<2	NT
04-031	Yes	83.4	<2	<2	<2	NT
04-032	Yes	74.9	<2	NT	NT	NT
04-033	Yes	74.9	<2	<2	<2	NT
04-034	No	NT	<1	<1	<1	NT
04-035	No	21.9	<2	<2	<2	NT
04-036	Yes	18.7	3	<2	<2	NT
04-054	Yes	49	<2	NT	NT	NT
04-067	Yes	25.9	2.2	NT	NT	NT
05-001	No	17.4	<2	NT	NT	NT
05-003	Yes	21.2	<2	NT	NT	NT
05-005	No	NT	<2	NT	NT	NT

Table B-5. Fly Ash Mercury Data

ID No.	Hg Control	Hg, µg/g	SGLP	30-Day LTL	60-Day LTL	TCLP
02-002	Yes	30.6	<0.01	NT	NT	<0.01
02-003	Yes	21.7	<0.01	NT	NT	<0.01
02-004	Yes	5.5	<0.01	<0.01	<0.01	<0.01
02-005	Yes	4.73	<0.01	<0.01	0.01	<0.01
02-006	Yes	5.81	0.064	NT	NT	<0.01
02-007	Yes	120	<0.01	NT	NT	NT
02-069	Yes	0.526	0.03	NT	NT	0.07
02-070	No	0.197	0.01	NT	NT	0.03
02-071	Yes	0.595	0.01	NT	NT	<0.01
02-072	No	0.158	0.02	NT	NT	0.02
02-073	No	0.205	0.05	NT	NT	0.02
02-074	No	0.526	0.01	NT	NT	<0.01
02-076	Yes	0.4	0.016	NT	NT	<0.01
03-004	No	<0.1	<0.01	NT	0.012	NT
03-005	No	<0.1	0.01	NT	0.239	NT
03-006	No	0.194	<0.01	NT	0.06	NT
03-007	No	0.141	<0.01	NT	<0.01	NT
03-008	No	0.119	<0.01	NT	NT	0.034
03-009	Yes	0.198	<0.01	NT	NT	<0.01
03-010	Yes	0.371	<0.01	NT	NT	<0.01
03-011	Yes	0.618	<0.01	NT	NT	0.17
03-012	Yes	1.09	<0.01	NT	NT	<0.01
03-013	Yes	0.362	<0.01	NT	NT	<0.01
03-014	Yes	1.21	0.018	NT	NT	0.01
03-015	Yes	NT	<0.01	NT	NT	<0.01
03-060	Yes	1.86	<0.01	<0.01	0.037	NT
03-061	No	0.578	<0.01	<0.01	0.325	NT
03-062	Yes	0.490	<0.01	<0.01	<0.01	NT
03-063	No	<0.1	<0.01	<0.01	0.038	NT
03-075	No	1.40	0.039	<0.01	0.13	NT
03-076	No	0.553	0.087	<0.01	0.027	NT
03-077	No	2.03	<0.01	<0.01	0.054	NT
03-078	No	0.662	<0.01	NT	NT	NT
03-079	No	0.785	<0.01	<0.01	0.02	NT
03-080	No	0.440	0.011	0.113	0.023	NT
03-081	No	0.469	0.083	0.013	0.018	NT
03-083	No	<0.1	<0.01	NT	NT	NT
03-085	No	<0.1	<0.01	NT	NT	NT
03-088	No	<0.1	0.029	<0.01	<0.01	NT
04-003	No	0.685	<0.01	0.04	<0.01	NT
04-004	No	<0.1	<0.01	<0.01	0.077	NT
04-006	No	0.144	<0.01	0.076	0.087	NT
04-007	No	0.521	0.021	0.035	<0.01	NT
04-029	No	0.261	0.023	<0.01	<0.01	NT
04-030	Yes	0.147	<0.01	<0.01	<0.01	NT
04-031	Yes	0.174	0.012	<0.01	0.028	NT
04-032	Yes	0.470	<0.01	NT	NT	NT
04-033	Yes	1.43	<0.01	<0.01	<0.01	NT
04-034	No	0.424	<0.2	<0.2	<0.2	NT
04-035	No	0.159	0.081	0.02	<0.01	NT
04-036	Yes	0.287	0.016	<0.01	<0.01	NT
04-054	Yes	17.7	<0.01	NT	NT	NT
04-067	Yes	0.640	<0.01	NT	NT	NT
05-001	No	<0.1	<0.01	NT	NT	NT
05-003	Yes	0.565	<0.01	NT	NT	NT
05-005	No	0.431	<0.01	NT	NT	NT

Table B-6. Fly Ash Nickel Data

ID No.	Hg Control	Ni, µg/g	SGLP	30-Day LTL	60-Day LTL	TCLP
02-006	Yes	50.6	<2	NT	NT	NT
03-004	No	68.3	50	NT	8.1	NT
03-005	No	85.7	63.2	NT	70	NT
03-006	No	60.4	40	NT	18.2	NT
03-007	No	71.3	50	NT	70	NT
03-011	Yes	NT	NT	NT	NT	279
03-060	Yes	67.6	<40	4.5	<2	NT
03-061	No	93.9	<40	4.1	<2	NT
03-062	Yes	57.6	<40	<2	<2	NT
03-063	No	23.3	<40	<2	<2	NT
03-075	No	25.4	<2	<2	<2	NT
03-076	No	24.6	<2	<2	<2	NT
03-077	No	17.8	<40	<2	<2	NT
03-078	No	NT	<40	NT	NT	NT
03-079	No	40.9	<40	<2	<2	NT
03-080	No	63.5	<2	<2	<2	NT
03-081	No	68.4	<2	<2	<2	NT
03-083	No	259	<40	NT	NT	NT
03-085	No	277	<40	NT	NT	NT
03-088	No	74.5	<2	5.4	5.6	NT
04-003	No	76.6	<2	<2	<2	NT
04-004	No	81.6	<2	<2	<2	NT
04-006	No	26.1	<2	<2	<2	NT
04-007	No	22	<2	10.6	10	NT
04-029	No	39.9	<2	4	4.8	NT
04-030	Yes	24.2	<2	5.6	3.3	NT
04-031	Yes	28.2	<2	4.4	2.9	NT
04-032	Yes	40	<2	NT	NT	NT
04-033	Yes	29.1	<2	5.8	4.7	NT
04-034	No	NT	5.97	4.07	<2	NT
04-035	No	17.2	<2	9.6	6.2	NT
04-036	Yes	23.5	<2	8.2	5.4	NT
04-054	Yes	94.5	5.6	NT	NT	NT
04-067	Yes	41.5	21	NT	NT	NT
05-001	No	30.3	43.6	NT	NT	NT
05-003	Yes	25.7	25.2	NT	NT	NT
05-005	No	NT	15.5	NT	NT	NT

Table B-7. Fly Ash Selenium Data

ID No.	Hg Control	Se, µg/g	SGLP	30-Day LTL	60-Day LTL	TCLP
02-006	Yes	36.6	57.1	NT	NT	NT
03-004	No	<1	16.7	NT	125	NT
03-005	No	<1	14.7	NT	48.9	NT
03-006	No	5.27	48.5	NT	212	NT
03-007	No	0.792	36.6	NT	86.9	NT
03-011	Yes	NT	NT	NT	NT	165
03-060	Yes	<1	8.4	8.5	11.4	NT
03-061	No	23.4	5.4	9.8	13.9	NT
03-062	Yes	<1	68	<2	3.8	NT
03-063	No	<1	29.1	42.6	37.4	NT
03-075	No	<1	40.3	41.9	41.6	NT
03-076	No	<1	19.1	16.6	13.8	NT
03-077	No	3.74	71.6	71.3	69.3	NT
03-078	No	NT	151	NT	NT	NT
03-079	No	<1	60.4	40.1	38.3	NT
03-080	No	<1	75.1	23.8	23.4	NT
03-081	No	<1	240	112	94.9	NT
03-083	No	<1	44.1	NT	NT	NT
03-085	No	<1	77.6	NT	NT	NT
03-088	No	<1	76.4	15.5	19	NT
04-003	No	3.39	412	489	503	NT
04-004	No	<1	166	186	180	NT
04-006	No	<1	160	111	76.2	NT
04-007	No	<1	265	26.7	17.4	NT
04-029	No	<1	2.1	<2	<2	NT
04-030	Yes	<1	222	53.2	63.4	NT
04-031	Yes	<1	177	54.4	60.3	NT
04-032	Yes	5.41	215	NT	NT	NT
04-033	Yes	5.67	156	64.8	71	NT
04-034	No	NT	113	12.8	21.1	NT
04-035	No	<1	17.8	<2	<2	NT
04-036	Yes	<1	19.9	<2	<2	NT
04-054	Yes	428	8620	NT	NT	NT
04-067	Yes	7.59	47.2	NT	NT	NT
05-001	No	3.38	12.9	NT	NT	NT
05-003	Yes	5.08	34.2	NT	NT	NT
05-005	No	NT	123	NT	NT	NT

Table B-8. FGD Material Arsenic Data

ID No.	Hg Control	As, ug/g	SGLP	30-Day LTL	60-Day LTL
99-188	No	14.7	3.5	2.6	2.2
03-065	No	<1	<2	NT	<2
03-082	No	<1	3.7	3.5	<2
03-084	No	53.4	4.9	5.2	<2
03-087	No	53.8	7	24	19.1
03-089	No	<1	<2	NT	<2
04-082	No	1.65	<2	NT	NT
04-083	No	<2	<2	NT	NT
05-002	No	22.6	2.1	NT	NT
05-004	Yes	21.8	4.3	NT	NT

Table B-9. FGD Material Cadmium Data

ID No.	Hg Control	Cd, ug/g	SGLP	30-Day LTL	60-Day LTL
99-188	No	<1	0.37	0.58	0.59
03-065	No	<1	<0.2	NT	<0.2
03-082	No	<1	<0.2	0.83	0.47
03-084	No	1.24	0.44	0.66	0.49
03-087	No	1.08	0.43	0.3	0.37
03-089	No	1.89	0.46	NT	<0.2
04-082	No	<0.5	0.33	NT	NT
04-083	No	<0.5	0.25	NT	NT
05-002	No	0.703	0.22	NT	NT
05-004	Yes	0.629	0.2	NT	NT

Table B-10. FGD Material Chromium Data

ID No.	Hg Control	Cr, ug/g	SGLP	30-Day LTL	60-Day LTL
99-188	No	26.3	111	215	223
03-065	No	2.9	<2	NT	<2
03-082	No	10.4	<2	<2	<2
03-084	No	53.6	4.7	3.1	2.45
03-087	No	51.6	3	2.2	3.3
03-089	No	4.13	<2	NT	<2
04-082	No	3.39	<2	NT	NT
04-083	No	3.95	<2	NT	NT
05-002	No	42.8	34.6	NT	NT
05-004	Yes	37.3	21.8	NT	NT

Table B-11. FGD Material Lead Data

ID No.	Hg Control	Pb, µg/g	SGLP	30-Day LTL	60-Day LTL
99-188	No	37	<2	<2	<2
03-065	No	<1	<2	NT	<2
03-082	No	2.22	<2	<2	<2
03-084	No	80.3	14.3	<2	<2
03-087	No	86.7	6.6	<2	<2
03-089	No	2.08	<2	NT	<2
04-082	No	<2.5	<2	NT	NT
04-083	No	<2.5	<2	NT	NT
05-002	No	18.6	<2	NT	NT
05-004	Yes	20.9	<2	NT	NT

Table B-12. FGD Material Mercury Data

ID No.	Hg Control	Hg, µg/g	SGLP	30-Day LTL	60-Day LTL
99-188	No	0.112	<0.01	<0.01	0.0428
03-065	No	<0.1	<0.01	NT	<0.01
03-082	No	0.218	0.404	<0.01	<0.01
03-084	No	0.18	0.289	<0.01	<0.01
03-087	No	0.136	0.237	<0.01	<0.01
03-089	No	<0.1	<0.01	NT	<0.01
04-082	No	<0.1	<0.01	NT	NT
04-083	No	0.103	<0.01	NT	NT
05-002	No	<0.1	<0.01	NT	NT
05-004	Yes	0.332	<0.01	NT	NT

Table B-13. FGD Material Nickel Data

ID No.	Hg Control	Ni, µg/g	SGLP	30-Day LTL	60-Day LTL
99-188	No	12.9	21.7	<2	<2
03-065	No	<1	<2	NT	10.1
03-082	No	3.5	7.4	32.1	25.4
03-084	No	87.2	<2	4	3.6
03-087	No	98.7	<2	<2	2.1
03-089	No	<1	<2	NT	12.6
04-082	No	6.83	28.4	NT	NT
04-083	No	6.81	23.3	NT	NT
05-002	No	29.7	39.1	NT	NT
05-004	Yes	25.3	29.3	NT	NT

Table B-14. FGD Material Selenium Data

ID No.	Hg Control	Se, µg/g	SGLP	30-Day LTL	60-Day LTL
99-188	No	<1	47.9	53.5	53.1
03-065	No	<1	3.3	NT	2.7
03-082	No	<1	71.2	55.2	45.3
03-084	No	<1	2.7	2.4	1.5
03-087	No	<1	2.1	3.4	<2
03-089	No	<1	9.4	NT	8.2
04-082	No	<2.5	12.5	NT	NT
04-083	No	<2.5	18.7	NT	NT
05-002	No	4.13	11.3	NT	NT
05-004	Yes	3.71	24.3	NT	NT

APPENDIX C

FIGURES

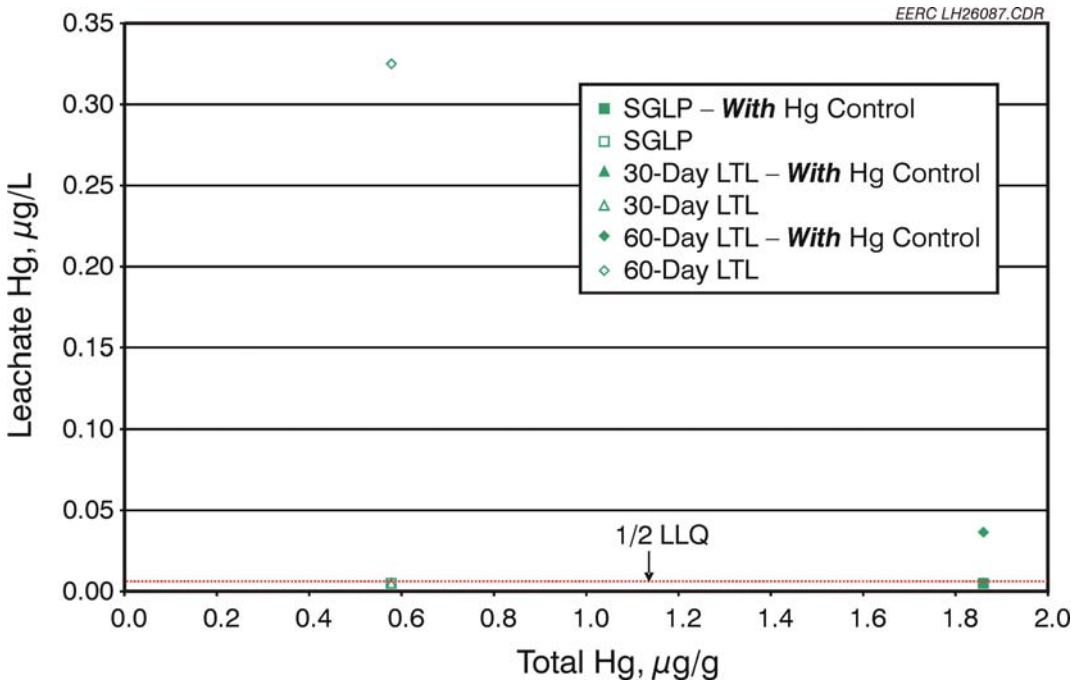

Figure C-1. Total mercury vs. short- and long-term leachable mercury: paired fly ash sample set ID Nos. 03-060 and 03-061.

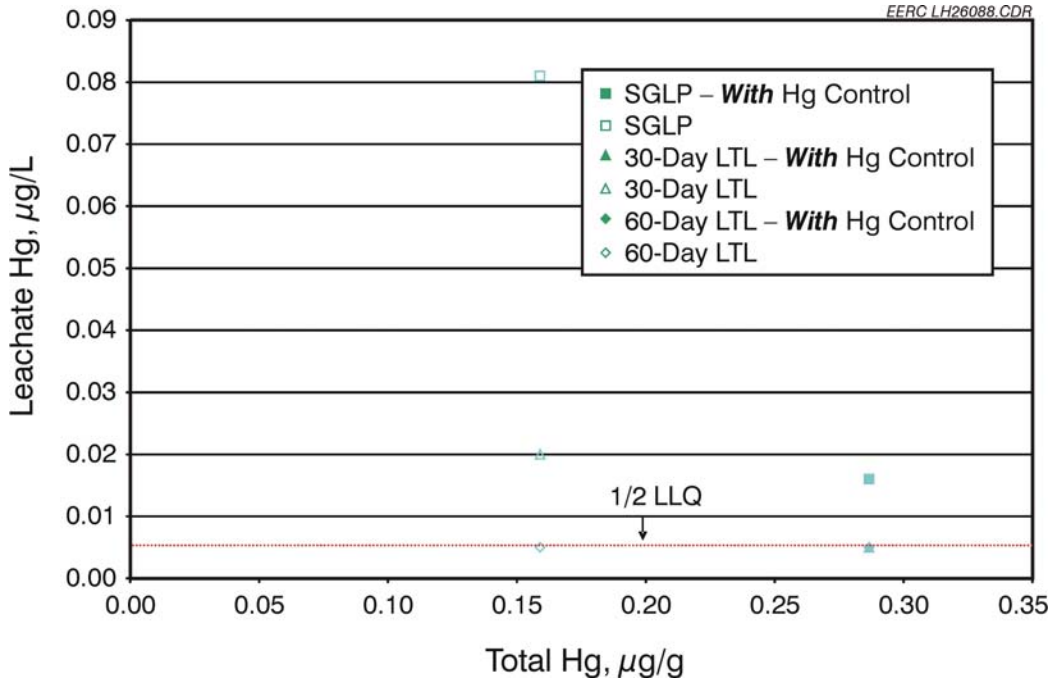

Figure C-2. Total mercury vs. short- and long-term leachable mercury: paired fly ash sample set ID Nos. 04-035 and 04-036.

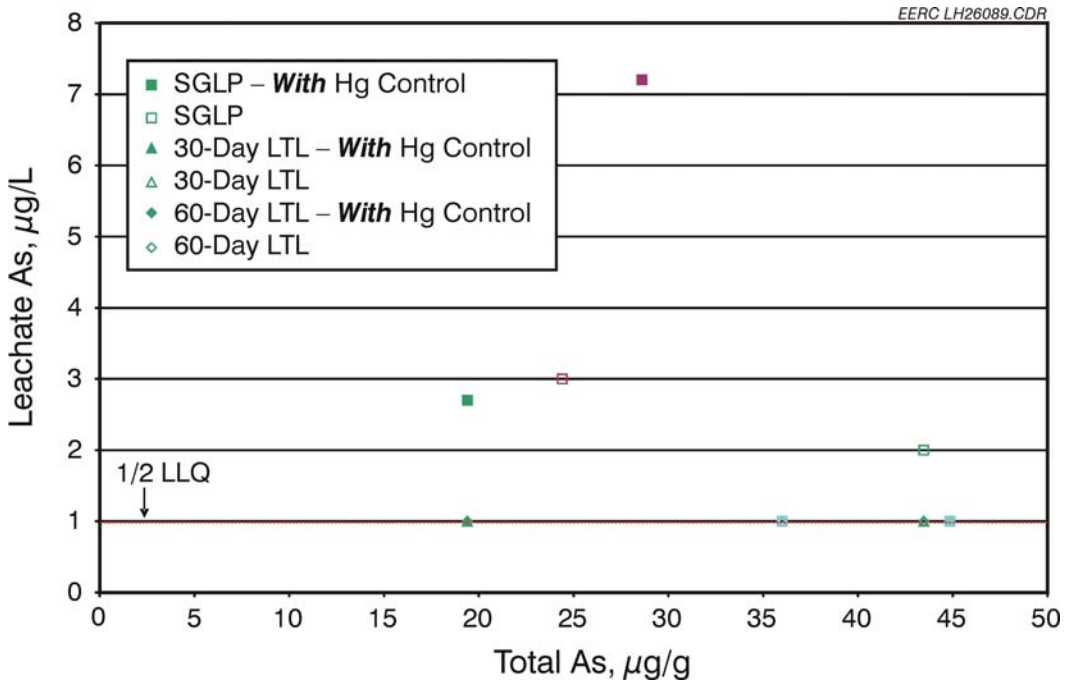

Figure C-3. Total arsenic vs. short- and long-term leachable arsenic: all available paired fly ash samples.

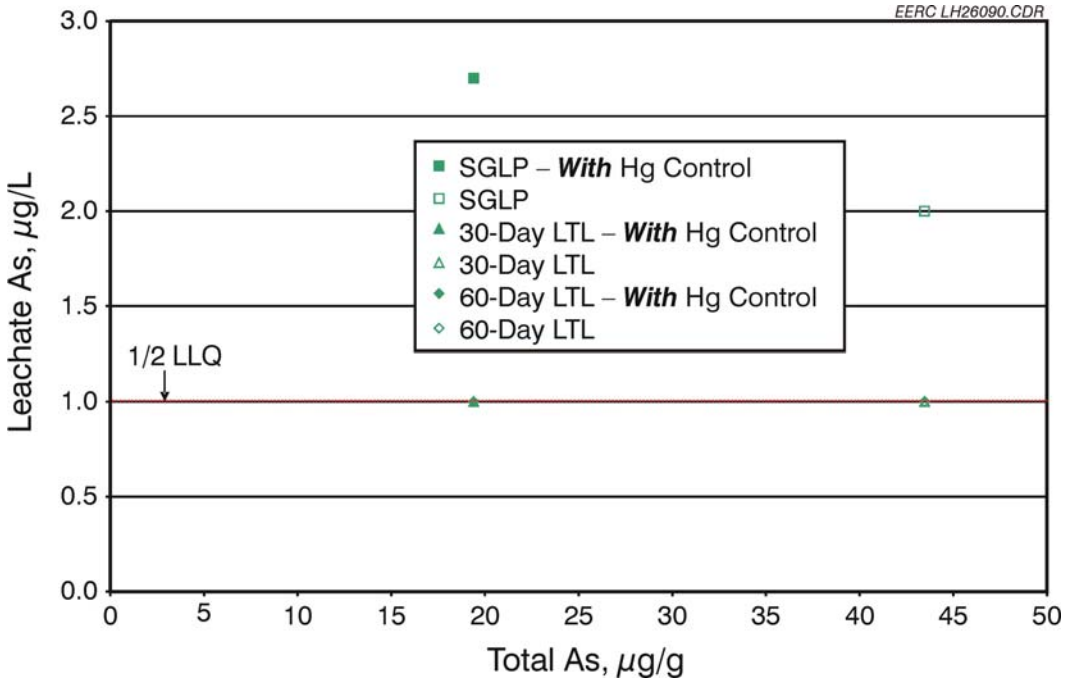

Figure C-4. Total arsenic vs. short- and long-term leachable arsenic: paired fly ash sample set ID Nos. 03-060 and 03-061.

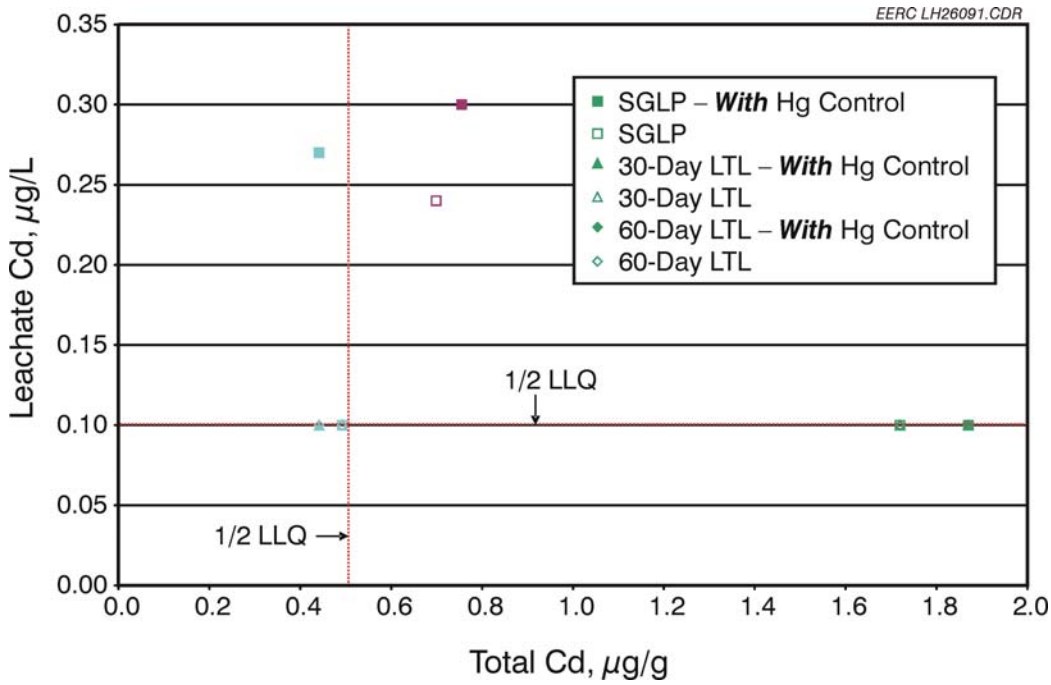

Figure C-5. Total cadmium vs. short- and long-term leachable cadmium: all available paired fly ash samples.

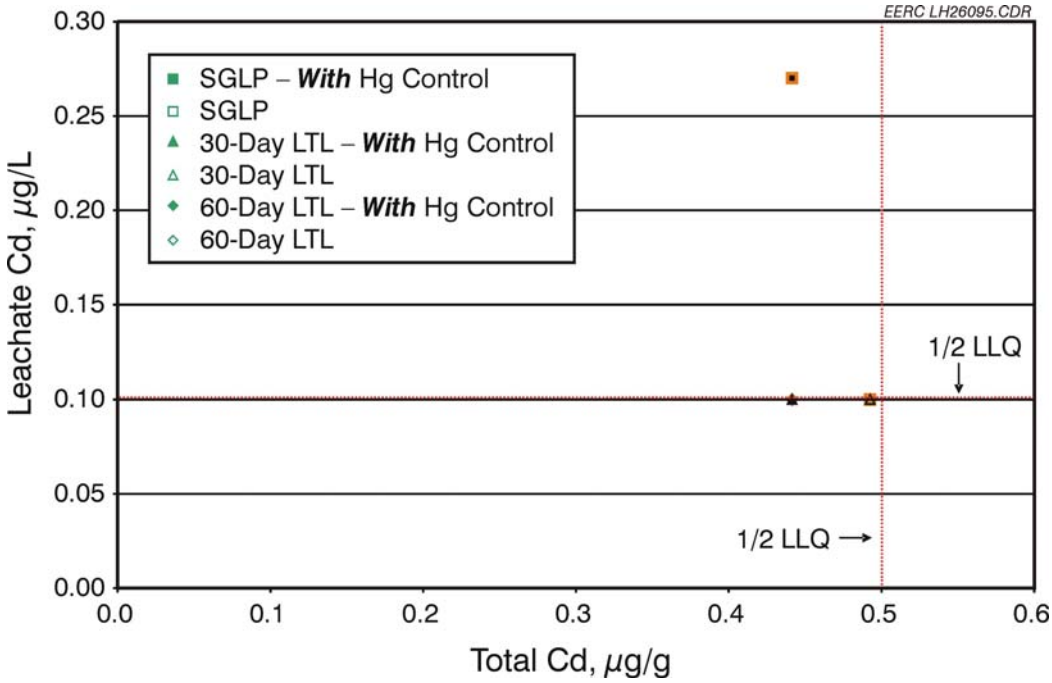

Figure C-6. Total cadmium vs. short- and long-term leachable cadmium: paired fly ash sample set ID Nos. 03-060 and 03-061.

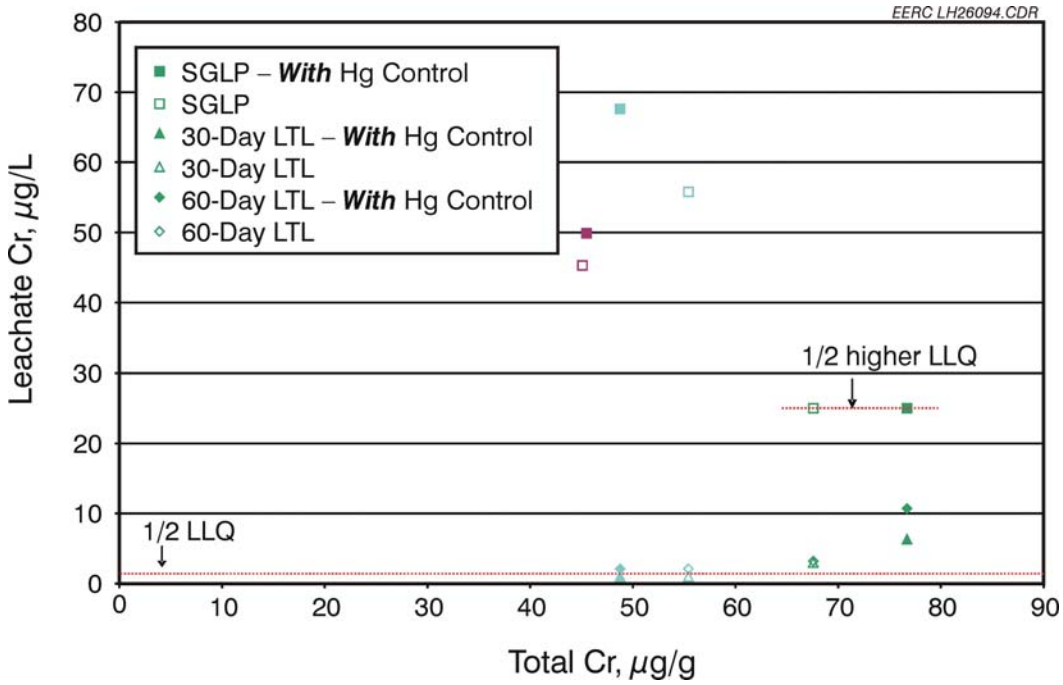

Figure C-7. Total chromium vs. short- and long-term leachable chromium: all available paired fly ash samples. One paired sample set had a leachable chromium LLQ higher than the reported values of other samples.

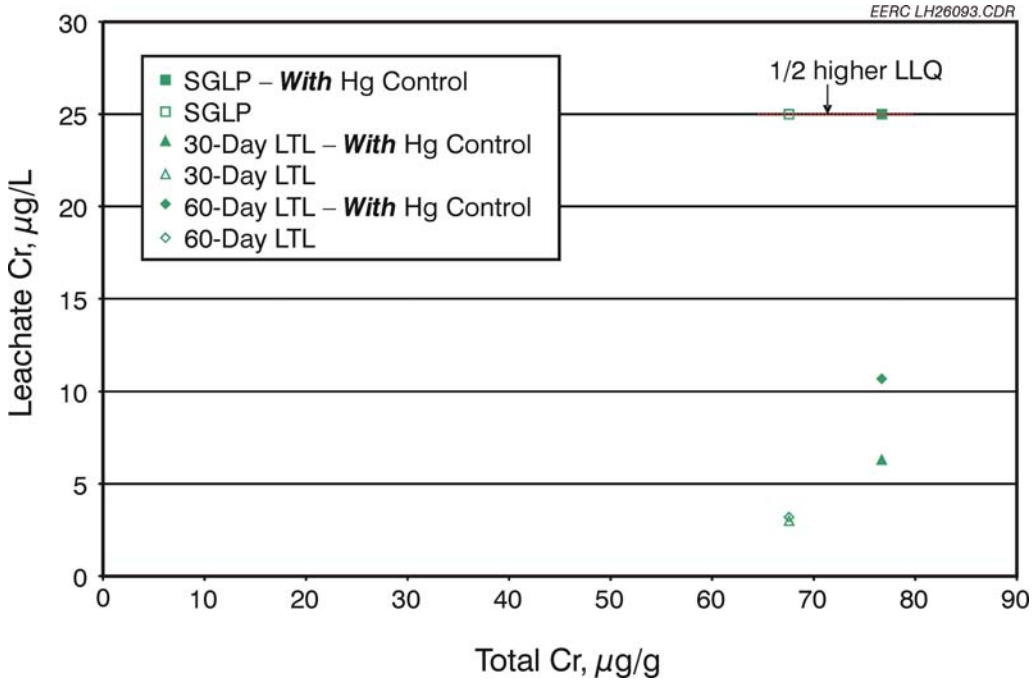

Figure C-8. Total chromium vs. short- and long-term leachable chromium: paired fly ash sample set ID Nos. 03-060 and 03-061. The SGLP leachable chromium LLQ was higher than the reported values of the long-term leachates.

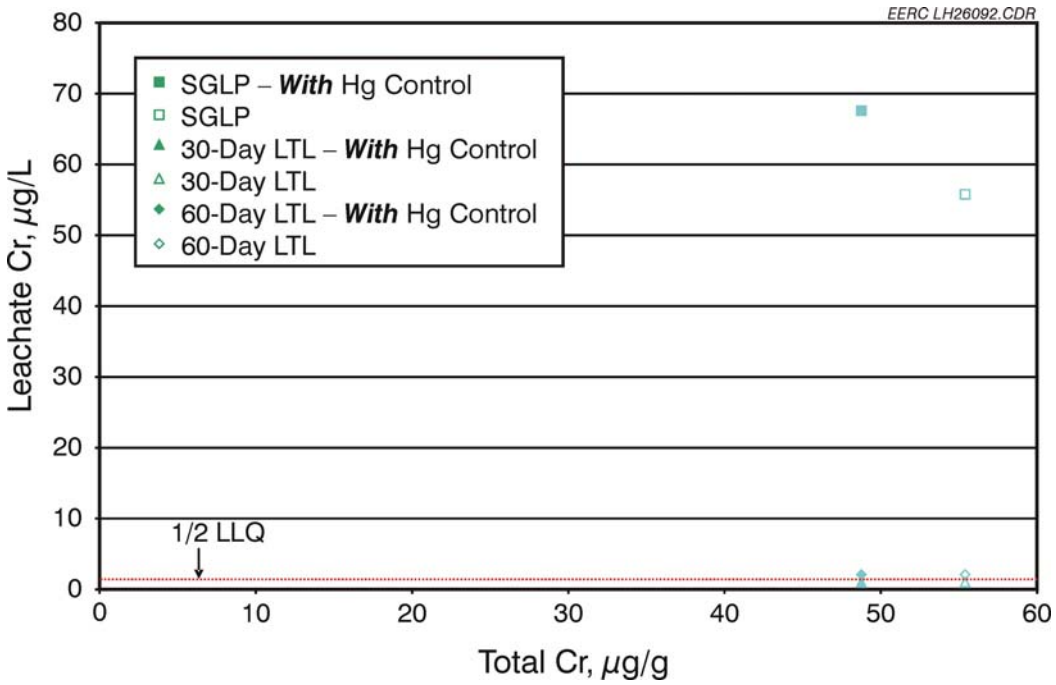

Figure C-9. Total chromium vs. short- and long-term leachable chromium: paired fly ash sample set ID Nos. 04-035 and 04-036.

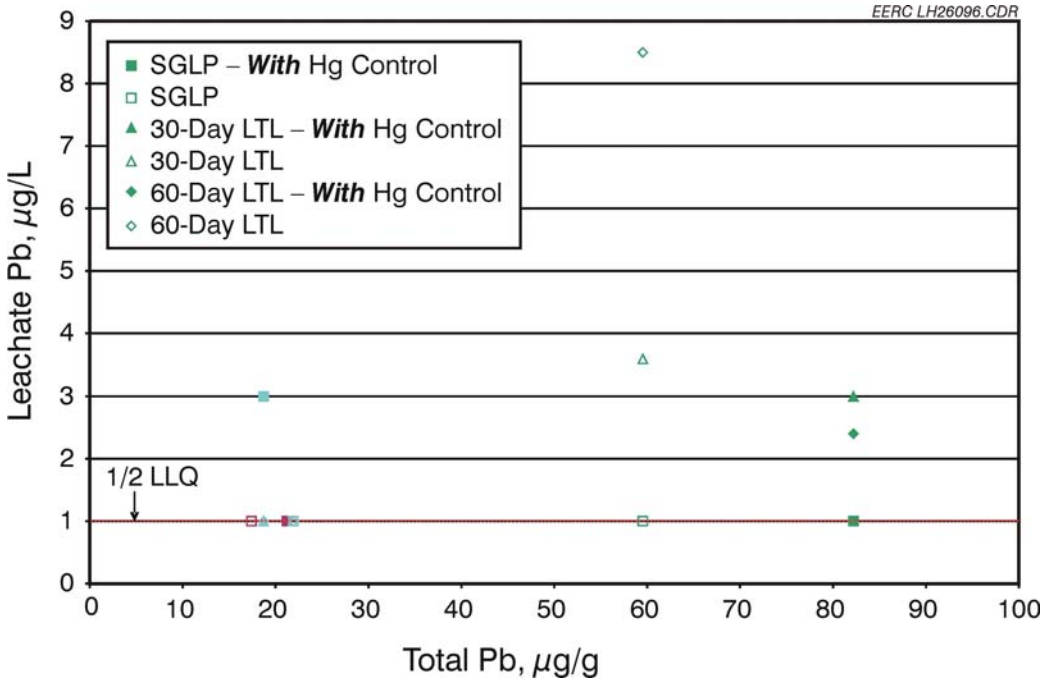

Figure C-10. Total lead vs. short- and long-term leachable lead: all available paired fly ash samples.

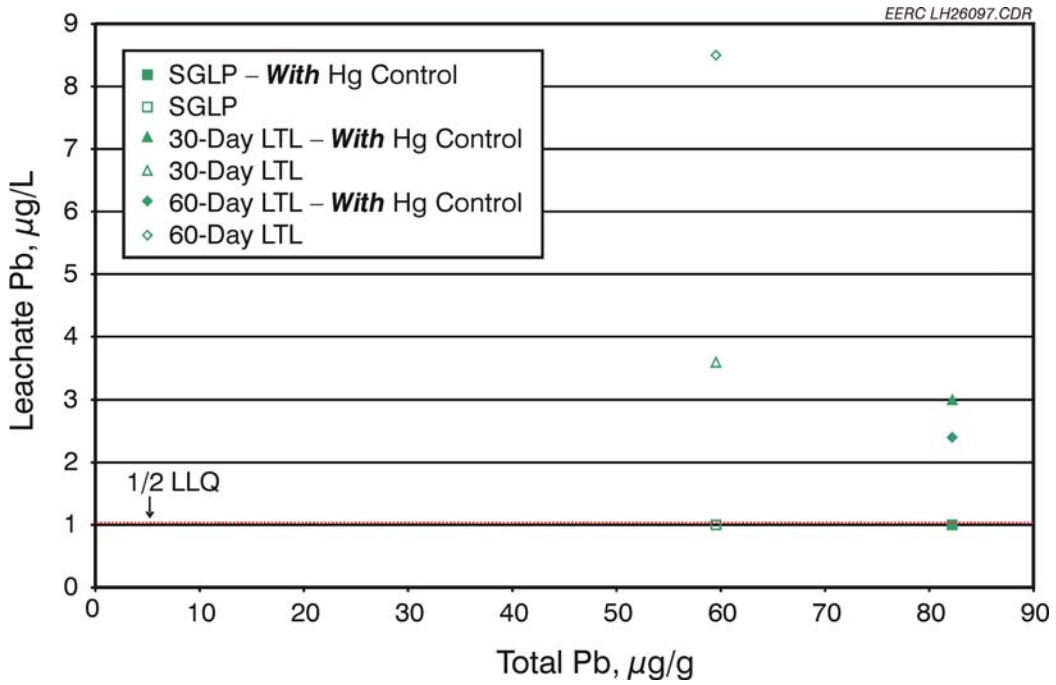

Figure C-11. Total lead vs. short- and long-term leachable lead: paired fly ash sample set ID Nos. 03-060 and 03-061.

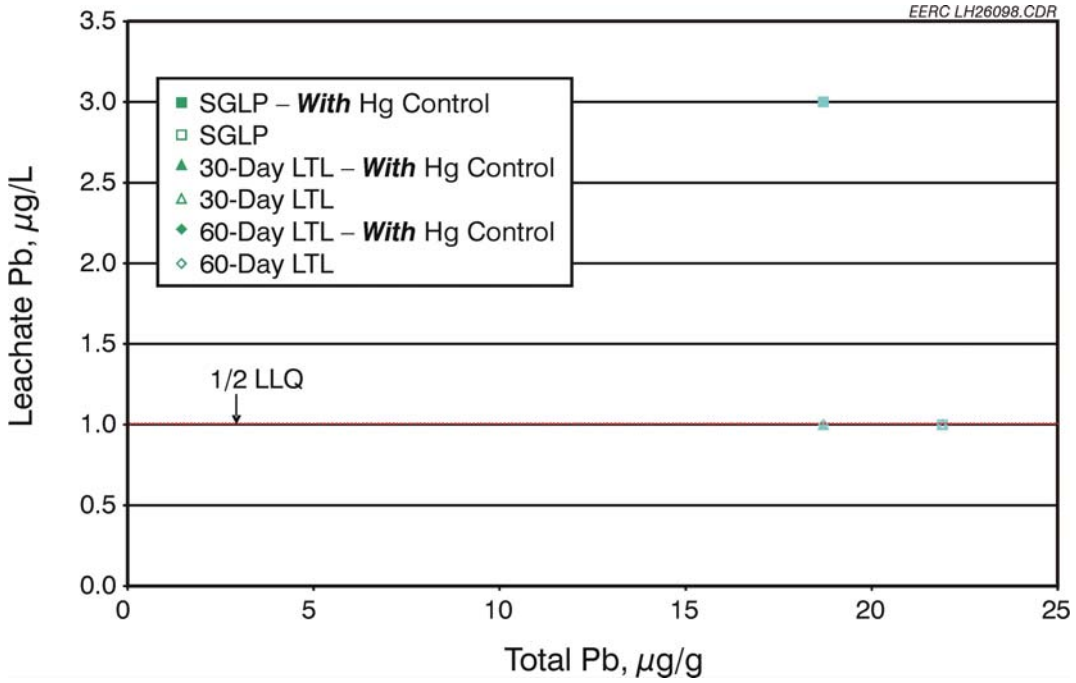

Figure C-12. Total lead vs. short- and long-term leachable lead: paired fly ash sample set ID Nos. 04-035 and 04-036.

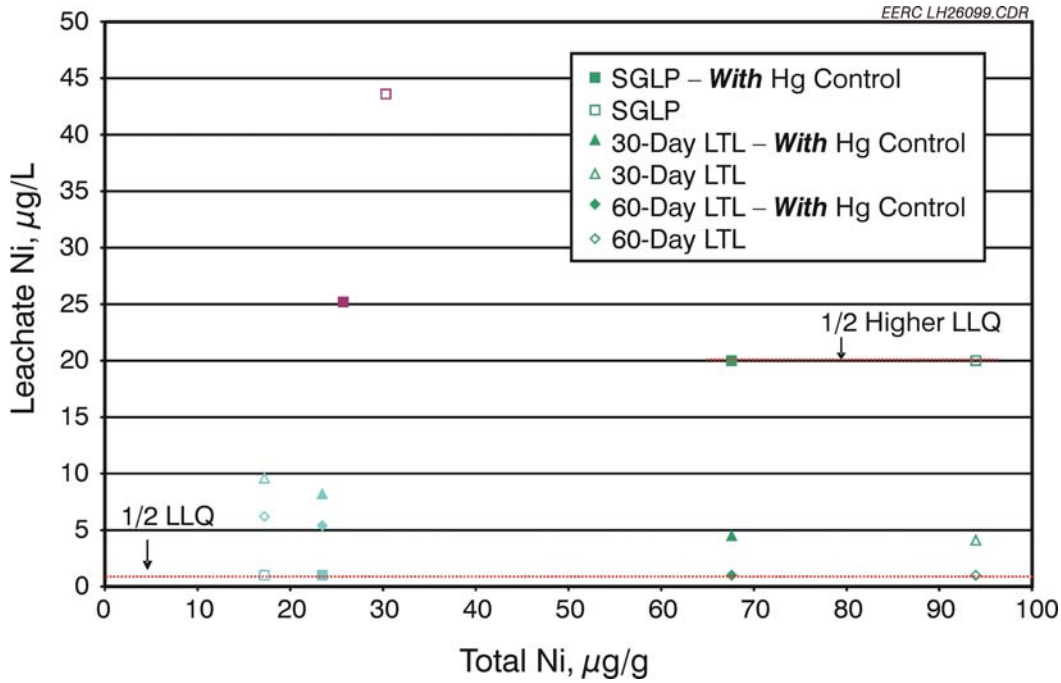

Figure C-13. Total nickel vs. short- and long-term leachable nickel: all available paired fly ash samples. One paired sample set had a leachable nickel LLQ higher than the reported values of other samples.

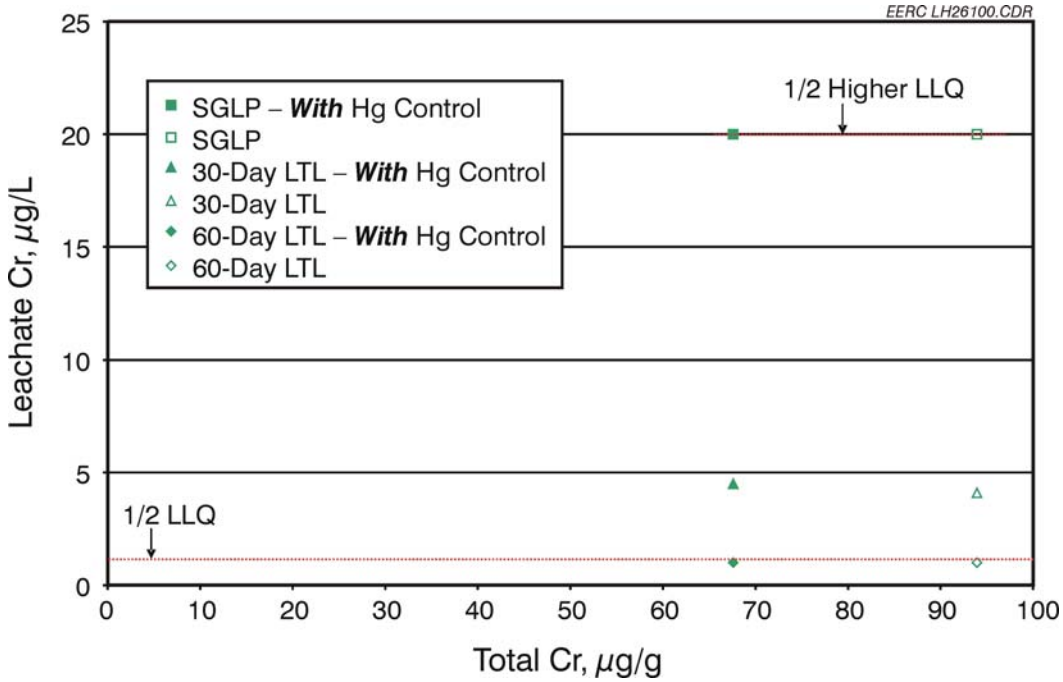

Figure C-14. Total nickel vs. short- and long-term leachable nickel: paired fly ash sample set ID Nos. 03-060 and 03-061. The SGLP leachable nickel LLQ was higher than the reported values of the long-term leachates.

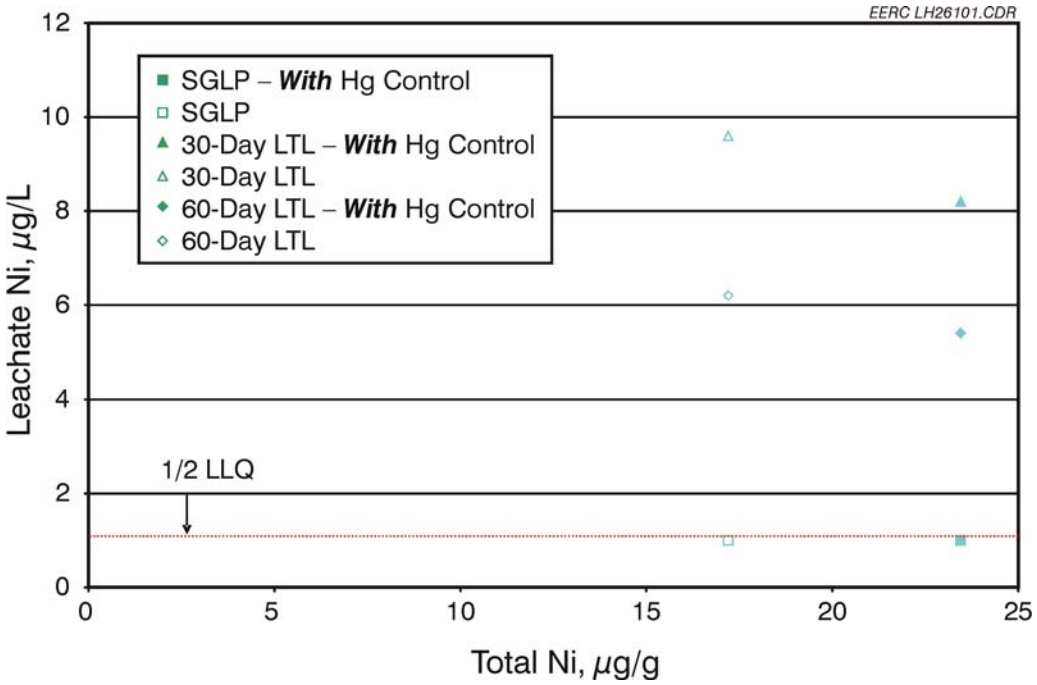

Figure C-15. Total nickel vs. short- and long-term leachable nickel: paired fly ash sample set ID Nos. 04-035 and 04-036.

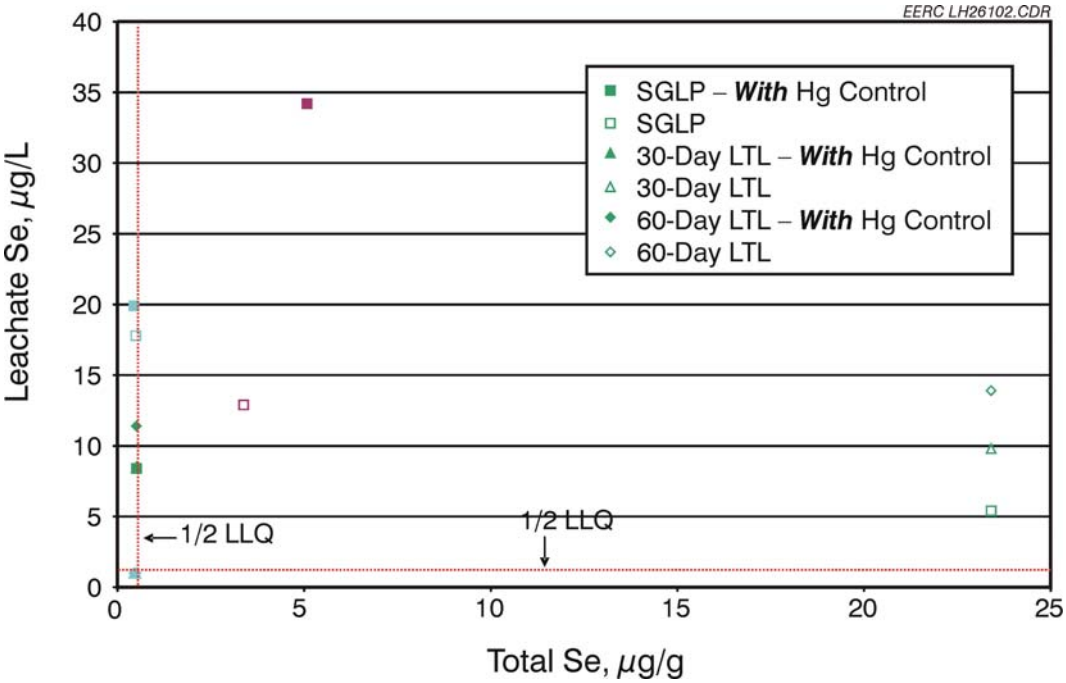

Figure C-16. Total selenium vs. short- and long-term leachable selenium: all available paired fly ash samples.

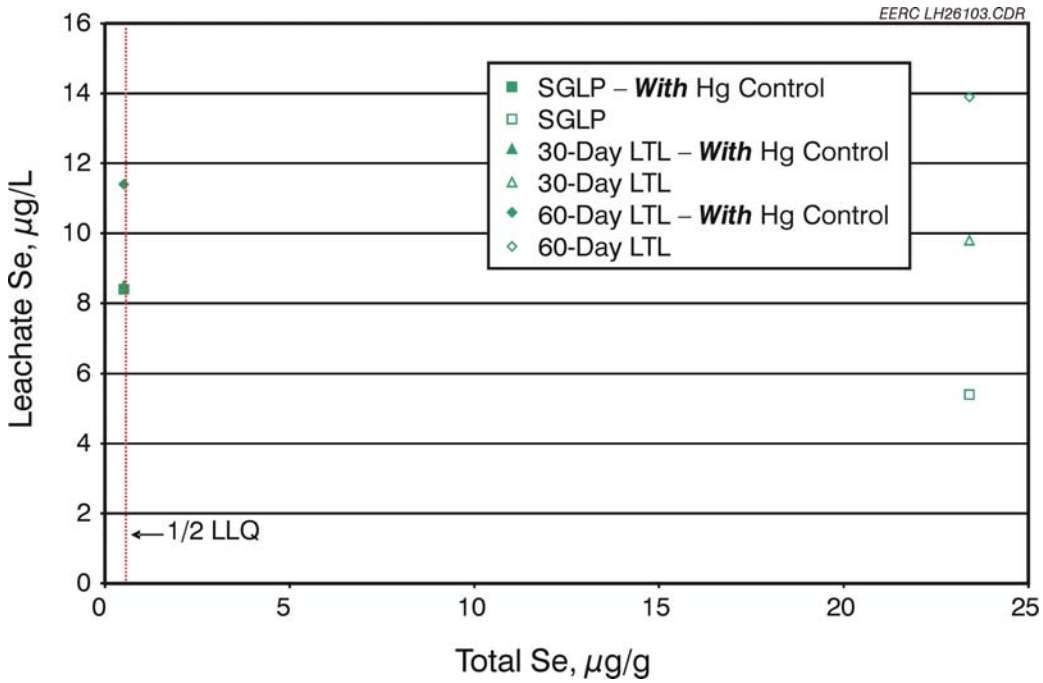

Figure C-17. Total selenium vs. short- and long-term leachable selenium: paired fly ash sample set ID Nos. 03-060 and 03-061.

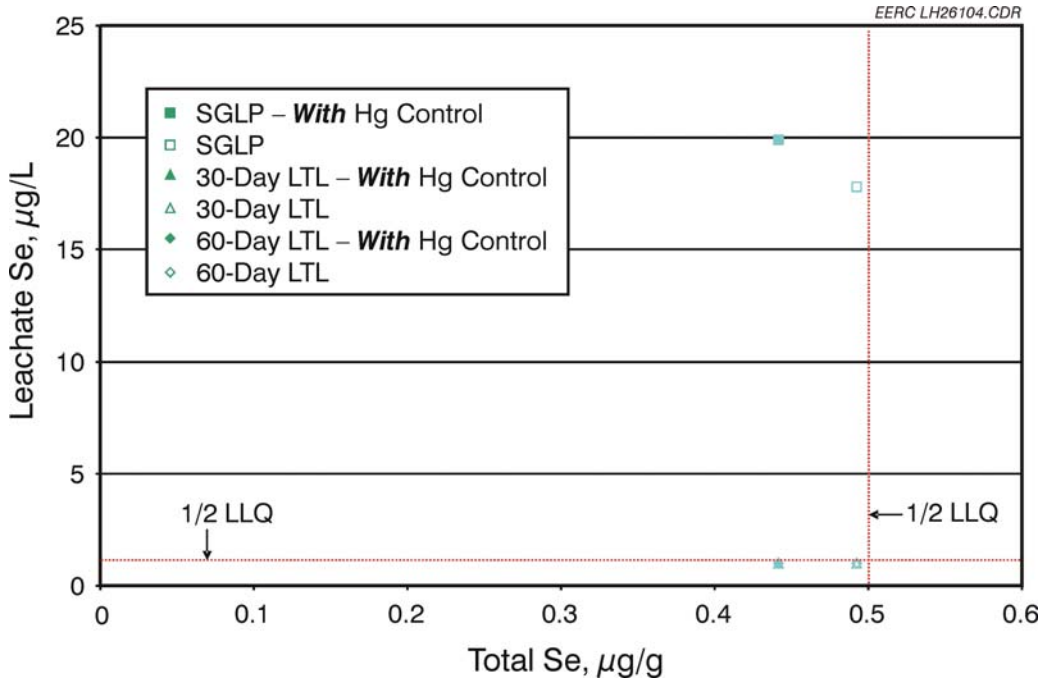

Figure C-18. Total selenium vs. short- and long-term leachable selenium: paired fly ash sample set ID Nos. 04-035 and 04-036

APPENDIX O

SUMMARY OF LONG-TERM AMBIENT-TEMPERATURE RELEASE DATA

ID No.	Replicate	Batch	Testing Period	No. Days in Testing Period	Total Hg on CCB (µg/g)	% Hg on CCB Released Over Testing Period	Years to Release 100% Hg on CCB at Measured Rate	Sorption or Release over Testing Period	Experiment Duration, Days	Cumulative % Hg on CCB Sorption or Release over Experiment	Years to Release 100% Hg on CCB at Measured Rate	Sorption or Release over Experiment
99-188	1	1	1	8	0.112	0%	NA	No sorption or release				
99-188	1	1	2	91	0.112	0%	NA	No sorption or release				
99-188	1	1	3	95	0.112	0.0000026%	9,864,357	Release	194	0.0000026%	20,144,056	Release
99-188	2	1	1	8	0.112	-0.0000281%	-77,875	Sorption				
99-188	2	1	2	91	0.112	-0.000300%	-83,232	Sorption				
99-188	2	1	3	95	0.112	-0.000329%	-79,095	Sorption	194	-0.000657%	-80,930	Sorption
99-456	1	1	1	8	1.39	-0.0000010%	-2,189,765	Sorption				
99-456	1	1	2	91	1.39	-0.0000106%	-2,361,255	Sorption				
99-456	1	1	3	95	1.39	-0.0000118%	-2,212,209	Sorption	194	-0.0000233%	-2,278,715	Sorption
99-456	2	1	1	8	1.39	-0.0000005%	-4,568,890	Sorption				
99-456	2	1	2	91	1.39	-0.0000049%	-5,046,768	Sorption				
99-456	2	1	3	95	1.39	-0.0000055%	-4,751,898	Sorption	194	-0.0000109%	-4,877,518	Sorption
00-048	1	1	1	8	0.361	-0.0000031%	-717,111	Sorption				
00-048	1	1	2	91	0.361	-0.0000293%	-850,697	Sorption				
00-048	1	1	3	95	0.361	-0.0000350%	-743,129	Sorption	194	-0.0000674%	-788,731	Sorption
00-048	2	1	1	8	0.361	0%	NA	No sorption or release				
00-048	2	1	2	91	0.361	0%	NA	No sorption or release				
00-048	2	1	3	95	0.361	0.0000018%	14,313,423	Release	194	0.0000018%	29,229,517	Release
01-002	1	1	1	8	0.187	-0.0000026%	-853,552	Sorption				
01-002	1	1	2	91	0.187	-0.0000613%	-406,857	Sorption				
01-002	1	1	3	95	0.187	-0.0000887%	-293,589	Sorption	194	-0.000152%	-348,532	Sorption
01-002	2	1	1	8	0.187	-0.0000069%	-319,622	Sorption				
01-002	2	1	2	91	0.187	-0.0000742%	-335,780	Sorption				
01-002	2	1	3	95	0.187	-0.0000762%	-341,639	Sorption	194	-0.000157%	-337,914	Sorption
01-008	1	1	1	8	1.22	0%	NA	No sorption or release				
01-008	1	1	2	91	1.22	0.0000020%	12,496,097	Release				
01-008	1	1	3	95	1.22	0.0000017%	15,517,310	Release	194	0.0000037%	14,472,785	Release
01-008	2	1	1	8	1.22	0%	NA	No sorption or release				
01-008	2	1	2	91	1.22	0%	NA	No sorption or release				
01-008	2	1	3	95	1.22	0%	NA	No sorption or release	194	0%	NA	No sorption or release
01-011	1	1	1	8	2.55	0%	NA	No sorption or release				
01-011	1	1	2	91	2.55	0.0000005%	53,747,404	Release				
01-011	1	1	3	95	2.55	0.0000002%	146,657,695	Release	194	0.0000006%	82,875,125	Release
01-011	2	1	1	8	2.55	0%	NA	No sorption or release				
01-011	2	1	2	91	2.55	0.0000005%	47,851,501	Release				
01-011	2	1	3	95	2.55	0.0000003%	100,452,715	Release	194	0.0000008%	68,131,501	Release
03-006	1	1	1	8	0.194	-0.0000047%	-468,182	Sorption				
03-006	1	1	2	91	0.194	-0.0000533%	-468,182	Sorption				
03-006	1	1	3	95	0.194	-0.0000520%	-500,495	Sorption	194	-0.000110%	-483,467	Sorption
03-006	2	1	1	8	0.194	-0.0000038%	-572,612	Sorption				
03-006	2	1	2	91	0.194	-0.0000382%	-652,696	Sorption				
03-006	2	1	3	95	0.194	-0.0000425%	-612,832	Sorption	194	-0.0000845%	-629,031	Sorption
03-017	1	1	1	8	0.225	0%	NA	No sorption or release				

ID No.	Replicate	Batch	Testing Period	No. Days in Testing Period	Total Hg on CCB (µg/g)	% Hg on CCB Released Over Testing Period	Years to Release 100% Hg on CCB at Measured Rate	Sorption or Release over Testing Period	Experiment Duration, Days	Cumulative % Hg on CCB Sorption or Release over Experiment	Years to Release 100% Hg on CCB at Measured Rate	Sorption or Release over Experiment
03-017	1	1	2	91	0.225	0.0000029%	8,554,255	Release				
03-017	1	1	3	95	0.225	0.0000016%	16,430,687	Release	194	0.0000045%	11,814,972	Release
03-017	2	1	1	8	0.225	-0.0000041%	-532,956	Sorption				
03-017	2	1	2	91	0.225	-0.0000447%	-557,211	Sorption				
03-017	2	1	3	95	0.225	-0.0000477%	-545,382	Sorption	194	-0.0000966%	-550,333	Sorption
03-018	1	1	1	8	0.289	0%	NA	No sorption or release				
03-018	1	1	2	91	0.289	0.0000032%	7,890,762	Release				
03-018	1	1	3	95	0.289	0.0000018%	14,840,697	Release	194	0.0000049%	10,817,569	Release
03-018	2	1	1	8	0.289	-0.0000051%	-427,244	Sorption				
03-018	2	1	2	91	0.289	-0.0000565%	-440,887	Sorption				
03-018	2	1	3	95	0.289	-0.0000602%	-432,098	Sorption	194	-0.000122%	-435,970	Sorption
03-060	1	1	1	8	1.86	0%	NA	No sorption or release				
03-060	1	1	2	91	1.86	0.0000006%	44,570,210	Release				
03-060	1	1	3	95	1.86	0.0000002%	170,208,032	Release	194	0.0000007%	74,619,320	Release
03-060	2	1	1	8	1.86	0%	NA	No sorption or release				
03-060	2	1	2	91	1.86	0.0000012%	20,994,849	Release				
03-060	2	1	3	95	1.86	0.0000009%	29,253,023	Release	194	0.0000021%	25,587,175	Release
03-061	1	1	1	8	0.578	0.0000040%	550,923	Release				
03-061	1	1	2	91	0.578	0.0000023%	10,729,242	Release				
03-061	1	1	3	95	0.578	0.0000013%	19,586,941	Release	194	0.0000076%	6,965,200	Release
03-061	2	1	1	8	0.578	-0.0000000428%	-51,176,729	Sorption				
03-061	2	1	2	91	0.578	-0.0000165%	-1,506,482	Sorption				
03-061	2	1	3	95	0.578	-0.0000164%	-1,590,529	Sorption	194	-0.0000330%	-1,612,762	Sorption
03-062	1	1	1	8	0.490	0%	NA	No sorption or release				
03-062	1	1	2	91	0.490	0.0000026%	9,609,441	Release				
03-062	1	1	3	95	0.490	0.0000005%	52,785,429	Release	194	0.0000031%	17,214,465	Release
03-062	2	1	1	8	0.490	0%	NA	No sorption or release				
03-062	2	1	2	91	0.490	0%	NA	No sorption or release				
03-062	2	1	3	95	0.490	0.0000004%	58,592,405	Release	194	0.0000004%	119,651,861	Release
03-065	1	3	1	7	0.044	0.000137%	13,985	Release				
03-065	1	3	2	90	0.044	0.00209%	11,794	Release				
03-065	1	3	3	90	0.044	0.00229%	10,788	Release				
03-065	1	3	4	44	0.044	0.00185%	6,509	Release				
03-065	1	3	5	46	0.044	0.000751%	16,778	Release				
03-065	1	3	6	48	0.044	0.000318%	41,353	Release				
03-065	1	3	7	43	0.044	0.000420%	28,059	Release				
03-065	1	3	8	58	0.044	-0.000149%	-106,573	Sorption				
03-065	1	3	9	47	0.044	-0.000142%	-90,856	Sorption	473	0.00756%	17,133	Release
03-065	2	3	1	7	0.044	0.000189%	10,142	Release				
03-065	2	3	2	90	0.044	0.000875%	28,181	Release				
03-065	2	3	3	90	0.044	0.00388%	6,350	Release				
03-065	2	3	4	44	0.044	0.00421%	2,863	Release				
03-065	2	3	5	46	0.044	0.00108%	11,624	Release				

ID No.	Replicate	Batch	Testing Period	No. Days in Testing Period	Total Hg on CCB (µg/g)	% Hg on CCB Released Over Testing Period	Years to Release 100% Hg on CCB at Measured Rate	Sorption or Release over Testing Period	Experiment Duration, Days	Cumulative % Hg on CCB Sorption or Release over Experiment	Years to Release 100% Hg on CCB at Measured Rate	Sorption or Release over Experiment
03-065	2	3	6	48	0.044	0.000229%	57,433	Release				
03-065	2	3	7	43	0.044	0.000310%	37,981	Release				
03-065	2	3	8	58	0.044	0.000341%	46,556	Release				
03-065	2	3	9	47	0.044	-0.0000260%	-494,826	Sorption	473	0.0111%	11,678	Release
03-082	1	2	1	7	0.248	0.000773%	2,480	Release				
03-082	1	2	2	44	0.248	0.0324%	372	Release				
03-082	1	2	3	46	0.248	0.0251%	501	Release				
03-082	1	2	4	46	0.248	0.0428%	294	Release				
03-082	1	2	5	45	0.248	0.0660%	187	Release				
03-082	1	2	6	58	0.248	0.0577%	275	Release				
03-082	1	2	7	33	0.248	0.0218%	415	Release				
03-082	1	2	8	45	0.248	0.0286%	431	Release				
03-082	1	2	9	47	0.248	0.0272%	473	Release				
03-082	1	2	10	43	0.248	0.0291%	405	Release				
03-082	1	2	11	44	0.248	0.0322%	375	Release				
03-082	1	2	12	46	0.248	0.0435%	290	Release				
03-082	1	2	13	45	0.248	0.0454%	272	Release				
03-082	1	2	14	45	0.248	0.0368%	335	Release				
03-082	1	2	15	59	0.248	0.0673%	240	Release				
03-082	1	2	16	46	0.248	0.0519%	243	Release	699	0.609%	315	Release
03-082	2	2	1	7	0.248	0.0000172%	111,680	Release				
03-082	2	2	2	44	0.248	0.00525%	2,297	Release				
03-082	2	2	3	46	0.248	0.00596%	2,115	Release				
03-082	2	2	4	46	0.248	0.0133%	948	Release				
03-082	2	2	5	45	0.248	0.0323%	381	Release				
03-082	2	2	6	58	0.248	0.0388%	409	Release				
03-082	2	2	7	33	0.248	0.0111%	818	Release				
03-082	2	2	8	45	0.248	0.0175%	705	Release				
03-082	2	2	9	47	0.248	0.0186%	694	Release				
03-082	2	2	10	43	0.248	0.0205%	576	Release				
03-082	2	2	11	44	0.248	0.0199%	605	Release				
03-082	2	2	12	46	0.248	0.0284%	443	Release				
03-082	2	2	13	45	0.248	0.0367%	336	Release				
03-082	2	2	14	45	0.248	0.0285%	432	Release				
03-082	2	2	15	59	0.248	0.0496%	326	Release				
03-082	2	2	16	46	0.248	0.121%	104	Release	699	0.448%	428	Release
03-082	3	3	1	7	0.248	0.0000234%	81,978	Release				
03-082	3	3	2	45	0.248	0.0170%	725	Release				
03-082	3	3	3	45	0.248	0.0380%	324	Release				
03-082	3	3	4	47	0.248	0.0489%	263	Release				
03-082	3	3	5	43	0.248	0.0562%	209	Release				
03-082	3	3	6	44	0.248	0.0511%	236	Release				
03-082	3	3	7	46	0.248	0.0766%	165	Release				

ID No.	Replicate	Batch	Testing Period	No. Days in Testing Period	Total Hg on CCB (µg/g)	% Hg on CCB Released Over Testing Period	Years to Release 100% Hg on CCB at Measured Rate	Sorption or Release over Testing Period	Experiment Duration, Days	Cumulative % Hg on CCB Sorption or Release over Experiment	Years to Release 100% Hg on CCB at Measured Rate	Sorption or Release over Experiment
03-082	3	3	8	45	0.248	0.0815%	151	Release				
03-082	3	3	9	45	0.248	0.0643%	192	Release				
03-082	3	3	10	59	0.248	0.375%	43.1	Release				
03-082	3	3	11	46	0.248	0.264%	47.7	Release	472	1.07%	120	Release
03-082	4	3	1	7	0.248	0.000759%	2,527	Release				
03-082	4	3	2	45	0.248	0.0426%	289	Release				
03-082	4	3	3	45	0.248	0.0436%	283	Release				
03-082	4	3	4	47	0.248	0.0436%	295	Release				
03-082	4	3	5	43	0.248	0.0481%	245	Release				
03-082	4	3	6	44	0.248	0.0493%	245	Release				
03-082	4	3	7	46	0.248	0.0661%	191	Release				
03-082	4	3	8	45	0.248	0.0798%	154	Release				
03-082	4	3	9	45	0.248	0.0643%	192	Release				
03-082	4	3	10	59	0.248	0.227%	71.2	Release				
03-082	4	3	11	46	0.248	0.202%	62.4	Release	472	0.867%	149	Release
03-082	5	3	1	7	0.248	0.000666%	2,878	Release				
03-082	5	3	2	45	0.248	0.0751%	164	Release				
03-082	5	3	3	45	0.248	0.0485%	254	Release				
03-082	5	3	4	47	0.248	0.0492%	262	Release				
03-082	5	3	5	43	0.248	0.0675%	175	Release				
03-082	5	3	6	44	0.248	0.0654%	184	Release				
03-082	5	3	7	46	0.248	0.103%	122	Release				
03-082	5	3	8	45	0.248	0.138%	89.5	Release				
03-082	5	3	9	45	0.248	0.0947%	130	Release				
03-082	5	3	10	63	0.248	0.217%	79.4	Release				
03-082	5	3	11	46	0.248	0.00652%	1,932	Release	476	0.866%	151	Release
03-082	6	3	1	7	0.248	0.0000897%	21,385	Release				
03-082	6	3	2	45	0.248	0.0685%	180	Release				
03-082	6	3	3	45	0.248	0.0618%	200	Release				
03-082	6	3	4	47	0.248	0.0397%	324	Release				
03-082	6	3	5	43	0.248	0.0625%	188	Release				
03-082	6	3	6	44	0.248	0.0621%	194	Release				
03-082	6	3	7	46	0.248	0.109%	115	Release				
03-082	6	3	8	45	0.248	0.131%	94.0	Release				
03-082	6	3	9	45	0.248	0.116%	106	Release				
03-082	6	3	10	63	0.248	0.310%	55.7	Release				
03-082	6	3	11	46	0.248	0.00210%	5,989	Release	476	0.963%	135	Release
04-006	1	2	1	7	0.144	-0.0000048%	-396,725	Sorption				
04-006	1	2	2	90	0.144	-0.0000622%	-396,725	Sorption				
04-006	1	2	3	91	0.144	-0.0000587%	-424,930	Sorption	188	-0.000126%	-409,894	Sorption
04-006	2	2	1	7	0.144	-0.0000089%	-214,953	Sorption				
04-006	2	2	2	90	0.144	-0.000113%	-219,087	Sorption				
04-006	2	2	3	91	0.144	-0.000114%	-218,809	Sorption	188	-0.000235%	-218,795	Sorption

ID No.	Replicate	Batch	Testing Period	No. Days in Testing Period	Total Hg on CCB (µg/g)	% Hg on CCB Released Over Testing Period	Years to Release 100% Hg on CCB at Measured Rate	Sorption or Release over Testing Period	Experiment Duration, Days	Cumulative % Hg on CCB Sorption or Release over Experiment	Years to Release 100% Hg on CCB at Measured Rate	Sorption or Release over Experiment
04-007	1	2	1	7	0.521	-0.0000020%	-958,159	Sorption				
04-007	1	2	2	90	0.521	-0.0000329%	-749,092	Sorption				
04-007	1	2	3	91	0.521	-0.0000336%	-742,965	Sorption	188	-0.0000685%	-752,201	Sorption
04-007	2	2	1	7	0.521	-0.0000007%	-2,748,990	Sorption				
04-007	2	2	2	90	0.521	-0.0000080%	-3,093,527	Sorption				
04-007	2	2	3	91	0.521	-0.0000081%	-3,079,637	Sorption	188	-0.0000168%	-3,072,481	Sorption
04-029	1	3	1	7	0.261	-0.0000006%	-3,115,851	Sorption				
04-029	1	3	2	90	0.261	-0.0000160%	-1,542,848	Sorption				
04-029	1	3	3	90	0.261	-0.0000138%	-1,782,759	Sorption	187	-0.0000304%	-1,683,717	Sorption
04-029	2	3	1	7	0.261	0.0000001%	33,539,583	Release				
04-029	2	3	2	90	0.261	-0.0000178%	-1,382,399	Sorption				
04-029	2	3	3	90	0.261	-0.0000155%	-1,590,153	Sorption	187	-0.0000333%	-1,539,173	Sorption
04-035	1	2	1	7	0.159	-0.0000026%	-750,237	Sorption				
04-035	1	2	2	90	0.159	-0.0000307%	-804,038	Sorption				
04-035	1	2	3	91	0.159	-0.0000313%	-795,294	Sorption	188	-0.0000646%	-797,663	Sorption
04-035	2	2	1	7	0.159	-0.0000030%	-630,077	Sorption				
04-035	2	2	2	90	0.159	-0.0000359%	-687,312	Sorption				
04-035	2	2	3	91	0.159	-0.0000374%	-667,237	Sorption	188	-0.0000763%	-675,195	Sorption
04-036	1	2	1	7	0.287	-0.0000005%	-3,523,638	Sorption				
04-036	1	2	2	90	0.287	-0.0000189%	-1,301,931	Sorption				
04-036	1	2	3	91	0.287	-0.0000197%	-1,262,661	Sorption	188	-0.0000392%	-1,312,989	Sorption
04-036	2	2	1	7	0.287	-0.0000017%	-1,120,108	Sorption				
04-036	2	2	2	90	0.287	-0.0000205%	-1,205,697	Sorption				
04-036	2	2	3	91	0.287	-0.0000212%	-1,176,251	Sorption	188	-0.0000434%	-1,187,922	Sorption
04-044	1	3	1	7	0.878	-0.0000010%	-1,912,355	Sorption				
04-044	1	3	2	90	0.878	-0.0000123%	-2,012,058	Sorption				
04-044	1	3	3	90	0.878	-0.0000113%	-2,188,197	Sorption	187	-0.0000245%	-2,088,908	Sorption
04-044	2	3	1	7	0.878	-0.0000003%	-5,752,628	Sorption				
04-044	2	3	2	90	0.878	-0.0000067%	-3,663,105	Sorption				
04-044	2	3	3	90	0.878	-0.0000059%	-4,205,365	Sorption	187	-0.0000129%	-3,962,923	Sorption
04-054	1	2	1	7	17.7	0.0000000%	-745,762,297	Sorption				
04-054	1	2	2	90	17.7	-0.0000004%	-60,558,141	Sorption				
04-054	1	2	3	91	17.7	-0.0000004%	-60,699,677	Sorption	188	-0.0000008%	-62,776,621	Sorption
04-054	2	2	1	7	17.7	0.0000000%	-1,390,309,949	Sorption				
04-054	2	2	2	90	17.7	-0.0000006%	-42,001,853	Sorption				
04-054	2	2	3	91	17.7	-0.0000006%	-39,302,048	Sorption	188	-0.0000012%	-42,122,262	Sorption
04-067	1	2	1	7	0.640	-0.0000010%	-2,018,590	Sorption				
04-067	1	2	2	90	0.640	-0.0000117%	-2,114,844	Sorption				
04-067	1	2	3	91	0.640	-0.0000120%	-2,077,249	Sorption	188	-0.0000246%	-2,092,795	Sorption
04-067	2	2	1	7	0.640	-0.0000011%	-1,805,535	Sorption				
04-067	2	2	2	90	0.640	-0.0000137%	-1,805,535	Sorption				
04-067	2	2	3	91	0.640	-0.0000132%	-1,882,177	Sorption	188	-0.0000280%	-1,841,838	Sorption
04-082	1	4	1	7	0.043	0.161%	11.9	Release				

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04-082	1	4	2	7	0.043	0.431%	4.45	Release				
04-082	1	4	3	7	0.043	0.572%	3.35	Release				
04-082	1	4	4	5	0.043	0.430%	3.18	Release				
04-082	1	4	5	7	0.043	0.684%	2.81	Release				
04-082	1	4	6	3	0.043	0.304%	2.71	Release				
04-082	1	4	7	5	0.043	0.500%	2.74	Release				
04-082	1	4	8	5	0.043	0.502%	2.73	Release				
04-082	1	4	9	4	0.043	0.288%	3.80	Release				
04-082	1	4	10	5	0.043	0.487%	2.81	Release				
04-082	1	4	11	5	0.043	0.497%	2.75	Release				
04-082	1	4	12	4	0.043	0.370%	2.96	Release				
04-082	1	4	13	5	0.043	0.319%	4.29	Release				
04-082	1	4	14	6	0.043	0.373%	4.41	Release				
04-082	1	4	15	13	0.043	0.558%	6.38	Release				
04-082	1	4	16	7	0.043	0.146%	13.1	Release				
04-082	1	4	17	7	0.043	0.297%	6.47	Release				
04-082	1	4	18	9	0.043	0.292%	8.44	Release				
04-082	1	4	19	14	0.043	0.299%	12.8	Release				
04-082	1	4	20	29	0.043	0.418%	19.0	Release				
04-082	1	4	21	46	0.043	0.486%	25.9	Release	200	8.41%	6.51	Release
04-082	2	4	1	7	0.043	0.183%	10.5	Release				
04-082	2	4	2	7	0.043	0.419%	4.58	Release				
04-082	2	4	3	7	0.043	0.593%	3.23	Release				
04-082	2	4	4	5	0.043	0.446%	3.07	Release				
04-082	2	4	5	7	0.043	0.694%	2.76	Release				
04-082	2	4	6	3	0.043	0.314%	2.62	Release				
04-082	2	4	7	5	0.043	0.536%	2.55	Release				
04-082	2	4	8	5	0.043	0.494%	2.78	Release				
04-082	2	4	9	4	0.043	0.300%	3.65	Release				
04-082	2	4	10	5	0.043	0.493%	2.78	Release				
04-082	2	4	11	5	0.043	0.510%	2.69	Release				
04-082	2	4	12	4	0.043	0.377%	2.91	Release				
04-082	2	4	13	5	0.043	0.321%	4.26	Release				
04-082	2	4	14	6	0.043	0.349%	4.71	Release				
04-082	2	4	15	13	0.043	0.550%	6.48	Release				
04-082	2	4	16	7	0.043	0.140%	13.7	Release				
04-082	2	4	17	7	0.043	0.288%	6.65	Release				
04-082	2	4	18	9	0.043	0.266%	9.29	Release				
04-082	2	4	19	14	0.043	0.294%	13.1	Release				
04-082	2	4	20	29	0.043	0.394%	20.2	Release				
04-082	2	4	21	46	0.043	0.419%	30.1	Release	200	8.38%	6.54	Release
04-083	1	4	1	7	0.103	0.00272%	706	Release				
04-083	1	4	2	43	0.103	0.0331%	356	Release				

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04-083	1	4	3	45	0.103	0.0563%	219	Release				
04-083	1	4	4	59	0.103	0.0676%	239	Release				
04-083	1	4	5	46	0.103	0.221%	56.9	Release	200	0.381%	144	Release
04-083	2	4	1	7	0.103	0.00305%	629	Release				
04-083	2	4	2	43	0.103	0.0609%	194	Release				
04-083	2	4	3	45	0.103	0.0487%	253	Release				
04-083	2	4	4	59	0.103	0.0712%	227	Release				
04-083	2	4	5	46	0.103	0.0986%	128	Release	200	0.282%	194	Release
05-001	1	3	1	7	<0.01	-0.000116%	-16,506	Sorption				
05-001	1	3	2	90	<0.01	-0.00116%	-21,251	Sorption				
05-001	1	3	3	90	<0.01	-0.00110%	-22,437	Sorption	187	-0.00238%	-21,567	Sorption
05-001	2	3	1	7	<0.01	-0.000105%	-18,212	Sorption				
05-001	2	3	2	90	<0.01	-0.00196%	-12,607	Sorption				
05-001	2	3	3	90	<0.01	-0.00186%	-13,287	Sorption	187	-0.00392%	-13,080	Sorption
05-002	1	3	1	7	<0.01	-0.000153%	-12,503	Sorption				
05-002	1	3	2	90	<0.01	-0.00275%	-8,975	Sorption				
05-002	1	3	3	90	<0.01	-0.00258%	-9,546	Sorption	187	-0.00548%	-9,343	Sorption
05-002	2	3	1	7	<0.01	0.0000577%	33,230	Release				
05-002	2	3	2	90	<0.01	-0.000685%	-35,990	Sorption				
05-002	2	3	3	90	<0.01	-0.000562%	-43,864	Sorption	187	-0.00119%	-43,069	Sorption
05-003	1	3	1	7	0.565	-0.0000007%	-2,744,055	Sorption				
05-003	1	3	2	90	0.565	-0.0000131%	-1,883,252	Sorption				
05-003	1	3	3	90	0.565	-0.0000096%	-2,578,508	Sorption	187	-0.0000234%	-2,193,689	Sorption
05-003	2	3	1	7	0.565	0.0000000%	49,463,677	Release				
05-003	2	3	2	90	0.565	-0.0000044%	-5,659,177	Sorption				
05-003	2	3	3	90	0.565	-0.0000029%	-8,416,414	Sorption	187	-0.0000072%	-7,068,541	Sorption
05-004	1	3	1	7	0.332	-0.0000018%	-1,076,757	Sorption				
05-004	1	3	2	90	0.332	-0.0000320%	-769,945	Sorption				
05-004	1	3	3	90	0.332	-0.0000272%	-904,992	Sorption	187	-0.0000611%	-839,164	Sorption
05-004	2	3	1	7	0.332	-0.0000017%	-1,151,710	Sorption				
05-004	2	3	2	90	0.332	-0.0000201%	-1,227,580	Sorption				
05-004	2	3	3	90	0.332	-0.0000192%	-1,285,465	Sorption	187	-0.0000409%	-1,251,619	Sorption
05-009	1	3	1	7	0.032	0.000863%	2,222	Release				
05-009	1	3	2	45	0.032	0.00672%	1,833	Release				
05-009	1	3	3	45	0.032	0.00202%	6,102	Release				
05-009	1	3	4	90	0.032	0.00535%	4,607	Release				
05-009	1	3	5	44	0.032	0.00817%	1,476	Release				
05-009	1	3	6	46	0.032	0.000506%	24,928	Release				
05-009	1	3	7	48	0.032	0.000169%	77,979	Release				
05-009	1	3	8	43	0.032	0.000117%	100,674	Release				
05-009	1	3	9	58	0.032	-0.000109%	-145,382	Sorption				
05-009	1	3	10	47	0.032	0.000056%	230,325	Release	473	0.0239%	5,430	Release
05-009	2	3	1	7	0.032	0.000816%	2,351	Release				

ID No.	Replicate	Batch	Testing Period	No. Days in Testing Period	Total Hg on CCB (µg/g)	% Hg on CCB Released Over Testing Period	Years to Release 100% Hg on CCB at Measured Rate	Sorption or Release over Testing Period	Experiment Duration, Days	Cumulative % Hg on CCB Sorption or Release over Experiment	Years to Release 100% Hg on CCB at Measured Rate	Sorption or Release over Experiment
05-009	2	3	2	45	0.032	0.00545%	2,263	Release				
05-009	2	3	3	45	0.032	0.00158%	7,781	Release				
05-009	2	3	4	90	0.032	0.00339%	7,265	Release				
05-009	2	3	5	44	0.032	0.00433%	2,783	Release				
05-009	2	3	6	46	0.032	0.00279%	4,524	Release				
05-009	2	3	7	48	0.032	0.000273%	48,232	Release				
05-009	2	3	8	43	0.032	0.000242%	48,780	Release				
05-009	2	3	9	58	0.032	-0.000177%	-89,646	Sorption				
05-009	2	3	10	47	0.032	0.000269%	47,862	Release	473	0.0190%	6,833	Release
05-013	1	4	1	7	39.0	0.0000001%	28,634,635	Release				
05-013	1	4	2	90	39.0	0.0000000%	894,186,303	Release				
05-013	1	4	3	90	39.0	0.0000000%	662,189,135	Release	187	0.0000001%	388,756,048	Release
05-013	2	4	1	7	39.0	0.0000000%	71,666,636	Release				
05-013	2	4	2	90	39.0	0.0000001%	289,972,871	Release				
05-013	2	4	3	90	39.0	0.0000000%	1,513,153,294	Release	187	0.0000001%	399,977,490	Release
05-023	1	4	1	7	12.7	0.0000001%	27,020,806	Release				
05-023	1	4	2	90	12.7	0.0000001%	217,423,321	Release				
05-023	1	4	3	90	12.7	0.0000001%	222,884,943	Release	187	0.0000003%	173,663,704	Release
05-023	2	4	1	7	12.7	0.0000001%	22,251,582	Release				
05-023	2	4	2	90	12.7	0.0000001%	192,511,093	Release				
05-023	2	4	3	90	12.7	0.0000002%	127,036,891	Release	187	0.0000004%	125,457,465	Release
05-024	1	4	1	7	35.9	0.0000000%	116,137,574	Release				
05-024	1	4	2	90	35.9	-0.0000001%	-320,866,834	Sorption				
05-024	1	4	3	90	35.9	0.0000000%	-736,059,867	Sorption	187	-0.0000001%	-546,002,953	Sorption
05-024	2	4	1	7	35.9	0.0000000%	97,478,007	Release				
05-024	2	4	2	90	35.9	-0.0000001%	-418,363,021	Sorption				
05-024	2	4	3	90	35.9	-0.0000001%	-460,332,617	Sorption	187	-0.0000001%	-551,909,510	Sorption
05-025	1	4	1	7	12.6	0.0000000%	-71,585,890	Sorption				
05-025	1	4	2	90	12.6	-0.0000009%	-27,276,514	Sorption				
05-025	1	4	3	90	12.6	-0.0000008%	-31,743,484	Sorption	187	-0.0000017%	-30,003,754	Sorption
05-025	2	4	1	7	12.6	0.0000000%	-86,636,216	Sorption				
05-025	2	4	2	90	12.6	-0.0000009%	-26,038,716	Sorption				
05-025	2	4	3	90	12.6	-0.0000010%	-25,362,355	Sorption	187	-0.0000019%	-26,390,978	Sorption
05-038	1	4	1	7	0.104	0.0000110%	175,125	Release				
05-038	1	4	2	90	0.104	0.0000155%	1,590,224	Release				
05-038	1	4	3	90	0.104	0.0000029%	8,600,047	Release	187	0.0000293%	1,747,138	Release
05-038	2	4	1	7	0.104	0.0000004%	4,284,755	Release				
05-038	2	4	2	90	0.104	-0.0000538%	-458,675	Sorption				
05-038	2	4	3	90	0.104	0.0000002%	117,631,310	Release	187	-0.0000531%	-964,820	Sorption
05-040	1	4	1	7	44.5	0.0000000%	592,394,110	Release				
05-040	1	4	2	90	44.5	0.0000000%	-839,331,007	Sorption				
05-040	1	4	3	90	44.5	0.0000000%	722,511,068	Release	187	0.0000000%	6,414,452,894	Release
05-040	2	4	1	7	44.5	0.0000000%	-105,422,344	Sorption				

ID No.	Replicate	Batch	Testing Period	No. Days in Testing Period	Total Hg on CCB (µg/g)	% Hg on CCB Released Over Testing Period	Years to Release 100% Hg on CCB at Measured Rate	Sorption or Release over Testing Period	Experiment Duration, Days	Cumulative % Hg on CCB Sorption or Release over Experiment	Years to Release 100% Hg on CCB at Measured Rate	Sorption or Release over Experiment
05-040	2	4	2	90	44.5	-0.0000003%	-83,152,524	Sorption				
05-040	2	4	3	90	44.5	-0.0000002%	-132,626,936	Sorption	187	-0.0000005%	-102,334,397	Sorption
06-001	1	4	1	7	64.5	0.0000000%	-207,793,209	Sorption				
06-001	1	4	2	90	64.5	-0.0000001%	-188,954,213	Sorption				
06-001	1	4	3	90	64.5	-0.0000001%	-196,211,436	Sorption	187	-0.0000003%	-193,045,902	Sorption
06-001	2	4	1	7	64.5	0.0000000%	-851,189,611	Sorption				
06-001	2	4	2	90	64.5	-0.0000002%	-135,031,899	Sorption				
06-001	2	4	3	90	64.5	-0.0000002%	-164,261,871	Sorption	187	-0.0000003%	-152,947,977	Sorption

APPENDIX P

ELEVATED-TEMPERATURE VAPOR-PHASE MERCURY MEASUREMENT FROM COAL COMBUSTION BY-PRODUCTS

ELEVATED-TEMPERATURE VAPOR-PHASE MERCURY MEASUREMENT FROM COAL COMBUSTION BY-PRODUCTS

Final Report

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ELEVATED-TEMPERATURE VAPOR-PHASE MERCURY MEASUREMENT FROM COAL COMBUSTION BY-PRODUCTS

ABSTRACT

Under an effort funded by the U.S. Department of Energy (DOE) and industry entitled "Mercury and Air Toxic Element Impacts of Coal Combustion By-Product Disposal and Utilization," the Energy & Environmental Research Center (EERC) is evaluating the impact of mercury and other air toxic elements on the management of (coal combustion by-products (CCBs). The EERC is measuring the release of mercury and other air toxic elements under different controlled laboratory conditions and investigating the release of these same air toxic elements in select field settings. One of the potential release mechanisms under investigation, and the subject of this report, is the elevated-temperature vapor-phase release of mercury from CCBs.

This report includes a summary of the method development and associated results for work performed under this project to assess the release of mercury from CCBs when exposed to elevated temperatures. The report includes descriptions of the apparatus and method developed. It also includes examples of real-time mercury release profiles generated when various fly ash and flue gas desulfurization material samples were subjected to temperatures up to 750°C. A discussion of work performed using the elevated-temperature releases to speciate mercury on the CCBs is presented. The report summarizes the various technical issues associated with performing the release experiments and data interpretation. A preliminary interpretation of the results generated is included.

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ELEVATED-TEMPERATURE VAPOR-PHASE MERCURY MEASUREMENT FROM COAL COMBUSTION BY-PRODUCTS

EXECUTIVE SUMMARY

Under an effort funded by the U.S. Department of Energy (DOE) and industry entitled "Mercury and Air Toxic Element Impacts of Coal Combustion By-Product Disposal and Utilization," the Energy & Environmental Research Center (EERC) is evaluating the impact of mercury and other air toxic elements on the management of coal combustion by-products (CCBs). The EERC is measuring the release of mercury and other air toxic elements under different controlled laboratory conditions and investigating the release of these same air toxic elements in select field settings. One of the potential release mechanisms under investigation, and the subject of this report, is the elevated-temperature vapor-phase release of mercury from CCBs.

Investigation of elevated-temperature mercury release from CCBs at the EERC began in 1999. The constructed apparatus heated an aliquot of CCB from ambient temperature to 750°C at a constant ramp rate. The mercury and mercury compounds desorbed from the CCB were carried with nitrogen to a heated analytical quartz cell operated at 800°C to thermally decompose compounds to form elemental mercury, which was detected by an atomic absorption spectrophotometer.

Early work under a DOE task showed that thermal desorption curves generated for 100% activated carbon sorbents loaded with mercury indicated a significant level of mercury desorbed from the sorbent with reproducible peaks. The curves generated under the early DOE work provided background information for this task.

A variety of CCBs were evaluated for the real-time elevated-temperature release of mercury. The CCBs were primarily fly ash but also included a limited number of flue gas desulfurization (FGD) materials. Most samples generated either one or two mercury peaks with a range of 0–4 peaks. The temperature of the primary mercury peak for fly ash samples ranged from 262° to 750°C, with an average of 468°C. Some samples actually continued to show increasing mercury release at 750°C, so the highest peak temperature at which the mercury was released could not be determined. More samples collected from mercury emission control tests continued to release mercury at 750°C than those collected under conditions without mercury emission control testing.

The use of elevated-temperature release of mercury was evaluated as a means of determining the speciation of mercury present on CCBs. Results indicated that the interaction of mercury with the CCBs at elevated temperatures may preclude speciation using this method on these complex materials.

Thermal desorption curves provided a comparative means of evaluating the elevated-temperature release of mercury from a variety of CCBs, but the method and results have not yet yielded an understanding of the mechanism of release over the temperature range evaluated.

ELEVATED-TEMPERATURE VAPOR-PHASE MERCURY MEASUREMENT FROM COAL COMBUSTION BY-PRODUCTS

INTRODUCTION

The stability of mercury associated with coal combustion by-products (CCBs) has become a prominent question as the coal-fired utility industry develops and tests mercury emission controls that may consequently increase the mercury associated with CCBs. The reasons for evaluating the release of mercury from CCBs are 1) to determine if mercury captured on CCBs is stable or if it will be released, thus negating the purpose of the removal of the mercury from the emissions, and 2) to aid utilities in determining and understanding changes in CCBs associated with mercury control and associated CCB management.

Under an effort funded by the U.S. Department of Energy (DOE) and industry entitled "Mercury and Air Toxic Element Impacts of Coal Combustion By-Product Disposal and Utilization," the Energy & Environmental Research Center (EERC) is evaluating the impact of mercury and other air toxic elements on the management of CCBs. The EERC is measuring the release of mercury and other air toxic elements under different controlled laboratory conditions and investigating the release of these same air toxic elements in select field settings. Results will be used to determine if mercury released from CCBs, both as currently produced and as produced with mercury and other emission controls in place, will impact CCB management practices.

Laboratory tasks were designed to address three primary potential release mechanisms for mercury over the life cycle of CCBs in a variety of management scenarios:

1. Direct leachability of air toxic constituents from CCBs.
2. Vapor release of mercury from CCBs at ambient and elevated temperatures.
3. Biologically mediated leachability and vapor release of mercury and other air toxic elements from CCBs.

This report focuses on the results generated from measuring mercury release at elevated temperatures. Elevated-temperature vapor-phase experiments simulated potential mercury release from high-temperature manufacturing processes such as wallboard and cement manufacturing. This report is a preliminary summary of elevated-temperature release results for the ongoing project entitled "Mercury and Air Toxic Element Impacts of Coal Combustion By-Product Disposal and Utilization."

BACKGROUND

Mercury emission controls will result in reapportioning the mercury that was previously released to the atmosphere into CCBs. The stability of mercury associated with CCBs is an issue that has only recently been under investigation, but has become a prominent question as the industry strives to determine if current management options for CCBs will need to be modified.

The release of mercury vapor, both at ambient and elevated temperatures, from CCBs resulting from the use of mercury control technologies has been evaluated on a limited basis. Samples of CCBs generated under emission control conditions were not readily available until DOE initiated field demonstrations of the control technologies. However, some work has been accomplished on samples primarily from pilot-scale and short-term tests. Methods of determining the release include measuring the mercury in the air, capturing the mercury released over extended periods, and evaluating the mercury contents of CCBs at varying periods, which generally require very sensitive analytical techniques.

Fly ash volatilization studies performed by Schwalb et al. (1) 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 1.

Limited information has been reported on the stability of mercury captured on sorbents (2). 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.

Investigation of elevated-temperature mercury release from CCBs at the EERC began in 1999. Most of the thermal curves generated were straightforward, containing only one or two major desorption peaks (3).

In early work performed under a DOE task (4), several samples of 100% activated carbon sorbents loaded with mercury were evaluated. Figure 1 shows a desorption curve generated for one of these sorbents. The desorption curve indicated that a significant level of mercury was

Table 1. Fly Ash Volatilization Results – Hg Concentration, ppm (1)

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

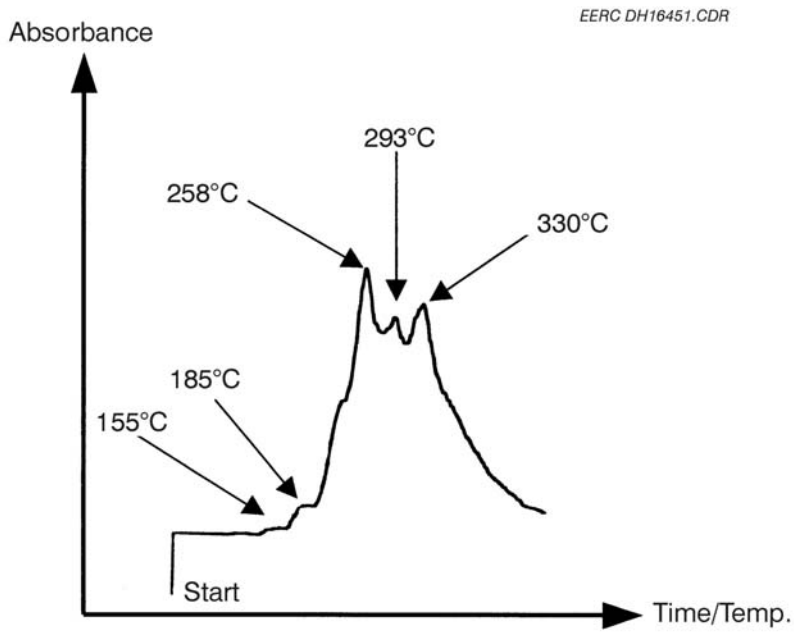


Figure 1. Mercury desorption curve for an activated carbon sorbent loaded with mercury.

desorbed from the sample and, as noted in Figure 1, five peaks were identified. These five peaks were reproducible. Other sorbent desorption curves were similar, and it was hypothesized as described above that there were multiple binding sites related to several mechanisms of sorption or bonding to additives in the carbon sorbents. At the time these curves were generated, the calibration of the elevated temperature apparatus had not yet been instituted, so the amount of mercury released was not quantitated.

No further elevated-temperature experiments were performed on 100% sorbent samples under this project, but the curves generated under the early DOE work provided background information for this task.

Determination of the speciation of mercury present on CCBs has been attempted at the EERC (5). Samples were spiked with mercuric oxide (HgO) or mercuric chloride ($HgCl_2$) powder. Experimental work was also done on determining the thermal curves for devolatilization of HgO and $HgCl_2$ compounds added to pulverized quartz powder to simulate an inert matrix. Thermal desorption of HgO produced a sharp, symmetric peak that desorbed at 250°–325°C. The peak from $HgCl_2$ desorption was less symmetric and desorbed at temperatures of 200°–250°C. When spiking ash samples with HgO and $HgCl_2$, it was found that the complex chemistry and/or matrix of the ash sample altered the decomposition of the mercury compounds. All spiked samples had peak desorption temperatures higher than that of the spike component alone. In all but one sample, the CCBs spiked with $HgCl_2$ eluted peaks at temperatures lower than the plain CCB. Spiking samples with HgO yielded variable decomposition temperatures. Unfortunately, this delayed desorption was not completely reproducible, making “peak matching” with desorption curves of the mercury compounds without ash difficult and problematic.

The use of fly ash in cement manufacture has become relatively common in recent years, and the use of FGD gypsum in wallboard has grown to the extent that new wallboard plants are almost exclusively using FGD and other by-product gypsum. The release of mercury in these uses where the CCB is exposed to elevated temperatures has the potential to impact the use applications and these industries. Laboratory information will be the starting point to understanding the impacts.

OBJECTIVES

The primary objective of the vapor-phase subtask was to evaluate the release of mercury from CCBs at ambient, near-ambient, and elevated temperatures to simulate possible mercury release in various disposal and utilization scenarios. The elevated-temperature experiments simulated high-temperature manufacturing scenarios such as wallboard and cement manufacturing. Mercury is more likely to be released at elevated temperatures, and this report only focuses on the elevated-temperature release experiments and results.

The objective of this report is to report on the method development for and results of experiments to evaluate the elevated-temperature vapor-phase release of mercury from CCBs.

METHODS

Mercury Desorption Apparatus and Method

Since mercury and mercury compounds are highly volatile, mercury was expected to be released from CCBs when they were exposed to elevated temperatures. Even mercury that is sorbed on fly ash, flue gas desulfurization (FGD) material, or sorbents developed to remove mercury in flue gas is expected to have high potential to be released if exposed to high enough temperatures. Instrumental and equipment constraints existed for the physical testing of elevated-temperature release of mercury from CCBs. These constraints were as follows:

- Furnaces available for the experimental apparatus could only achieve maximum temperatures of 750°C.
- Fittings and connecting tubing needed to be heated in order to minimize the loss of mercury in the system.
- Gas flow to remove the mercury from the heated sample cell to the analytical cell needed to be constant.
- Temperature ramping needed to be controlled and consistent between sample runs.

The apparatus for the investigation of real-time mercury release was constructed as shown in Figure 2. The CCB sample was weighed into a quartz tube with quartz wool used to keep the sample in place in the tube. Nominal sample size was approximately 1 gram. The sample tube

was then placed into a small tube furnace capable of achieving a maximum temperature of 750°C. The furnace was controlled with a temperature controller programmed to ramp the furnace from ambient to maximum temperature at a rate of 25°C per minute. In preliminary experiments, the maximum temperature achievable was 700°C, but an improved furnace was incorporated into the apparatus to increase the maximum achievable temperature to 750°C. A nitrogen gas flow of 5 cm^3/min was introduced into the tube furnace. As the mercury and mercury compounds desorbed from the CCB in the sample tube, the nitrogen flow carried them through the system to the electrically heated quartz analytical cell. The quartz analytical cell was operated at 800°C, allowing the detection of mercury compounds by thermally decomposing compounds to form elemental mercury, which can be detected by atomic absorption spectrophotometer (AAS). The analytical cell was placed in the center-focused beam path of an AAS. A mercury hollow cathode lamp was used as the light source, and the AAS detector was set to the 253.7-nm line for mercury. A Hewlett Packard 3395 integrator was used for data collection.

Calibration of the AAS with elemental mercury vapor sorbed onto gold-coated quartz produced a peak that was very symmetric and well-defined, decomposing at an average temperature of 350°–375°C. Calibration allows quantitation of the amount of mercury desorbed from the sample being evaluated.

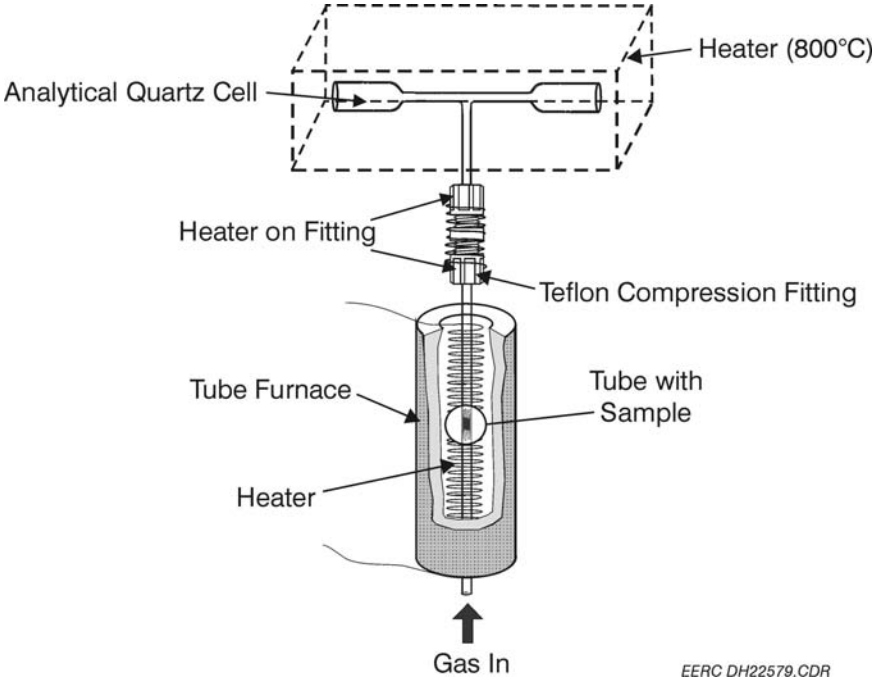


Figure 2. Mercury thermal desorption apparatus.

Mercury Speciation Method

It has been hypothesized that the mercury species associated with fly ash, FGD material, or carbon can be identified using thermal desorption techniques. EERC researchers performed several experiments to confirm or refute this hypothesis. The experimental design focused on the use of analytical spikes using mercuric chloride and elemental mercury. CCB samples, quartz sand, and quartz powder were all used as a base sample for these evaluations. Mercuric chloride was dissolved in ether and then added to the base samples. Elemental mercury was added in a gaseous form to CCB samples. The spiked samples were then desorbed using the same apparatus and protocol for the mercury release experiments described above.

RESULTS AND DISCUSSION

Samples Evaluated for Elevated-Temperature Release

Mercury thermal desorption curves were generated for 39 CCBs, including 18 samples without mercury control and 18 samples with mercury control. The sample set included primarily fly ash but also included various types of FGD materials. Several sorbents were evaluated under earlier EERC work, and data from some of these samples are included for comparison and discussion purposes. A list of the samples included in the elevated-temperature release experiments is included in Appendix A. Table 2 lists numbers of each sample type based relative to coal source and mercury control. It was determined early in the elevated-temperature

Table 2. Summary of Samples Evaluated in Elevated-Temperature Mercury Release Experiments

Coal Type	Sample Type	Mercury Control	No. of Samples Tested	Total Mercury Content Range, µg/g	Average Total Mercury, µg/g	Loss on Ignition (LOI), %
Eastern Bituminous	Fly ash	Yes	6	0.4–120	31.8	12.61–23.91
Eastern Bituminous	Fly ash	No	7	0.01–0.685	0.199	1.07–8.44
Eastern Bituminous	Fly ash	Unknown	3	0.362–1.21	0.730	10.49–10.90
Lignite	Fly ash	Yes	7	0.147–2.22	0.857	1.04–4.21
Lignite	Fly ash	No	6	<0.01–0.785	0.343	0.34–2.54
Lignite	FGD material	Yes	1	0.332	0.332	1.12
Lignite	FGD material	No	0	<0.01	<0.01	0.95
Subbituminous	Fly ash	Yes	4	0.64–5.5	3.18	2.11–4.14
Subbituminous	Fly ash	No	2	0.261–0.578	0.420	0.48–1.08
Subbituminous	FGD material	No	1	0.112	0.112	2.07
Western Bituminous	Fly ash	No	1	0.521	0.521	2.46

experiments that total mercury content of <0.01 µg/g generally did not allow for a desorption curve to be generated with any level of reproducibility. The absolute quantitation limit of the apparatus was approximately 10 nanograms. Using a maximum of 1 gram of sample, the quantitation limit was used to determine the lower concentration limit of 0.01 µg/g. The bulk of the samples evaluated had total mercury content of >0.01 µg/g and, after some preliminary attempts to evaluate samples with a lower total mercury content, low mercury samples were screened out and not evaluated.

Elevated-Temperature Release Desorption Curves for Fly Ash

As already noted, the release of mercury at elevated temperatures was evaluated by heating a sample in a temperature-controlled tube furnace and detecting the emitted mercury or mercury compounds with AAS in a t-cell heated to 800°C. Over the duration of the project, the apparatus for elevated-temperature release experiments has been modified to increase the achievable maximum temperature from 700° to 750°C. During the developmental stages of this apparatus, it was also determined that good control of gas flow was essential for good quantitation. Since the pressure drop across the sample increases as temperature increases, a mass flow controller was added to maintain a constant gas flow. The release of mercury from CCBs at temperatures up to 750°C is essentially quantitative. Mercury thermal desorption curves were generated throughout the project. However, only those generated after the installation of the mass flow controller are included in this report to give a better comparison of obtained results. Representative curves are shown in Figures 1–8.

For this project, most samples desorbed were fly ash samples, and most samples generated either one or two mercury peaks with a range of 0–4 peaks. Table 3 summarizes the information on the mercury thermal desorption curves by samples with and without mercury control testing. The temperature of the primary mercury peak ranged from 262° to 750°C, with an average of 468°C. Some samples actually continued to show increasing mercury release at 750°C, so the highest peak temperature at which the mercury was released could not be determined. More samples from mercury control testing continued to release mercury at 750°C

Table 3. Summary of Fly Ash Mercury Thermal Desorption Curves Generated to Date

Coal Type	Mercury Control	No. of Samples Tested	No. of Peaks Noted	Range of All Peaks, °C	Total Mercury Content Range, µg/g	LOI, %
Eastern Bituminous	Yes	6	1–4	262–750	0.4–120	12.61–23.91
Eastern Bituminous	No	7	0–3	302–750	0.01–0.685	1.07–8.44
Eastern Bituminous	Unknown	3	1–2	351–750	0.362–1.21	10.49–10.90
Lignite	Yes	7	1–2	325–632	0.147–2.22	1.04–4.21
Lignite	No	6	0–2	334–750	<0.01–0.785	0.34–2.54
Subbituminous	Yes	4	1–2	318–750	0.64–5.5	2.11–4.14
Subbituminous	No	2	1	333–404	0.261–0.578	0.48–1.08
Western Bituminous	No	1	1	330–335	0.521	2.46

than those without mercury control testing. Although the lowest mercury absorbance peak occurred at 262°C for a fly ash sample, some samples showed mercury release beginning before 250°C.

Examples of desorption curves with one and two peaks are shown in Figures 3 and 4, respectively. As can be seen in these figures, the single or first peaks tended to rise relatively sharply at the initiation of the peak but tailed off with time. In curves where two or more peaks were noted, peaks after the initial peak tended to show slightly less definition and were usually broader.

Examples of replicate desorption curves are noted in Figures 5–8. Figures 5 and 6 are replicate curves for a sample of lignite fly ash generated during mercury control technology testing and show excellent reproducibility. Figures 7 and 8 are replicate curves for a sample of eastern bituminous fly ash and show relatively poor reproducibility. While replicates were not performed on every sample in the task sample set (Appendix A), where replicates were performed, results were generally good. Poor replication generally indicated a highly variable sample.

Table 4 presents a breakdown of sample reproducibility for replicate mercury thermal desorption curves generated for fly ash. Just over half of the samples show a reproducible number of peaks generated in replicate runs. However, the remaining samples produced an inconsistent number of peaks in replicate runs and are reported as generating a range of peak numbers.

Table 4. Breakdown of Number of Peaks Generated for Fly Ash Mercury Thermal Desorption Curves to Date

Coal Type	Mercury Control	No. of Samples Tested	No. of Samples with Designated No. of Peaks							
			<DL[1]	1	2	3	4	1–2	2–3	1–3
Eastern Bituminous	Yes	6			1	1	1		2	1
Eastern Bituminous	No	7	1		1			2	1	2
Eastern Bituminous	Unknown	3		1				2		
Lignite	Yes	7		5				2		
Lignite	No	6	1	2				2		
Subbituminous	Yes	4		3				1		
Subbituminous	No	2		2						
Western Bituminous	No	1		1						

[1] Detection limit.

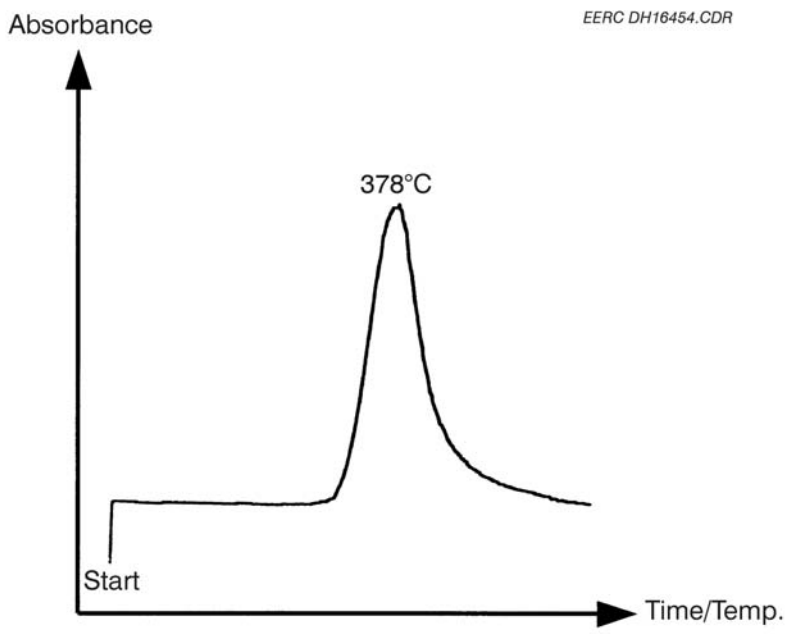


Figure 3. Typical one-peak mercury desorption curve for fly ash.

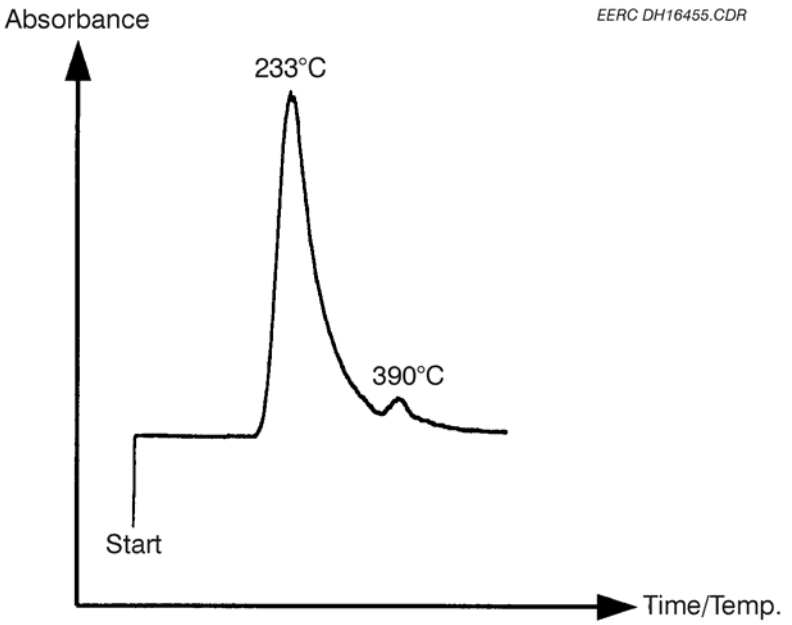
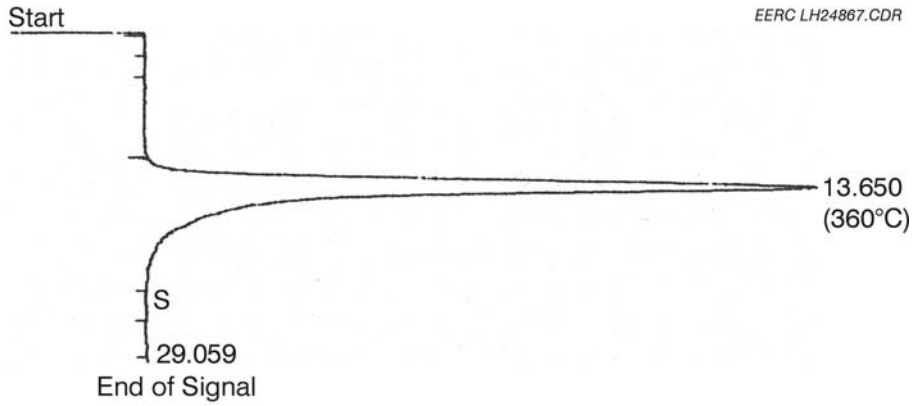


Figure 4. Typical two-peak mercury desorption curve for fly ash.



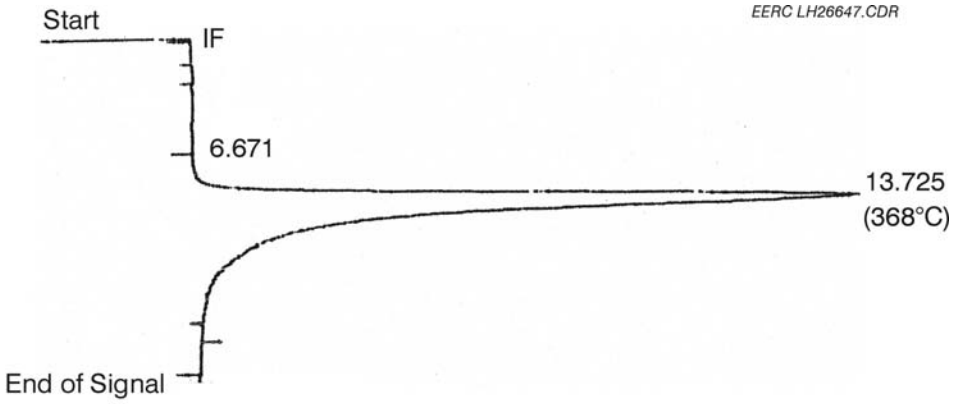
Run No. 1203 January 24, 2005, 15:44:27

ESTD-AREA

RT	Type	Area	Width	Cal#	Amount	Name
13.650	SBB	368,748,000	1.788	1R	132.440	Hg
29.059	VV	1,451,010	1.857		.530	

Total Area = 3.7020E + 08
Mul. Factor = 1.0000E + 00

Figure 5. Replicate 1 of a reproducible sample mercury desorption curve, using 640.3 mg of sample.



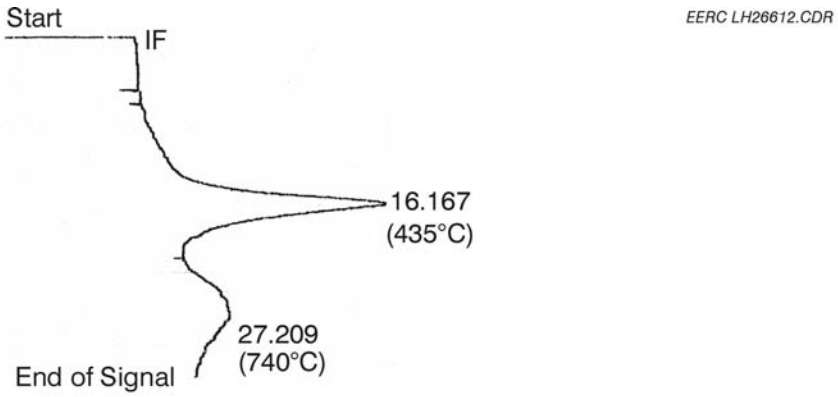
Run No. 1204 January 24, 2005, 16:33:30

ESTD-AREA

RT	Type	Area	Width	Cal#	Amount	Name
6.671	I PB	675616	1.520		.247	
13.725	SBB	382155200	2.085	1R	137.255	Hg

Total Area = 3.8283E+ 08
Mul. Factor = 1.0000E + 00

Figure 6. Replicate 2 of a reproducible sample mercury desorption curve, using 634.2 mg of sample.



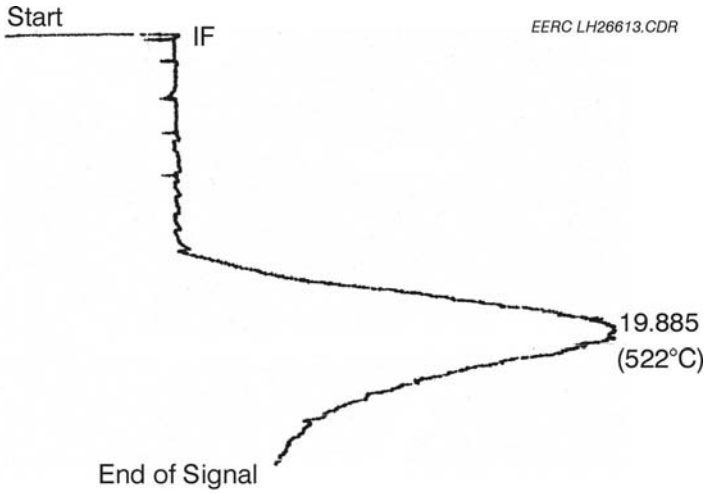
Run No. 1074 September 28, 2004, 21:56:11

ESTD-AREA

RT	Type	Area	Width	Cal#	Amount	Name
16.167	VV	77,480,832	3.941	1R	49.293	NG
27.209	I VH	68,920,960	9.372		43.847	

Total Area = 1.4640E+ 08
Mul. Factor = 1.0000E + 00

Figure 7. Replicate 1 of an irreproducible sample mercury desorption curve, using 788.9 mg of sample.



Run No. 1103 October 18, 2004, 10:08:38

Total Area = 1.7421E+ 08
Mul. Factor = 1.0000E + 00

Figure 8. Replicate 2 of an irreproducible sample mercury desorption curve, using 581.6 mg of sample.

Samples that have shown the most variability are those that contain activated carbon sorbents. The nature of the ash–carbon mixture is to separate, with the carbon moving preferentially to the surface of any container in which the sample is stored. The research team was aware of this issue, and it was sometimes easily observed in the laboratory handling of the samples; however, even very careful mixing and sampling were not adequate to alleviate this variability for the small sample size used for thermal desorption experiments. In later thermal runs, samples containing no visible carbon showed improved reproducibility after grinding. We believe that in these samples the carbon particles may have been coated with ash and, for this reason, could not be easily seen. During grinding, the carbon particles became evident as black swirls as the material was being ground. The variability of the sample was also readily noted in experiments to quantitate mercury releases. In some samples with activated carbon present, mercury concentrations determined based on the peaks identified by the integrator (after apparatus calibration) were not consistent. This phenomenon was exacerbated as carbon particles in the individual samples were noted to be larger. It was determined that this problem could be overcome by carefully grinding the samples in a mortar and pestle to allow a more homogeneous samples to be placed in the thermal desorption sample tubes.

An example of the many problems associated with thermal desorption is a fly ash sample containing sulfur-impregnated activated carbon. A sample like this would be expected to produce a thermal curve containing more than one peak. The reasons that multiple peaks might occur on a thermal desorption profile include the following:

- Flue gas can contain elemental and oxidized mercury. The oxidized mercury may be present as a chloride, oxide, nitrate, or sulfate, and each of these compounds could result in a discreet peak on its vaporization.

- Sorbents may contain other compounds by design as in sulfur- or halogen-impregnated activated carbon, which may cause formation of additional mercury compounds, each releasing at a discreet temperature.

Elemental mercury is known to sorb as an oxidized species on activated carbon. Additives such as sulfur or iodine, for example, could lead to the formation of additional compounds such as mercuric sulfide or mercuric iodide. During thermal desorption, there are many additional things that might happen:

- Elemental mercury and mercuric chloride can desorb unchanged.

- Other mercury compounds can decompose into their components as would happen with mercuric oxide, which would decompose into oxygen and elemental mercury prior to desorption.

All of these factors combine in practice to produce thermal desorption curves that, while we may not completely understand the process, provide valuable data.

Elevated-Temperature Release Desorption Curves for FGD Material

Some FGD material samples were also subjected to the elevated-temperature protocol. A summary of the information on the mercury thermal desorption curves by sample is provided in Table 5. Table 6 contains a breakdown of the identified mercury peaks from several sample runs. The three samples tested showed a wide variety of mercury release profiles.

Figure 9 is an example of a desorption curve for a spray dryer absorber (SDA) material. This sample was collected during demonstration of mercury emission control testing using activated carbon injection at a lignite-fired power plant. Fly ash is recycled into the SCA system at the power plant where these samples were obtained, which is relatively common.

FGD materials are difficult to analyze with the current elevated-temperature release system because of sulfur interferences, moisture, and other possible problems as noted above.

Mercury-Spiked Desorption Curves

Quartz sand and pure quartz powder where spiked with mercuric chloride as an inert material similar to CCBs. A single sharp peak was recorded when the mercuric chloride was added to the quartz sand. However, when mercuric chloride was spiked onto pure quartz powder, a double peak was noted. This suggests that matrix effects may make determination of species very unlikely.

Table 5. Summary of FGD Material Mercury Thermal Desorption Curves Generated to Date

Coal Type	Mercury Control	No. of Samples Tested	No. of Peaks Noted	Range of All Peaks, °C	Total Mercury Content, µg/g	LOI, %
Lignite	Yes	1	1	312–354	0.332	1.12
Lignite	No	1	0	NA[1]	<0.01	0.95
Subbituminous	No	1	2–3	270–695	0.112	2.07

[1] Not applicable.

Table 6. Identified Peak Ranges for FGD Material Mercury Thermal Desorption Curves to Date

Coal Type	Mercury Control	Identified Peak Ranges	No. of Samples Tested
Lignite	Yes	312–354	1
Lignite	No	NA	1
Subbituminous	No	270–280 430–475 695	1

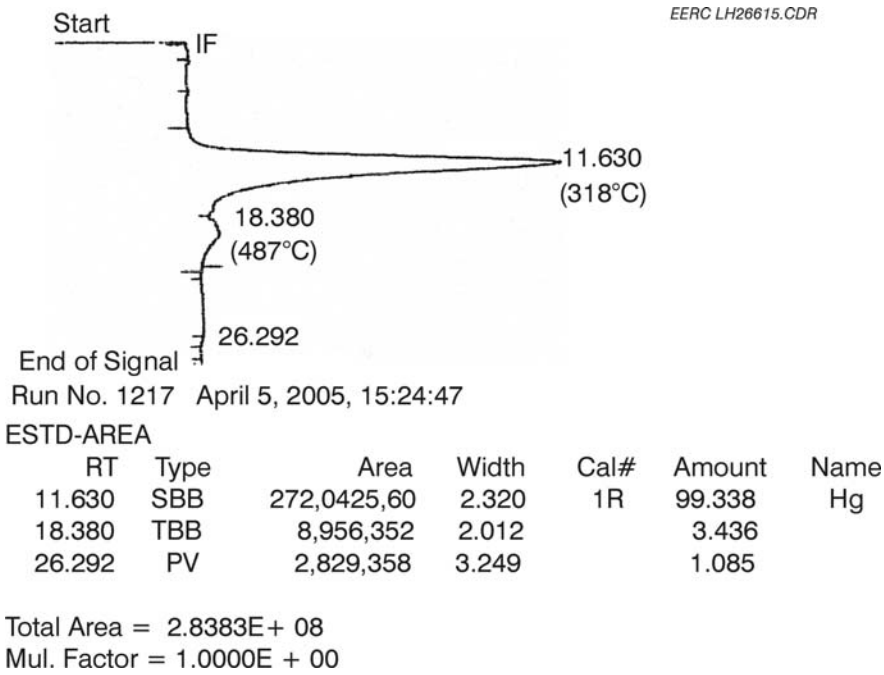
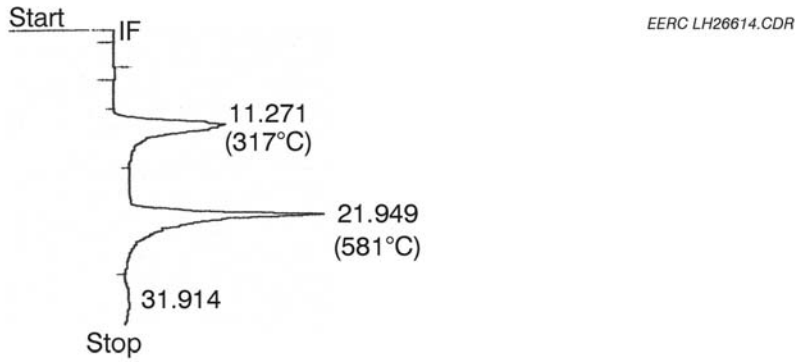


Figure 9. Mercury desorption curve for an SDA material generated during injection of activated carbon, using 458.7 mg of sample.

Additional elevated-temperature release experiments were also performed on CCB samples spiked with mercury. All samples used in this experiment were fly ash, some of which contained activated carbon from mercury emission control demonstrations. The addition of mercuric chloride or elemental mercury to the CCBs resulted in a shift of the mercury release peaks noted previously from the samples without any added mercury. The peak temperatures measured for spiked CCB samples shifted to higher temperatures for some samples and to lower temperatures for other samples.

Figures 10 and 11 are an example of a fly ash sample tested as described earlier compared to a separate aliquot spiked with mercuric chloride. This was done by mixing a single aliquot of the CCB, just less than 2 grams, and dividing it into two small, nearly equal portions. One portion was left untreated while the other portion was spiked with 50 µL of an ether solution of mercuric chloride containing 10 ng/µL of mercuric chloride. This is equivalent to the addition of 370 ng of mercury as mercuric chloride. Spiking was done in this manner to minimize nonhomogeneity between the two aliquots of sample. Mercuric chloride spiking of this fly ash sample produced an additional peak to those noted on the original fly ash sample. The reasons for an additional peak noted in the spiked sample are the same as why a fly ash sample may release multiple peaks of mercury.



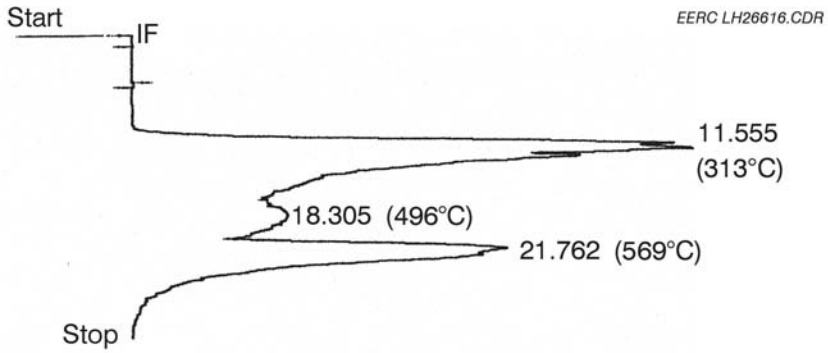
Run No. 3003 December 27, 2005, 14:26:21

ESTD-AREA

RT	Type	Area	Width	Cal#	Amount	Name
11.271	SPB	99,109,312	2.269		30.797	
21.949	ISHH	208,283,120	2.529	1R	53.205	Hg
31.914	ITBB	6,458,282	3.213		2.007	

Total Area = 3.1385E+ 08
Mul. Factor = 1.0000E + 00

Figure 10. Mercury desorption curve for a baseline (no mercury control) eastern bituminous fly ash, using 855.9 mg of sample.



Run No. 3004 December 27, 2005, 15:44:46

ESTD-AREA

RT	Type	Area	Width	Cal#	Amount	Name
11.555	SBH	781,830,720	4.166	1R	199.714	Hg
18.305	IBB	33,633,760	2.603		10.451	
21.762	ISHH	345,580,480	2.760		107.386	

Total Area = 1.160E+ 09
Mul. Factor = 1.0000E + 00

Figure 11. Mercury desorption curve for a baseline (no mercury control) eastern bituminous fly ash spiked with 500 ng of mercuric chloride, using 811.1 mg of sample.

CONCLUSIONS

Thermal desorption curves provided a comparative means of evaluating the elevated-temperature release of mercury from a variety of CCBs, but the method and results have not yet yielded an understanding of the mechanism of release over the temperature range evaluated. The possible scenarios for release are as follows:

- Mercury and mercury compounds, as sorbed, are being released unchanged during the thermal desorption procedure.

- Mercury compounds are being desorbed by a mechanism of thermal decomposition whereby sorbed compounds such as HgO are thermally decomposed to mercury and oxygen during the thermal desorption.

- Mercury or mercury compounds are chemically reacting with the CCB components then thermally desorbed according to the first or second scenario as described above.

The results indicated that the mercury present on CCBs is expected to be released at temperatures between 262° and 750°C. In most cases, all the sorbed mercury will be released, although some samples did retain some mercury after exposure to 750°C. Some samples showed continued release at 750°C so they might not release all their mercury until a higher temperature is achieved. While not investigated under this project, the amount of time the CCB is exposed to certain temperatures may also impact the amount of mercury released. It is recommended that this be investigated, especially for FGD gypsum, which may be exposed to elevated temperatures for short times during the preparation for use in wallboard. The use of fly ash that contains measurable mercury (with or without sorbent carbon) for cement manufacture has high potential to release that mercury based on the results presented. It is recommended that the CCB industry work with cement manufacturers to investigate solutions that will facilitate maintenance of this market for fly ash.

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4. Pavlish, J.H. Task 1.2 – Mercury Stability in the Environment; Final Report for U.S. Department of Energy National Energy Technology Laboratory, July 1999.

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APPENDIX A

LIST OF SAMPLES TESTED WITH MERCURY THERMAL DESORPTION APPARATUS

Table A1. List of Samples Tested with Mercury Thermal Desorption Apparatus

ID No.	Sample Type	Coal Type	Mercury Control	Total Mercury, µg/g	LOI, %
02-002	Fly ash	Eastern bituminous	Yes	30.6	22.17
02-003	Fly ash	Eastern bituminous	Yes	21.7	19.38
02-004	Fly ash	Subbituminous	Yes	5.5	2.84
02-005	Fly ash	Subbituminous	Yes	4.73	4.14
02-007	Fly ash	Eastern bituminous	Yes	120	23.91
02-069	Fly ash	Eastern bituminous	Yes	0.634	12.61
02-070	Fly ash	Eastern bituminous	No	0.193	5.88
02-072	Fly ash	Eastern bituminous	No	0.16	5.39
02-076	Fly ash	Eastern bituminous	Yes	0.4	21.15
03-005	Fly ash	Eastern bituminous	No	0.084	3.60
03-007	Fly ash	Eastern bituminous	No	0.141	4.41
03-011	Fly ash	Eastern bituminous	Unknown	0.618	10.49
03-013	Fly ash	Eastern bituminous	Unknown	0.362	10.90
03-014	Fly ash	Eastern bituminous	Unknown	1.21	10.88
03-016	Fly ash	Lignite	No	0.016	0.34
03-018	Fly ash	Lignite	Yes	0.289	1.17
03-019	Fly ash	Lignite	Yes	2.22	4.21
03-060	Fly ash	Subbituminous	Yes	1.86	2.47
03-061	Fly ash	Subbituminous	No	0.578	1.08
03-062	Fly ash	Lignite	Yes	0.49	1.29
03-078	Fly ash	Lignite	No	0.662	1.47
03-079	Fly ash	Lignite	No	0.785	2.54
03-088	Fly ash	Eastern bituminous	No	0.01	1.07
04-003	Fly ash	Eastern bituminous	No	0.685	8.44
04-007	Fly ash	Western bituminous	No	0.521	2.46
04-029	Fly ash	Subbituminous	No	0.261	0.48
04-033	Fly ash	Lignite	Yes	1.43	1.39
04-035	Fly ash	Lignite	No	0.159	2.24
04-036	Fly ash	Lignite	Yes	0.287	2.16
04-054	Fly ash	Eastern bituminous	Yes	17.7	18.60
04-067	Fly ash	Subbituminous	Yes	0.64	2.11
05-001	Fly ash	Lignite	No	<0.01	0.90
05-002	Fly ash + FGD-SDA	Lignite	No	<0.01	0.95
05-003	Fly ash	Lignite	Yes	0.565	1.04
05-004	Fly ash + FGD-SDA	Lignite	Yes	0.332	1.12
05-005	Fly ash	Lignite	No	0.431	1.29
05-017	Fly ash	Lignite	Yes	0.717	1.70
05-018	Fly ash	Eastern bituminous	No	0.123	3.01
99-188	Fly ash + FGD-SDA	Subbituminous	No	0.112	2.07

APPENDIX Q

ELEVATED-TEMPERATURE MERCURY RELEASE DATA

Table Q-1. Elevated-Temperature Mercury Release Results

ID No.	Run #	Sample Amount (mg)	Peak 1 (°C)	Peak 2 (°C)	Peak 3 (°C)	Peak 4 (°C)	Comments	Sample Type	Hg Control Configuration	Fuel Type
99-188	1154	765.7	270	475	695			FGD-SDA		PRB Subbituminous
99-188	1181	1018.7	280	440				FGD-SDA		PRB Subbituminous
99-188	1182	1087.1	275	430				FGD-SDA		PRB Subbituminous
02-002	1050	116.1	262	330	411	736		Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous
02-002	1051	71	278	352	470	740		Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous
02-003	1052	138.7	290	400	519	750	Peak 1 very small	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous
02-003	1053	54.4	390	509	748		additional peak evolved after heated at 750° for extended period	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous
02-004	1054	155.2	318	552				Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous
02-004	1101	154	334	363			Very close double peak	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous
02-004	2879	257	366				start of curve noticed at end of run	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous
02-005	1056	99.5	326					Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous
02-005	2880	87.8	358	750				Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous
02-006	1058	53.9	302				very fine double peak	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous
02-006	3015	83.4	702				peak tip not very defined	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous
02-007	1060	19.6	400	518				Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous
02-007	2877	13.2	433	571			2nd peak is large tailing peak	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous
02-069	1061	655.2	481	750			high absorbance	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous
02-069	2921	429.5	474	722	750		Hg release continued when held at 750°C	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous
02-069	2957	442.4	478					Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous
02-069	2958	446.8	700				peak was essentially a small bump	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous
02-069	2959	444.4	750					Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous
02-069	2960	442	350	685	747		all peaks very small	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous
02-069	2963	520	410	429	543	705		Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous
02-069	2965	484.5	415	450	619	739		Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous
02-069	2966	488.8	445	597	750			Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous
02-070	1062	707.7	473	741				Fly Ash		Eastern Bituminous
02-070	2993	856.4	473					Fly Ash		Eastern Bituminous
02-071	1063	541	427	675				Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous
02-072	1064	792.9	411	558	590			Fly Ash		Eastern Bituminous
02-072	2971	770.3	420	645				Fly Ash		Eastern Bituminous
02-072	2973	778	612					Fly Ash		Eastern Bituminous
02-073	1065	636.3	404					Fly Ash		Eastern Bituminous
02-073	2989	912.1	406	524	750		Hg release continued when held at 750°C	Fly Ash		Eastern Bituminous
02-074	1068	606.2	399					Fly Ash		Eastern Bituminous
02-074	3016	706.2	750					Fly Ash		Eastern Bituminous
02-076	1069	710.5	405	750			Hg release continuing at 750°C	Fly Ash		South American Bituminous
02-076	1070	741	417	750				Fly Ash		South American Bituminous
02-076	2990	709.1	386	602				Fly Ash		South American Bituminous
02-076	2997	735.3	356	750			Hg release continued when held at 750°C	Fly Ash		South American Bituminous
02-076	2999	722.2	358	708	750		Hg release continued when held at 750°C	Fly Ash		South American Bituminous
02-076	3000	722.5	396	750				Fly Ash		South American Bituminous
02-076	3006	702.6	365	750				Fly Ash		South American Bituminous
02-076	3028	363.7	361	750				Fly Ash		South American Bituminous
03-004	1071	994.7	378	720				Fly Ash		Eastern Bituminous
03-004	3014	1070.2	537					Fly Ash		Eastern Bituminous
03-005	1072	956.4	384	711				Fly Ash		Eastern Bituminous
03-005	1080	530.2	376	750			Hg release continuing at 750°C	Fly Ash		Eastern Bituminous
03-006	1073	767.7	443					Fly Ash		Eastern Bituminous
03-006	2987	894	450					Fly Ash		Eastern Bituminous

ID No.	Run #	Sample Amount (mg)	Peak 1 (°C)	Peak 2 (°C)	Peak 3 (°C)	Peak 4 (°C)	Comments	Sample Type	Hg Control Configuration	Fuel Type
03-006	2988	884.1	412	575	625			Fly Ash		Eastern Bituminous
03-007	1074	788.9	435	740				Fly Ash		Eastern Bituminous
03-007	1102	936.2	452	527	718			Fly Ash		Eastern Bituminous
03-007	1103	581.6	522					Fly Ash		Eastern Bituminous
03-008	1075	942.8	362					Fly Ash		South American Bituminous
03-016	1082	1001.1	368					Fly Ash		Fort Union Lignite
03-016	2904	408.1	354					Fly Ash		Fort Union Lignite
03-016	2905	964.8	383				very small bump	Fly Ash		Fort Union Lignite
03-017	1083	697.1	350				slight peak start at end of run	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite
03-018	1084	649.2	325					Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite
03-018	1085	649.3	335					Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite
03-018	1108	438.1	350					Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite
03-018	1200	616.4	346					Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite
03-018	1202	647.6	339				slight increase at end of run	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite
03-018	2931	638.8	358					Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite
03-018	2932	639.5	363					Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite
03-019	1086	221.2	375					Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite
03-019	1250	186.1	382					Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite
03-019	1251	167.1	375					Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite
03-060	1087	197.6	395					Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous
03-060	1247	202.4	400					Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous
03-060	1248	196.3	392					Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous
03-061	1088	556.7	383					Fly Ash		PRB Subbituminous
03-061	2908	269.4	404					Fly Ash		PRB Subbituminous
03-061	2926	276.9	378					Fly Ash		PRB Subbituminous
03-062	1089	629.7	334					Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite
03-062	1230	595.8	358					Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite
03-062	1231	596.3	357				sharp peak	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite
03-062	1239	598.2	346				sharp peak	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite
03-062	2933	603	398					Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite
03-062	2934	604.8	368				ground sample	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite
03-062	2935	602.7	361					Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite
03-062	2942	606.3	331					Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite
03-062	2943	604.4	333				jagged peak	Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite
03-062	2945	600	356					Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite
03-063	1090	990.1	675				no real peak	Fly Ash		Eastern Bituminous
03-065	1111	1000.9	329					FGD Gypsum		Eastern Bituminous
03-078	1044	494.6	350					Fly Ash		Fort Union Lignite
03-078	1120	498.4	334					Fly Ash		Fort Union Lignite
03-078	1171	505.7	355				jagged top of peak	Fly Ash		Fort Union Lignite
03-079	1043	236.7	356					Fly Ash		Fort Union Lignite
03-079	1121	465.4	361	750			peak not complete at end of run	Fly Ash		Fort Union Lignite
03-079	2916	506.1	345					Fly Ash		Fort Union Lignite
03-080	1122	677.4	380	443			slight increase at end of run	Fly Ash		Fort Union Lignite
03-080	3018	1105	750					Fly Ash		Fort Union Lignite
03-080	3019	1044.7	347					Fly Ash		Fort Union Lignite
03-081	1123	641.3	275	346	592			Fly Ash		Fort Union Lignite
03-081	2984	479.5	296	750			peak not complete at end of run	Fly Ash		Fort Union Lignite
03-083	1124	1005.9	413				very broad peak	Fly Ash		Eastern Bituminous
03-083	3021	1364.2	358					Fly Ash		Eastern Bituminous

ID No.	Run #	Sample Amount (mg)	Peak 1 (°C)	Peak 2 (°C)	Peak 3 (°C)	Peak 4 (°C)	Comments	Sample Type	Hg Control Configuration	Fuel Type
03-084	1125	750.1	256	460	720			Fixated FGD		Eastern Bituminous
03-085	1126	1003.5	354	748				Fly Ash		Eastern Bituminous
03-085	3020	1558.2	392	750				Fly Ash		Eastern Bituminous
03-088	1127	1862.8	273	350	551	747		Fly Ash		Eastern Bituminous
03-088	1173	1323.1	742					Fly Ash		Eastern Bituminous
03-088	1175	1315	487	737			all peaks very small	Fly Ash		Eastern Bituminous
03-088	1177	1327.8	285	750			all peaks very small	Fly Ash		Eastern Bituminous
03-089	1128	756.8	298					FGD Gypsum		Eastern Bituminous
04-003	1129	467.7	434					Fly Ash		Eastern Bituminous
04-003	1178	507.7	393	750				Fly Ash		Eastern Bituminous
04-003	1180	504.8	449					Fly Ash		Eastern Bituminous
04-003	2918	253	444					Fly Ash		Eastern Bituminous
04-004	1130	1606.1	300					Fly Ash		Eastern Bituminous
04-006	1131	752.1	378					Fly Ash		Western Bituminous
04-007	1132	620.5	330					Fly Ash		Western Bituminous
04-007	2954	626.7	335					Fly Ash		Western Bituminous
04-029	1133	623.5	352					Fly Ash		PRB Subbituminous
04-029	2910	317.3	333				very small peak	Fly Ash		PRB Subbituminous
04-030	1143	1308.5	397	750			peak not complete at end of run	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite
04-030	3013	1011.2	563					Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite
04-031	3010	890	555					Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite
04-032	1145	788.2	448	572	747			Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite
04-032	3009	806.3	318	576				Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite
04-033	1149	293.5	477					Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite
04-033	2867	251.4	632					Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite
04-033	2868	284.9	499	603				Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite
04-033	2883	251.3	528					Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite
04-035	1150	715	336					Fly Ash		Fort Union Lignite
04-035	1209	558.2	356					Fly Ash		Fort Union Lignite
04-035	1215	623.5	362					Fly Ash		Fort Union Lignite
04-035	2912	852	370				sample had visible unburned C particles	Fly Ash		Fort Union Lignite
04-035	2936	768.6	341				jagged peak	Fly Ash		Fort Union Lignite
04-035	2940	771.2	365					Fly Ash		Fort Union Lignite
04-035	2941	769.4	353				jagged peak	Fly Ash		Fort Union Lignite
04-036	1151	619.7	336					Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite
04-036	1203	640.3	360					Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite
04-036	1204	634.2	368					Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite
04-036	2946	635.2	339					Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite
04-036	2947	632.5	344					Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite
04-036	3022	704.8	324	750				Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite
04-036	3023	885.9	324				ground sample	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite
04-036	3025	711.8	330					Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite

ID No.	Run #	Sample Amount (mg)	Peak 1 (°C)	Peak 2 (°C)	Peak 3 (°C)	Peak 4 (°C)	Comments	Sample Type	Hg Control Configuration	Fuel Type
04-054	1153	60.5	385	435	720			Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous
04-054	1190	99.4	490					Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous
04-054	1191	115.4	477					Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous
04-054	1193	104.3	344	500	750		peak not complete at end of run	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous
04-067	1206	543.9	377				high absorbance	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite
04-067	1207	482.3	397				high absorbance	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite
04-067	2884	374.1	433					Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite
04-067	2928	504.1	422				sharp peak	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite
05-001	1211	532.8					no real peak recorded	Fly Ash		Fort Union Lignite
05-001	2861	1033.1	289	442				Fly Ash		Fort Union Lignite
05-001	2862	1179.5	459					Fly Ash		Fort Union Lignite
05-002	1228	453.9					no real peak recorded	FGD-SDA		Fort Union Lignite
05-003	1223	490.9	335					Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite
05-003	1225	474.8	345					Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite
05-003	1226	496.6	329					Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite
05-003	2890	206.5	385				broad tailing	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite
05-004	1217	458.7	318	487				FGD-SDA + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite
05-004	2891	287.8	354					FGD-SDA + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite
05-004	2953	291.9	312					FGD-SDA + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite
05-005	1219	405.3	365					Fly Ash		Fort Union Lignite
05-005	1220	428.3	377					Fly Ash		Fort Union Lignite
05-005	2892	265.2	384					Fly Ash		Fort Union Lignite
05-005	2924	520.5	379				all peaks small; sample run through 100-mesh sieve	Fly Ash		Fort Union Lignite
05-005	3030	778.7	332				sample run through 100-mesh sieve	Fly Ash		Fort Union Lignite
05-005	3034	729.2	316				sample run through 100-mesh sieve	Fly Ash		Fort Union Lignite
05-005	3042	673.4	316				sample run through 100-mesh sieve	Fly Ash		Fort Union Lignite
05-010	2864	782.1	328	393			broad curve with two peaks	Fly Ash		Eastern Bituminous
05-010	2865	762.9	311					Fly Ash		Eastern Bituminous
05-010	3007	777.1	334	750				Fly Ash		Eastern Bituminous
05-013	3075	6.2	423					Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite
05-013	3076	4.8	457	751				Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite
05-013	3077	5.6	451	526			very jagged	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite
05-017	2853	341.8	417	578				Fly Ash + Enhancing Agent	Enhancing Agent on Coal	Fort Union Lignite
05-017	2854	523.5	405	561				Fly Ash + Enhancing Agent	Enhancing Agent on Coal	Fort Union Lignite
05-017	2858	338	403	590				Fly Ash + Enhancing Agent	Enhancing Agent on Coal	Fort Union Lignite
05-017	2863	320.5	406					Fly Ash + Enhancing Agent	Enhancing Agent on Coal	Fort Union Lignite
05-017	3039	485	391	684				Fly Ash + Enhancing Agent	Enhancing Agent on Coal	Fort Union Lignite
05-017	3040	560	399					Fly Ash + Enhancing Agent	Enhancing Agent on Coal	Fort Union Lignite
05-017	3041	403.5	393	666				Fly Ash + Enhancing Agent	Enhancing Agent on Coal	Fort Union Lignite

ID No.	Run #	Sample Amount (mg)	Peak 1 (°C)	Peak 2 (°C)	Peak 3 (°C)	Peak 4 (°C)	Comments	Sample Type	Hg Control Configuration	Fuel Type
05-018	2855	788.4	317	747			1st peak high absorbance; Hg release continuing at 750°C	Fly Ash		Eastern Bituminous
05-018	2857	787.4	340	703				Fly Ash		Eastern Bituminous
05-018	2995	822.7	302	564	643		3rd peak on tail of 2nd peak	Fly Ash		Eastern Bituminous
05-018	3003	855.9	317	581				Fly Ash		Eastern Bituminous
05-023	3046	167.2	497	749			high absorbance	Fly Ash + Activated Carbon	Post-Primary PCD: High Fly Ash Content	Fort Union Lignite
05-023	3048	55.5	454	746	750		great amount of Hg release after 750°C reached	Fly Ash + Activated Carbon	Post-Primary PCD: High Fly Ash Content	Fort Union Lignite
05-023	3050	86.9	471				high absorbance	Fly Ash + Activated Carbon	Post-Primary PCD: High Fly Ash Content	Fort Union Lignite
05-023	3053	102.1		471			high absorbance	Fly Ash + Activated Carbon	Post-Primary PCD: High Fly Ash Content	Fort Union Lignite
05-023	3054	75.5	469				high absorbance; Hg release continued when held at 750°C	Fly Ash + Activated Carbon	Post-Primary PCD: High Fly Ash Content	Fort Union Lignite
05-023	3059	102.1	441	682			Sx in 1008.5 mg quartz sand; high absorbance; Hg release continued when held at 750°C	Fly Ash + Activated Carbon	Post-Primary PCD: High Fly Ash Content	Fort Union Lignite
05-023	3062	29	388				Sx in 1002.8 mg quartz sand	Fly Ash + Activated Carbon	Post-Primary PCD: High Fly Ash Content	Fort Union Lignite
05-023	3063	32.8	460	586			Hg release continuing at 750°C	Fly Ash + Activated Carbon	Post-Primary PCD: High Fly Ash Content	Fort Union Lignite
05-023	3065	19.6	459	577				Fly Ash + Activated Carbon	Post-Primary PCD: High Fly Ash Content	Fort Union Lignite
05-023	3067	13.7	468					Fly Ash + Activated Carbon	Post-Primary PCD: High Fly Ash Content	Fort Union Lignite
05-024	3071	16.2	436				high absorbance	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite
05-024	3072	9.2	444					Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite
05-024	3073	8.5	443					Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite
05-025	3068	31.2	437					Fly Ash + Activated Carbon	Post-Primary PCD: High Fly Ash Content	Fort Union Lignite
05-025	3069	18.6	353	430	704			Fly Ash + Activated Carbon	Post-Primary PCD: High Fly Ash Content	Fort Union Lignite
05-025	3070	20.7	438	684				Fly Ash + Activated Carbon	Post-Primary PCD: High Fly Ash Content	Fort Union Lignite
05-038	3056	941.6	376	697			Hg release continuing at 750°C	Fly Ash		Fort Union Lignite
05-040	3078	2.9	427					Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite
05-040	3079	2.2	447	750				Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite
06-001	3080	1.3	385					Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite
06-001	3081	1.2	423					Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite
Quartz Sand	3058	1008.5					no peaks	Quartz Sand		
Quartz Sand	3084	494					no peaks	Quartz Sand		
Quartz Sand	3090	495.8					no peaks	Quartz Sand		
Quartz Sand	3108	531.9					no peaks	Quartz Sand		
Fly Ash Std.	1139	526.9	292					NIST 1633b Fly Ash Standard		
Fly Ash Std.	2951	806.4	450	750			all peaks very small	NIST 1633b Fly Ash Standard		

Table Q-2. Elevated-Temperature Mercury Release Results for Mercury Spiked Samples

ID No.	Run #	Sample Amount (mg)	Spiked with	Peak 1 (°C)	Peak 2 (°C)	Peak 3 (°C)	Peak 4 (°C)	Comments	Sample Type	Hg Control Configuration	Fuel Type
02-004	1099	155.6	$HgCl_2$ in ether	307				plateau noted half way down tail of peak	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous
02-004	1100	157.5	$HgCl_2$ in ether	307				plateau noted half way down tail of peak	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous
02-069	2968	494.7	$HgCl_2$ in ether	306	419	698	750	Hg release continued when held at 750°C	Fly Ash + Activated Carbon	Post-Primary PCD	Eastern Bituminous
02-070	2994	778.6	$HgCl_2$ in ether	483	596				Fly Ash		Eastern Bituminous
02-076	2991	713.4	$HgCl_2$ in ether	364	651				Fly Ash		South American Bituminous
02-076	3001	722	$HgCl_2$ in ether	410	750				Fly Ash		South American Bituminous
02-076	3002	760.3	$HgCl_2$ in ether	401					Fly Ash		South American Bituminous
02-076	3027	614.3	$HgCl_2$ in ether	367					Fly Ash		South American Bituminous
03-007	1104	593.1	$HgCl_2$ in ether	597					Fly Ash		Eastern Bituminous
03-007	1105	581.6	Hg^0	403	577			1st peak very sharp, 2nd peak broad	Fly Ash		Eastern Bituminous
03-007	1106	548.8	Hg^0	406	572			1st peak very sharp, 2nd peak broad	Fly Ash		Eastern Bituminous
03-007	1107	573.9	$HgCl_2$ in ether	431	750			Hg release continued when held at 750°C	Fly Ash		Eastern Bituminous
03-016	2907	458.6	$HgCl_2$ in ether	315					Fly Ash		Fort Union Lignite
03-018	1109	438.8	Hg^0	350					Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite
03-018	1110	436.3	$HgCl_2$ in ether	323					Fly Ash + Activated Carbon	Pre-Primary PCD	Fort Union Lignite
03-061	2909	222.4	$HgCl_2$ in ether	387				broad peak with narrow lip at top	Fly Ash		PRB Subbituminous
03-061	2927	277	$HgCl_2$ in ether	392					Fly Ash		PRB Subbituminous
03-063	1096	975.2	$HgCl_2$ in ether	307	450			very broad; 2nd peak on tail of 1st peak	Fly Ash		Eastern Bituminous
03-063	1097	479.4	$HgCl_2$ in ether	260				tailing peak	Fly Ash		Eastern Bituminous
03-081	2985	454.2	$HgCl_2$ in ether	320	664			Hg release continued when held at 750°C	Fly Ash		Fort Union Lignite
04-029	2911	331.8	$HgCl_2$ in ether	361				jagged peak	Fly Ash		PRB Subbituminous
04-033	2887	105	$HgCl_2$ in ether	331	475	498		all peaks very small	Fly Ash + Activated Carbon	Post-Primary PCD	Fort Union Lignite
04-035	2914	892.5	$HgCl_2$ in ether	351					Fly Ash		Fort Union Lignite
04-036	3024	777.1	$HgCl_2$ in ether	307	750				Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite
04-036	3026	774.2	$HgCl_2$ in ether	306					Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite
04-067	2903	393.9	$HgCl_2$ in ether	388					Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite
04-067	2929	506.7	$HgCl_2$ in ether	407	750				Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite
05-003	2899	205.7	$HgCl_2$ in ether	370					Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite
05-004	2900	298	$HgCl_2$ in ether	321					FGD-SDA + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite
05-005	2901	271	$HgCl_2$ in ether	376					Fly Ash		Fort Union Lignite
05-005	2923	519	$HgCl_2$ in ether	377				sample run through 100-mesh sieve	Fly Ash		Fort Union Lignite
05-010	3008	770.4	$HgCl_2$ in ether	286	382	750			Fly Ash		Eastern Bituminous
05-018	2996	885.6	$HgCl_2$ in ether	317	583				Fly Ash		Eastern Bituminous
05-018	3004	811.1	$HgCl_2$ in ether	313	496	569			Fly Ash		Eastern Bituminous
05-038	3055	800	$HgCl_2$ in ether	339	711				Fly Ash		Fort Union Lignite
Blank Tube	2889	1	$HgCl_2$ in ether								

ID No.	Run #	Sample Amount (mg)	Spiked with	Peak 1 (°C)	Peak 2 (°C)	Peak 3 (°C)	Peak 4 (°C)	Comments	Sample Type	Hg Control Configuration	Fuel Type
Blank Tube	2969	1	$HgCl_2$ in ether	408							
Blank Tube	2978	1	$HgCl_2$ in ether	287							
Blank Tube	2979	1	$HgCl_2$ in ether	132	228			very jagged			
Blank Tube	2980	1	$HgCl_2$ in ether	203	237	315		very jagged			
Quartz Powder	1093	513.6	$HgCl_2$ in ether	218	260				Quartz Powder		
Quartz Powder	1094	501.1	$HgCl_2$ in ether	219					Quartz Powder		
Quartz Sand	1092	511.2	$HgCl_2$ in ether	268					Quartz Sand		
Quartz Sand	1095	507.2	$HgCl_2$ in ether	264					Quartz Sand		
Quartz Sand	2894	1009.5	$HgCl_2$ in ether	175	218				Quartz Sand		
Quartz Sand	2895	1003.6	$HgCl_2$ in ether	285					Quartz Sand		
Quartz Sand	2896	1014.4	$HgCl_2$ in ether	270					Quartz Sand		
Quartz Sand	3085	492.2	$HgCl_2$ in ether	209					Quartz Sand		
Quartz Sand	3086	460.4	$HgCl_2$ in ether	189	750				Quartz Sand		
Quartz Sand	3087	501.6	$HgCl_2$ in ether	213	240	713			Quartz Sand		
Quartz Sand	3089	477.4	$HgCl_2$ in ether	193	236			very jagged	Quartz Sand		
Quartz Sand	3091	487	$HgCl_2$ in ether	173					Quartz Sand		
Quartz Sand	3092	497.2	$HgCl_2$ in ether	168	202	662	734	very jagged	Quartz Sand		
Quartz Sand	3093	495.2	$HgCl_2$ in ether	216					Quartz Sand		
Quartz Sand	3097	471.1	$HgCl_2$ in ether	191	228			very jagged	Quartz Sand		
Quartz Sand	3098	488	$HgCl_2$ in ether	200				very jagged	Quartz Sand		
Quartz Sand	3101	488.1	$HgCl_2$ in ether	199					Quartz Sand		
Quartz Sand	3102	478.6	$HgCl_2$ in ether	207	691			Hg release continued at 750°C	Quartz Sand		
Quartz Sand	3104	478.8	$HgCl_2$ in ether	199					Quartz Sand		
Quartz Sand	3105	482.2	$HgCl_2$ in ether	204					Quartz Sand		
Quartz Sand	3106	470.2	$HgCl_2$ in ether	190					Quartz Sand		
Quartz Sand	3109	489.5	$HgCl_2$ in ether	152	183				Quartz Sand		
Quartz Sand	3110	489.3	$HgCl_2$ in ether	197					Quartz Sand		
Quartz Sand	3111	496.6	$HgCl_2$ in ether	188					Quartz Sand		
Quartz Sand	3112	453.1	$HgCl_2$ in ether	202					Quartz Sand		
Quartz Sand	3113	476.1	$HgCl_2$ in ether	197					Quartz Sand		

APPENDIX R

MICROBIOLOGICALLY MEDIATED MERCURY AND AIR TOXIC ELEMENT RERELEASES FROM COAL COMBUSTION BY-PRODUCTS

MICROBIOLOGICALLY MEDIATED MERCURY AND AIR TOXIC ELEMENT RERELEASES FROM COAL COMBUSTION BY-PRODUCTS

Final Report

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MICROBIOLOGICALLY MEDIATED MERCURY AND AIR TOXIC ELEMENT RERELEASES FROM COAL COMBUSTION BY-PRODUCTS

ABSTRACT

Under an effort funded by the U.S. Department of Energy (DOE) and industry entitled "Mercury and Air Toxic Element Impacts of Coal Combustion By-Product Disposal and Utilization," the Energy & Environmental Research Center (EERC) is evaluating the impact of mercury and other air toxic elements on the management of coal combustion by-products (CCBs). The EERC is measuring the release of mercury and other air toxic elements under different controlled laboratory conditions and investigating the release of these same air toxic elements in select field settings. One of the potential release mechanisms under investigation, and the subject of this report, is the biologically mediated leachability and vapor release of mercury and other air toxic elements from CCBs.

This report includes a summary of the method development over the course of this project and the associated results. It also summarizes the various technical issues associated with performing the release experiments and the analyses of the mercury released in both the vapor and liquid phases. A preliminary interpretation of the results generated is also included, but a final data analysis and interpretation will be included in the final report for the ongoing project.

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MICROBIOLOGICALLY MEDIATED MERCURY AND AIR TOXIC ELEMENT RERELEASES FROM COAL COMBUSTION BY-PRODUCTS

EXECUTIVE SUMMARY

Under an effort funded by the U.S. Department of Energy (DOE) and industry entitled "Mercury and Air Toxic Element Impacts of Coal Combustion By-Product Disposal and Utilization," the Energy & Environmental Research Center (EERC) is evaluating the impact of mercury and other air toxic elements on the management of coal combustion by-products (CCBs). The EERC is measuring the release of mercury and other air toxic elements under different controlled laboratory conditions and investigating the release of these same air toxic elements in select field settings. One of the potential release mechanisms under investigation, and the subject of this report, is the biologically mediated leachability and vapor release of mercury and other air toxic elements from CCBs.

The EERC's method to evaluate the mercury release potential from CCBs by leaching and offgassing under microbiologically mediated conditions has undergone several modifications since it was first developed in 1999. The current apparatus uses a 9-place stir plate to facilitate mixing of the CCB, a buffer, and microbes. An improved buffer uses 100 ppm of phosphate and potassium glutamate as the nitrogen source. Early experiments with starved microbes did not promote microbial growth; therefore, all samples in later experiments were fed with glucose. An innoculum from a local brackish wetland added to 10 mL of 0.9% NaCl and vortexed was introduced to the samples. Sulfuric acid was added to neutralize alkaline samples prior to introducing the microbes. The sample mixtures were allowed to incubate in sealed flasks at room temperature for 4 weeks. Experiments were all performed in triplicate.

Several methods were used to collect, measure, and speciate the mercury release from CCBs. Vapor-phase organomercury compounds were trapped on Supelco Carbotrap™ collection traps, with the remaining mercury collected on gold-coated quartz collection traps. The Carbotrap™ collection traps were analyzed for total mercury by heating the trap to approximately 300°C, passing the released organomercury through a tube at about 800°C, and collecting the mercury vapor on a gold-coated quartz trap. All gold-coated quartz traps were desorbed for analysis by heating to approximately 500°C and determining the mass of mercury released with atomic fluorescence (AF). Total mercury concentrations of the leachate were determined using cold-vapor atomic fluorescence spectroscopy (CVAFS). Solid-phase microextraction (SPME) was used to determine organomercury species of the mercury present in leachates. The air toxic element—arsenic, cadmium, chromium, lead, nickel, and selenium—concentrations of the leachate were determined by inductively coupled plasma (ICP) and ICP–mass spectrometry (ICP–MS).

A variety of CCB samples were evaluated for microbiologically mediated mercury releases using the methods described. Aerobic and anaerobic glucose-fed conditions were used in the experiments on fly ash and wet limestone flue gas desulfurization (FGD) filter cake material. The fly ash samples evaluated were from eastern bituminous, subbituminous, and lignite coal-fired power plants, with total mercury contents ranging from 0.004–1.86 µg/g. The FGD material

had a 0.218-μg/g mercury content and a significant natural population of sulfate-reducing bacteria. Data collected to date are variable, and work will continue on the experimental release method and the analytical methods.

MICROBIOLOGICALLY MEDIATED MERCURY AND AIR TOXIC ELEMENT RERELEASES FROM COAL COMBUSTION BY-PRODUCTS

INTRODUCTION

The stability of mercury associated with coal combustion by-products (CCBs) has become a prominent question as the coal-fired utility industry develops and tests mercury emission controls that may consequently increase the mercury associated with CCBs. The reasons for evaluating the release of mercury from CCBs are 1) to determine if mercury captured on CCBs is stable or if it will be released, thus negating the purpose of the removal of the mercury from the emissions, and 2) to aid utilities in determining and understanding changes in CCBs associated with mercury control and associated CCB management.

Under an effort funded by the U.S. Department of Energy (DOE) and industry entitled "Mercury and Air Toxic Element Impacts of Coal Combustion By-Product Disposal and Utilization," the Energy & Environmental Research Center (EERC) is evaluating the impact of mercury and other air toxic elements on the management of CCBs. The EERC is measuring the release of mercury and other air toxic elements under different controlled laboratory conditions and investigating the release of these same air toxic elements in select field settings. Results will be used to determine if mercury released from CCBs, both as currently produced and as produced with mercury and other emission controls in place, will impact CCB management practices.

Laboratory tasks were designed to address three primary potential release mechanisms for mercury over the life cycle of CCBs in a variety of management scenarios. These release mechanisms are:

1. Direct leachability of air toxic constituents from CCBs.

2. Vapor release of mercury from CCBs at ambient and elevated temperatures.

3. Biologically mediated leachability and vapor release of mercury and other air toxic elements from CCBs.

This report focuses on the methods development for and results generated from microbiologically mediated experiments to measure rerelease of mercury from CCBs. This report includes a summary of the methods development over the course of this project and the associated results. It also summarizes the various technical issues associated with performing the release experiments and the analyses of the mercury released in both the vapor and liquid phases. A preliminary interpretation of the results generated is also included, but final data analysis and interpretation will be included in the final report for the ongoing project entitled "Mercury and Air Toxic Element Impacts of Coal Combustion By-Product Disposal and Utilization" Under which this work was performed.

BACKGROUND

A majority of mercury emission controls currently being developed and demonstrated in the United States are expected to result in reapportioning of mercury that was previously released to the atmosphere into CCBs. Research on CCBs has not previously focused on mercury, primarily because the levels of mercury were low and difficult to quantitate, but the potential for significantly increased levels of mercury to be present on CCBs, especially fly ash and FGD, has raised the question of its potential to be rereleased from the CCBs under standard management scenarios. This question should have been addressed prior to implementing mercury emission controls at coal-fired power plants because rerelease or emission from the CCBs could potentially negate the use of the mercury emission controls. Preliminary work in the area of direct leaching and direct vapor-phase rerelease of mercury from CCBs indicated that these releases were expected to be very low (1–5). However, the investigation of the microbiologically mediated rerelease of mercury from CCBs had only been initiated on a preliminary level when this project was developed (2–4). Since the chemistry of mercury is unique in that it can form extremely toxic organomercury compounds when exposed to a variety of microorganisms, the rerelease of mercury from CCBs exposed to microbes, including filamentous fungi, is of great interest both from the fundamental chemistry standpoint and from the CCB management standpoint.

There is a wide distribution and variety of microorganisms in the environment that can promote the rerelease of mercury from many sources including CCBs, and many of these microorganisms have been found to be present in CCB disposal sites and certainly are present in environments where CCBs may be used such as in combination with soils for various use applications. A wide variety of specific microbe interactions can affect key elements associated with CCBs, including oxidation/reduction and alkylation/dealkylation reactions. Additionally, in order for microbes to be metabolically active, a few constraints must be satisfied. These include a food source, water, and an appropriate pH. For some CCBs and in some CCB management scenarios, these criteria are unlikely to be met, but for scenarios where they can be met, laboratory experiments can be used to simulate appropriate scenarios. Designing these experiments is a challenge as reported previously by the EERC (2–4, 6). The experiments needed to address a variety of materials and take into consideration the microbiological processes that are expected to allow mercury to be rereleased from CCBs.

Microbiological processes that can affect mercury associated with CCBs are:

- Methylation–demethylation type reactions involving sulfate-reducing bacteria.

- Formation of:
  - Methylmercuric chloride.
  - Dimethyl mercury.
  - Ethylmercuric chloride.
  - Diethyl mercury.
  - Many possible others.

OBJECTIVES

The overall goal of the project under which this work was accomplished is to support continued environmentally responsible management of CCBs and appropriate federal regulation of CCBs. Results will provide an indication of appropriate utilization guidelines and disposal requirements. If the environmental performance of CCBs from conventional and advanced emission control systems is similar, it will facilitate the maintenance of current CCB markets and minimize the potential for an additional barrier to utilization of CCBs. If the environmental performance changes, the proposed project will facilitate an understanding of appropriate management options and provide direction for any future regulatory assessment of CCBs. Supporting objectives of the project are to 1) determine the release potential of selected air toxic elements, including mercury and other air toxic elements, from CCBs under specific environmental conditions; 2) increase the database of information on mercury and other air toxic element releases for CCBs; 3) develop comparative laboratory and field data; and 4) develop appropriate laboratory and field protocols.

The objective of this report is to provide information on the methods development for and results of experiments to evaluate the microbiologically mediated rerelease of mercury, arsenic, cadmium, chromium, lead, nickel, and selenium from CCBs. Primary work was accomplished on release of mercury.

METHODS

Early work at the EERC resulted in development of a preliminary method to determine vapor-phase rerelease of mercury from CCBs under microbiologically mediated conditions. Development of the method took into consideration the properties of CCBs, the chemistry of mercury, and the microbiological processes that could occur under CCB disposal or land application. The methodology, developed at the EERC, required the CCB or CCB–soil mixture to be buffered to near neutral with phosphate buffer. The sample was dosed with glucose as a carbon and energy source and salts to stimulate microbial growth and inoculated with a source of microbes. The inoculated sample is sparged with mercury-free gas (either air or argon) and monitored for the release of elements from the mixture.

In the EERC review of published data on the release of mercury from CCBs (1), it was reported that the method developed by the EERC was the only published method developed and demonstrated for use in evaluating the release of mercury from CCBs on exposure to natural biota. The EERC method has been under development since approximately 1999 and has undergone numerous modifications to achieve the goal of evaluating the mercury release potential by leaching and offgassing when CCBs are under microbiologically mediated conditions. The first experiments performed using early versions of the apparatus focused on mercury releases by offgassing. Over the duration of this project, it was decided that the apparatus and experiments could also be used to determine if microbiologically mediated leaching of mercury was occurring, and measurement of organomercury compounds and air toxic elements in leachate was included as part of the methods development and analysis.

Description of Initial Apparatus and Method

The first apparatus assembled to conduct microbiologically mediated vapor-phase mercury release used a 250-mL Erlenmeyer flask fitted with an impinger inlet/outlet tube with the inlet center shortened to 6 cm below the standard taper. Cylinder gas was passed through several sets of gold-coated quartz traps for mercury removal and admitted to each of the flasks through a gas distribution manifold that routed the gas through 0.25-mm gas chromatography (GC) capillary tubing to each of the individual flasks. A GC capillary length of approximately 60 cm, when pressurized to between 1 and 2 psig through a gas distribution manifold, provided a convenient means of regulating gas flow to approximately 2 cm^3/min. The gas passed mercury vapor from the head space of the flasks to a mercury vapor collection system at the outlet of the flasks, consisting of two traps. A gold-coated quartz trap (for collection of elemental mercury) and a Supelco Carbotrap™ (for collection of organomercury compounds) were used to collect mercury released in the vapor phase from the flasks.

The flasks were placed on a 16-flask wrist action shaker. The experimental matrix consisted of eight flasks under anaerobic conditions (using argon) and eight flasks under aerobic conditions (using breathing-quality air). In each set of eight flasks, two contained only buffer, three contained the CCB with buffer (starved), and three contained the CCB with buffer and glucose (fed). A 50-gram aliquot of CCB was placed in the flasks, and ~100 mL of a phosphate buffer (with or without glucose, as appropriate) was added to create a neutral pH. The CCB-containing flasks also had 100 µL of mixed bacterial culture added. The source of bacteria was a mixed bacterial inoculum from a brackish wetland. This setup is illustrated in Figure 1.

Figure 1. Early microbiologically mediated mercury vapor-phase collection apparatus utilizing a wrist action shaker to facilitate mixing.

Modifications of the Apparatus and Experimental Design

The apparatus as described underwent several iterations as difficulties were identified and solutions developed. The wrist-action shaker was abandoned, as it was inadequate to suspend the sample during the experiments. Instead of the wrist action shaker, samples were placed in Erlenmeyer flasks on a 9-place stir plate. This was operated for about 20 minutes every 3 hours to maintain sample agitation over the 30-day experiment period. Additionally, the sample size was reduced to 20 grams and the buffer increased to 135–150 mL to provide adequate sample volume for additional trace element analyses. The buffer composition was also altered. It was found that phosphate and nitrate interfered with a derivitization step in the determination of organomercury compounds in the solid-phase microextraction (SPME) process using gas chromatographic separation followed by detection of the mercury compounds by atomic fluorescence. This technique is described later. The original buffer utilized nominal concentrations of phosphate and nitrate salts. The improved buffer used only 100 ppm of phosphate and substituted potassium glutamate as the nitrogen source. This simple change appeared to remove the interferences. Additionally, later experiments did not involve the use of starved control samples. In current experiments, all samples are fed with glucose. Table 1 summarizes the modifications and indicates the experimental difficulties that the modifications were employed to correct or improve. The final experimental apparatus used for the majority of the project microbiological experiments is illustrated in Figure 2.

CCB Preparation Methods

Some CCBs, especially fly ash, can be alkaline in nature. CCB alkalinity can be attributed to the dissolution of alkaline metal oxides that react with water to generate net alkalinity. Water-soluble calcium content contributes most of a CCB's net alkalinity. This trend can be seen in the classification of fly ashes; Class C fly ash is enriched in Ca and Mg and subsequently generates pH values considerably higher than Class F fly ash (e.g., pH >10).

Table 1. Microbiological Rerelease Apparatus Modifications

Original Experiment or Apparatus Component	Difficulty or Unmet Need	Modified Experiment or Apparatus Component
Wrist Action Shaker, Continuous Shaking	Inadequate suspension of sample.	Magnetic stir plate, intermittent stirring.
50–80-gram Sample Size + ~100-mL Buffer	Inadequate volume of liquid to recover for leachate analysis.	~20 gram sample + 135–150 mL buffer.
Phosphate Nitrate Buffer Solution	Interference with the determination of the organomercury compounds in leachate.	Lower concentration of phosphate with potassium glutamate as nitrogen source.
Glucose-Fed and Starved Experiments	Starved experiments did not promote microbial growth so were deemed unnecessary.	All experiments fed with glucose.
Gold-Coated Quartz Trap Was Followed by Carbotrap at Gas Exit (only in Experiment 1)	Organomercury was trapped on the gold-coated quartz so organomercury could note be measured.	Carbotrap was followed by gold-coated quartz trap at gas exit.

Figure 2. Current microbiologically mediated mercury vapor-phase collection apparatus utilizing a stir plate to facilitate mixing.

In order for a CCB, or any material, to support biological activity, it must be near neutral pH. Microbiological activity of sulfate-reducing bacteria is viable only in the pH range of 6.5 to 8.5, requiring substantial neutralization of some CCBs. Prior to initiation of experiments, the buffer for that experiment was added to individual samples, pH of the ash–buffer mixture was measured, and an appropriate volume of acid was added over a period of time to achieve a neutral pH.

Microbiological Innoculum Growth Conditions and Media

Since the microbes that promote the release of mercury are ubiquitous, freshly collected sediment from a local brackish wetland was used as the innoculum. This innoculum contained a variety of microbes including both aerobic and anaerobic bacteria and, therefore, was identified as an appropriate innoculum. The source of the innoculum was the same for all experiments.

The innoculum was prepared by using 1 gram of sediment taken approximately 2 mm from the surface of the sample so that is was more likely that a high concentration of anaerobic organisms would be present. This sample was added to 10 mL of 0.9 % NaCl and vortexed. This suspension was then used to inoculate the CCB slurry samples.

Experimental Incubation Conditions

Samples were allowed to incubate in sealed flasks at room temperature for 4 weeks. Experiments were all performed in triplicate. Table 2 provides information on the incubation conditions for microbiological rerelease experiments performed under this project.

Table 2. Experimental Incubation Conditions

Experiment	Number of Samples Run in Triplicate	Apparatus Used	Acid Addition	Buffer	Ash-to-Buffer Ratio	Incubation Conditions
Experiment 1	1	Original apparatus		Phosphate/nitrate buffer	50 g to 94 mL	Anaerobic and aerobic both with glucose-fed and starved conditions
Experiment 2	1	Original apparatus		Phosphate/nitrate buffer	50 g to 100 mL	Anaerobic and aerobic both with glucose-fed and starved conditions
Experiment 3	1	Original apparatus	Phosphoric acid added to neutralize solution pH to allow microbial growth	Phosphate/nitrate buffer	80 g to 100 mL	Anaerobic and aerobic both with glucose-fed and starved conditions
Experiment 4	3	Modified apparatus	Sulfuric acid added to neutralize solution pH to allow microbial growth	Phosphate/glutamic acid buffer	20 g to 150 mL	Anaerobic and aerobic with glucose-fed conditions
Experiment 5	3	Modified apparatus	Sulfuric acid added to neutralize solution pH to allow microbial growth for fly ash samples	Phosphate/glutamic acid buffer	20 g to 150 mL	Anaerobic and aerobic with glucose-fed conditions; no bacterial innoculum for flue gas desulfurization (FGD) sample
Experiment 6	4	Modified apparatus	Sulfuric acid added to neutralize solution pH to allow microbial growth	Phosphate/glutamic acid buffer	18 g to 135 mL	Anaerobic and aerobic with glucose-fed conditions

Mercury Analyses

The mercury collected in the traps designed to collect mercury released in the vapor phase was quantitated at the conclusion of each experiment. The gold-coated quartz collection traps were desorbed for analysis by heating to approximately 500°C, and the mass of mercury released was determined using atomic fluorescence (AF) yielding a result indicating the elemental mercury vapor-phase release. The Carbotrap™ collection traps were analyzed for total mercury by heating the trap to approximately 300°C, passing the released organomercury through a tube at about 800°C, and collecting the mercury vapor on a gold-coated quartz trap, which was analyzed as described above. The result from this analysis was reported as vapor-phase organomercury released.

The leachate was separated from the sample in order to determine the concentrations of mercury in solution. Total mercury concentrations of the leachate were determined using CVAFS (cold-vapor atomic florescence spectroscopy).

In order to determine organomercury species of the mercury present in the leachates, SPME was used. SPME is a sample collection technique utilizing a fiber coated with polydimethylsiloxane. Samples containing organomercury compounds are first derivatized to increase the volatility of organomercury halides such as methylmercuric chloride. The derivitization reagents used were sodium tetraethyl borate, sodium tetrapropyl borate, and sodium tetraphenyl borate. Sodium tetraethyl borate was most commonly used. In the derivitization procedure, derivatizing agent, acetate buffer, an internal standard (usually propyl mercuric chloride), and sample were mixed in a septum-capped vial. In a relatively fast reaction, the halide is replaced with the appropriate alkyl or aryl group, depending on which derivatizing agent is chosen. A SPME fiber was inserted through the septum cap, and the sample was stirred using a Teflon-coated stir bar for 20 minutes. After this equilibration time, the SPME fiber was introduced into the heated inlet zone of a GC. Sample separation can be accomplished using a 0.53-mm capillary column 15 or 30 meters in length. The exit end of the column was connected to a heated quartz tube (800°C), and makeup helium gas was added to increase the total flow to between 25 and 30 mL per minute. The gas was then routed to an AF detector for determination of the separated mercury compounds.

Five mL of the liquid plus an aliquot of ethylmercuric chloride as an internal standard was placed into a 15-mL septum-capped nonactinic vial containing a Teflon-coated stir bar. 500 µL of a pH 4.5 acetate buffer was added followed by 200 µL of a 1% solution of sodium tetrapropylborate. SPME sampling was accomplished using a 100-µm polydimethylsiloxane-coated fiber and sampler from Supelco (Bellefonte, Pennsylvania). The head space was sampled for 20 minutes after which the SPME fiber was directly introduced into the GC.

Microbiological Analysis

Bacterial counts were performed upon completion of the experiments to determine if there were adequate active microbes present at the completion of the experiment to account for any mercury releases found. A 1-mL aliquot of solution was taken from each flask. The aqueous supernate was serially diluted in 0.1% sodium pyrophosphate buffer (pH 7) and then used to

inoculate a series of tubes containing 1% PTYG (peptone, tryptone, yeast extract, glucose) broth. The tubes were incubated at 25°C, and growth, as turbidity, was monitored over a 3-week period.

Of the 18 samples, half were grown under anaerobic conditions and the other half were grown under aerobic conditions. Ash samples were removed from the shaker table and a 1-mL aliquot was removed for further processing.

Prior to processing, the ash sample was stored in a flask at 4°C. When processing, 100 µL was removed and added to 9.9 mL sodium pyrophosphate (PP) buffer (0.1% w/v) pH 7.0 with three glass beads in each test tube. This was vortexed for 30 s then serially diluted into PP buffer (up to 1/1000 dilution). These dilutions were used to inoculate a 3-tube most probable number (MPN) assay with 1% peptone–tryptone–yeast extract–glucose (PTYG) buffer. 4 mL of PTYG were placed in each 13 × 100-mm tube along with innoculum and incubated at room temperature. Tubes and plates (peptone–yeast extract–glucose [PYG] agar) inoculated with samples from the anaerobic ash suspension were incubated under anaerobic conditions (anaerobic hood), and aerobic ash suspension samples were exposed to atmospheric oxygen. At week intervals, they were scored based on turbidity.

RESULTS AND DISCUSSION

A variety of CCB samples were evaluated for microbiologically mediated mercury releases using the methods described. The results of experiments are presented for each experiment so the results can be discussed relative to the methods modifications that were required over the course of the project. Samples included primarily coal combustion fly ash. A complete summary of the samples evaluated and identifying information is included in Appendix A.

Microbiologically Mediated Release of Mercury from CCBs – Experiment 1

The first microbiologically mediated mercury release experiment was performed on one CCB buffered to near neutral with a phosphate–nitrate buffer. The CCB tested in Experiment 1 is listed in Table 3. The sample was dosed with glucose as a carbon and energy source and salts to stimulate microbial growth and inoculated with a source of microbes. The inoculated sample was sparged with mercury-free gas and monitored for the release of mercury from the mixture. Mercury vapor-phase releases only were quantitated from Experiment 1.

The results from the experiment using Sample 99-188, a subbituminous fly ash neutralized prior to the experiment, are shown in Table 4. AF instrument problems resulted in incomplete results for the elemental mercury captured on some of the gold-coated quartz traps because of the

Table 3. CCB Sample Description and Total Mercury Content, Experiment 1

Sample	Sample Type	Coal Type	Mercury Control	Additional Information	Total Mercury, µg/g
99-188	Fly ash + FGD-SDA	Subbituminous	No	Neutralized	0.131

Table 4. Results of Microbiologically Released Mercury from Sample 99-188, Experiment 1

Anaerobic	Gold Trap Hg, pg	Gold Trap Hg, pg/g/day	Carbotrap™ Hg, pg	Carbotrap™ Hg, pg/g/day
Blank	3920	NA[a]	300	NA
Blank	3980	NA	190	NA
Fed	63,100	43.5	720	0.50
Fed	45,600[b]	31.5[b]	2320	1.60
Fed	69,200	47.7	4140[c]	2.86[c]
Starved	NT[d]	NT	1830	1.26
Starved	47,700[b]	32.9[b]	5620	3.88
Starved	66,300	45.7	2070	1.43
Aerobic				
Blank	23,700	NA	80	NA
Blank	16,500	NA	60	NA
Fed	31,500	1090	1060	36.5
Fed	61,300	2110	860	29.5
Fed	33,200	1140	1930	66.4
Starved	45,000	1550	660	22.8
Starved	42,200	1460	500	17.3
Starved	44,900	1550	890	30.8

[a] Not applicable.
[b] Low value because of analyzing conditions.
[c] High value because of analyzing conditions.
[d] Not tested.

unexpected high masses of mercury. The elemental mercury release results appear to be higher from the anaerobic condition. No trend is apparent for the organomercury results. This may be because the order of the gold-coated quartz and Carbotrap™ collection traps was incorrect. The gold-coated quartz traps were placed nearest the flask outlet during the experimentation; therefore, it is believed that some of the organomercury was trapped on the gold-coated quartz traps before the gas passed to the Carbotrap™ collection traps. The bacterial count showed more bacteria in the flasks in which the bacteria were fed glucose in both the anaerobic and aerobic conditions.

Microbiologically Mediated Release of Mercury from CCBs – Experiment 2

The second microbiologically mediated mercury release experiment was performed the same as Experiment 1, using Sample 01-002, described in Table 5.

Table 5. CCB Sample Description and Total Mercury Content, Experiment 2

Sample	Sample Type	Coal Type	Mercury Control	Total Mercury, µg/g
01-002	Fly ash	Eastern bituminous	No	0.234

The results from the experiment using Sample 01-002, an eastern bituminous fly ash, are shown in Table 6. The blank flasks, containing only buffer, yielded higher mercury release values than those containing the CCB slurry. The mercury release results show that more elemental mercury was released from flasks in which the bacteria were fed with glucose versus starved. These values are much lower than those from Sample 99-188, pg/g/day versus ng/g/day. The bacterial count results show that the bacteria were able to survive in the aerobic environment and that within the aerobic environment, the bacterial count was higher at the end of the experiment in the flasks where the bacteria were fed with glucose.

Microbiologically Mediated Release of Mercury from CCBs – Experiment 3

The third microbiologically mediated mercury release experiment was performed similarly to Experiments 1 and 2. However, phosphoric acid was added to the flasks to neutralize the slurry pH. The sample tested is shown in Table 7.

Table 6. Results of Microbiologically Released Mercury from Sample 01-002, Experiment 2

Anaerobic	Gold Trap Hg, pg	Gold Trap Hg, pg/g/day	Carbotrap™ Hg, pg	Carbotrap™ Hg, pg/g/day
Blank	1280	NAa	95.47	NA
Blank	2303	NA	203	NA
Fed	155	0.0968	13.45	0.00840
Fed	177.3	0.111	14.12	0.00882
Fed	376.9	0.236	12.66	0.00791
Starved	66.49	0.0415	13.16	0.00822
Starved	45[d]	0.0281	22.29	0.0139
Starved	56.28	0.0352	19.9	0.0124
Aerobic				
Blank	1096	NA	36.16	NA
Blank	1160	NA	44.52	NA
Fed	405.71	0.253	13.76	0.00860
Fed	1758	1.10	52[d]	0.0325
Fed	136.1	0.0851	13.16	0.00822
Starved	48[d]	0.0300	5.876	0.00367
Starved	79.39	0.0496	13.59	0.00849
Starved	30.48	0.0190	4.739	0.00296

Table 7. CCB Sample Description and Total Mercury Content, Experiment 3

Sample	Sample Type	Coal Type	Mercury Control	Total Mercury, µg/g
03-060	Fly ash	Subbituminous	Yes	1.86

Results from CCB 03-060, a subbituminous fly ash collected during a mercury control test, are shown in Table 8. These results show that elemental mercury is being released from the CCB-containing flasks in the aerobic environment in which the bacteria are fed with glucose. The mass of mercury released from the blank flasks in the aerobic environment was much lower than in the anaerobic environment.

The results of Experiments 1–3 (Tables 4, 6, and 8) showed some general trends. The mercury released from the CCB slurry was generally higher in the samples fed with glucose versus starved samples and in aerobic versus anaerobic conditions. The bacterial count followed a similar trend. The flasks containing buffer only were used as blanks.

Microbiologically Mediated Release of Mercury and Air Toxic Elements from CCBs – Experiment 4

Three samples (see Table 9) were evaluated under aerobic and anaerobic glucose-fed conditions in triplicate. A 20-gram sample, 150-mL buffer solution, a sample-dependent amount of sulfuric acid, and a 100-µL aliquot of a sulfate-reducing bacteria culture were used for evaluation. The bacteria were added 4 days after the addition of the buffer and acid to allow the systems to neutralize. The system was stirred intermittently over the duration of the experiment. Vapor-phase organomercury released from the system was captured in tubes containing Supelco Carbotrap™, and elemental mercury releases were captured on gold-coated quartz traps.

Three days after the bacteria was introduced to the experimental vessels, Sample 03-082 under anaerobic conditions exhibited notable changes. The CCB changed from a cream to a gray color, and a hydrogen sulfide smell was emanating from the flasks. The gas from these flasks was directed to flasks containing zinc acetate to capture the hydrogen sulfide being produced.

Table 8. Results of Microbiologically Mediated Release of Vapor-Phase Mercury and Total Bacterial Counts for Sample 03-060, Experiment 3

Anaerobic			Aerobic		
Condition	Elemental Mercury, pg/g/day	Organomercury, pg/g/day	Condition	Elemental Mercury, pg/g/day	Organomercury, pg/g/day
Fed	0.069	0.008	Fed	1.7	0.010
Fed	0.092	0.007	Fed	0.65	0.018
Fed	0.033	0.002	Fed	1.3	0.007
Starved	0.025	0.001	Starved	0.024	0.003
Starved	0.021	0.001	Starved	0.020	0.002
Starved	0.049	0.002	Starved	0.038	0.002

Table 9. CCB Sample Description and Total Mercury Content, Experiment 4

ID No.	Sample Type	Coal Type	Mercury Control	Total Mercury, µg/g
03-079	Fly ash	Lignite	No	0.785
03-082	FGD filtercake	Eastern bituminous	No	0.218
04-043	Fly ash	Lignite	No	0.689

Fifteen days after the addition of bacteria, crystal-like formations were noted on the liquid surface layer from Sample 04-043, two flasks under anaerobic and one under aerobic conditions.

In this experiment, 3 weeks elapsed before the addition of the buffer solution; therefore, the gold-coated quartz traps were analyzed to determine the amount of initial elemental mercury released from the samples in the interim period (see Table 10). Sample and blank flasks generally released similarly low quantities of mercury, but Sample 03-082 under aerobic conditions released significantly more elemental mercury than the other samples. This wet FGD sample was determined to contain a significant population of sulfate-reducing bacteria. The now mercury-free gold-coated quartz traps were then replaced on the flasks for collection of elemental mercury over the duration of the experiment.

Upon completion of the experiment, evaluations included pH, Eh, elemental and organomercury vapor releases, solution organomercury content, and solution elemental concentrations.

A description of the contents of each sample flask upon completion of the experiment is included in Table 11. After the liquid was filtered from the solid, the pH and Eh values were determined. For Samples 03-079 and 03-082, the pH was higher under anaerobic conditions than aerobic; the opposite was true for Sample 04-043. A greater amount of mold was noted in the Sample 04-043 aerobic flasks that yielded a higher pH.

Table 10. Initial Elemental Mercury Release, pg/g/day, Experiment 4

Anaerobic		Aerobic	
ID No.	Initial Elemental	ID No.	Initial Elemental
03-079	0.0534	03-079	0.0732
03-079	0.0417	03-079	0.0622
03-079	0.0358	03-079	0.0204
03-082	0.264	03-082	9.20
03-082	0.0341	03-082	9.29
03-082	0.178	03-082	9.83
04-043	0.0454	04-043	0.0313
04-043	0.0245	04-043	0.0356
04-043	0.0358	04-043	0.0588

[a] One flask broke; therefore, only two samples were evaluated.

Table 11. Results Including Eh, pH, and Ending Sample Description, Experiment 4

Anaerobic				Aerobic			
ID No.	Eh, mV	pH	Sample Description	ID No.	Eh, mV	pH	Sample Description
03-079	164	8.23	Black layer on top of clear liquid; liquid bubbles; brown ash	03-079	374	8.09	Very slightly brown liquid; black and brown coatings on flask; dark brown ash
03-079	179	8.30	Black layer on top of clear liquid; liquid bubbles; brown ash	03-079	314	8.02	Film on top of liquid; very slightly brown liquid; black and brown coatings on flask; dark brown ash
03-079	189	8.45	Black layer on top of clear liquid; liquid bubbles; brown ash	03-079	354	7.97	Two spots of mold; film on top of liquid; very slightly brown liquid; black and brown coatings on flask; dark brown ash
03-082	−176	8.39	Gray liquid and ash; H_2S smell; crusted bubbles on top of liquid—round on top and broken on bottom	03-082	[a]	[a]	[a]
03-082	−161	8.55	Gray liquid and ash; H_2S smell; slightly crusted bubbles on top of liquid	03-082	39	7.89	Slightly gray liquid with gold crust on top; smelled like baby formula; gray ash
03-082	−146	8.51	Gray liquid and ash; H_2S smell; slimy on top of liquid	03-082	44	7.92	Slightly yellow liquid; smelled like baby formula; gray ash
04-043	164	6.85	Some carbon particles on top of clear liquid; no noticeable smell; grayish-brown ash	04-043	354	7.61	Layer of mold on top of slightly gray liquid confirmed by smell; grayish-brown ash
04-043	154	6.95	Some carbon particles on top of clear liquid; no noticeable smell; grayish-brown ash	04-043	279	7.15	No mold smell; grayish liquid; carbon granules on top of liquid; grayish-brown ash
04-043	149	6.81	Some carbon particles on top of clear liquid; no noticeable smell; grayish-brown ash	04-043	134	7.36	Patch of mold on top of gray liquid; grayish-brown ash

[a] One flask broke; therefore, only two samples were evaluated.

The results from the three samples evaluated under the modified method are shown in Table 12 and reported as picograms of mercury per grams of CCB. In some instances, the results were highly variable for the replicate flasks. The highest release of both elemental and organomercury was from Sample 03-082 under aerobic conditions. Analysis of the gold-coated quartz traps from Sample 03-082 under anaerobic conditions resulted in a white, sulfur-smelling deposit on the gold trap. Analyzing the Carbotrap™ tubes from Sample 03-082 aerobic condition caused a sulfur smell to be released with no deposit formed. Analyzing the Carbotrap™ tubes from Sample 03-082 anaerobic condition resulted in a noticeable sulfur-smelling smoke to be released, and a subsequent formation of a white- to yellow-colored deposit on both the Carbotrap™ and pyrolysis tube. The amount of vapor-phase elemental mercury released coincided with the amount of mold present in the Sample 04-043 aerobic flasks at the completion of the experiment.

SPME was used to determine organomercury compounds in the liquid remaining in the flasks after the experimental collection period. Results are shown in Table 13.

Solution elemental concentrations are shown in Table 14.

Microbiologically Mediated Release of Mercury and Air Toxic Elements from CCBs – Experiment 5

Three samples (Table 15) were evaluated in aerobic and anaerobic glucose-fed conditions in triplicate. A 20-g sample, a 150-mL buffer solution, a sample-dependent amount of sulfuric acid, and a 100-µL aliquot of a sulfate-reducing bacteria culture were used for evaluation. The experimental systems were brought to a neutral pH by addition of the buffer solution and sulfuric acid. The bacteria were added after neutral pH conditions were found to be stable. The remainder of the protocol and setup were the same as in Experiment 4 for Samples 04-035 and 04-036. Samples 04-035 and 04-036 were a paired sample set, collected before and during mercury emission control testing, respectively. Sample 03-082, a moist FGD sample evaluated in

Table 12. Vapor-Phase Mercury Release Results, Experiment 4

Anaerobic			Aerobic		
ID No.	Elemental Mercury, pg/g	Organomercury, pg/g	ID No.	Elemental Mercury, pg/g	Organomercury, pg/g
03-079	4.1	5.7	03-079	14.7	9.1
03-079	2.8	5.0	03-079	11.3	30.8
03-079	5.3	6.7	03-079	19.8	2.5
03-082	12.7	41.3	03-082	[a]	[a]
03-082	0.7	2.6	03-082	486	90.0
03-082	1.5	102	03-082	648	110
04-043	1.3	1.1	04-043	46.5	4.5
04-043	2.2	0.6	04-043	4.0	1.4
04-043	1.9	1.0	04-043	9.1	1.3

[a] One flask broke; therefore, only two samples were evaluated.

Table 13. Solution Organomercury Results, Experiment 4

Anaerobic			Aerobic		
ID No.	Methylmercury Measured, pg/mL	Methylmercury Released, pg/g/day	ID No.	Methylmercury Measured, pg/mL	Methylmercury Released, pg/g/day
03-079	13	2.65	03-079	32	6.67
03-079	15	3.05	03-079	7	1.47
03-079	<5	<1	03-079	12	2.50
03-082	[a]	[a]	03-082	[b]	[b]
03-082	250	50.7	03-082	18	3.75
03-082	[a]	[a]	03-082	99	20.6
04-043	31	6.30	04-043	<5	<1
04-043	19	3.86	04-043	65	13.6
04-043	18	3.65	04-043	13	2.72

[a] Samples precipitated colloidal sulfur on standing and were not analyzed.
[b] One flask broke; therefore, only two samples were evaluated.

Table 14. Leached Total Trace Element Results, µg/L, Experiment 4

Anaerobic								Aerobic							
ID No.	As	Cd	Cr	Pb	Hg	Ni	Se	ID No.	As	Cd	Cr	Pb	Hg	Ni	Se
03-079	99	15	10	<2.0	0.15	350	200	03-079	76	16	2.0	<2.0	<0.01	24	48
03-079	95	15	9.6	<2.0	<0.01	330	200	03-079	49	17	<2.0	<2.0	0.095	36	37
03-079	87	16	8.8	<2.0	<0.01	320	190	03-079	56	17	2.0	<2.0	<0.01	27	14
03-082	12	<0.2	7.7	<2.0	[a]	25	16	03-082	[b]	[b]	[b]	[b]	[b]	[b]	[b]
03-082	14	<0.2	20	<2.0	[a]	25	9.9	03-082	17	<0.2	37	<2.0	0.024	33	17
03-082	11	<0.2	6.8	<2.0	[a]	27	8.5	03-082	28	<0.2	11	<2.0	0.070	31	20
04-043	12	5.5	8.0	<2.0	<0.01	260	79	04-043	140	5.9	7.1	<2.0	0.020	140	190
04-043	11	5.2	7.8	<2.0	<0.01	250	79	04-043	90	4.2	3.8	<2.0	4.9	130	170
04-043	11	4.7	7.7	<2.0	<0.01	250	78	04-043	71	3.4	3.8	<2.0	0.013	100	210

[a] Samples precipitated colloidal sulfur on standing and were not analyzed.
[b] One flask broke; therefore, only two samples were evaluated.

Table 15. Samples Included in Microbiological Release Experiment 5

ID No.	Sample Type	Coal Type	Mercury Control	Total Hg, µg/g
03-082	FGD filtercake	Eastern bituminous	No	0.218
04-035	Fly ash	Lignite	No	0.160
04-036	Fly ash	Lignite	Yes	0.287

Experiment 4, required minor revisions to the protocol. The amount of sample was increased from 20 to 22 g to account for the moisture present, and no acid or bacteria were added to this sample. Sulfate-reducing bacteria were found to be present in the sample as received, and this experiment was designed to take advantage of these natural conditions to serve as a comparison to the experiment run previously under the standard protocol.

Upon completion of the experiment, evaluations included pH, Eh, elemental and organomercury vapor releases, solution mercury and trace element concentrations, and a bacterial count.

Vapor-phase elemental and organomercury releases were determined using the method described earlier.

Sample 03-082 under anaerobic conditions changed from a cream color to gray and began to release hydrogen sulfide within 5 days of buffer addition. As noted previously, this sample was not inoculated and had no acid addition. In the previous experiment, this sample was inoculated 4 days after buffer and acid addition, with hydrogen sulfide release 3 days after inoculation. Therefore, it appears that the pH of Sample 03-082 with the buffer addition and the natural bacteria in the sample is sufficient to produce hydrogen sulfide.

The results for Experiment 5 are shown in Tables 16–19. A summary of microbiological results for the anaerobic and aerobic experiments is noted in Figure 3.

Table 16. Microbiological Eh and pH Results, Experiment 5

Anaerobic			Aerobic		
ID No.	Eh, mV	pH	ID No.	Eh, mV	pH
03-082	−10	8.52	03-082	92	7.81
03-082	−94	8.52	03-082	81	7.83
03-082	105	8.41	03-082	86	7.83
04-035	−11	11.26	04-035	12	10.56
04-035	−21	11.17	04-035	10	10.39
04-035	−13	11.20	04-035	−10	10.53
04-036	−8	11.29	04-036	−25	10.74
04-036	−14	11.14	04-036	−3	10.68
04-036	−12	11.25	04-036	−18	10.53

Table 17. Vapor-Phase Mercury Release Results, pg/g/day, Experiment 5

Anaerobic			Aerobic		
ID No.	Elemental Mercury	Organomercury	ID No.	Elemental Mercury	Organomercury
03-082	NT*	NT	03-082	4.64	0.935
03-082	1.54	NT	03-082	9.69	1.62
03-082	NT	NT	03-082	8.98	1.01
04-035	0.0279	0.0364	04-035	0.190	0.113
04-035	0.0366	0.0251	04-035	0.150	0.0876
04-035	0.0317	0.135	04-035	0.202	0.0153
04-036	0.0352	0.0242	04-036	0.449	0.0482
04-036	0.147	0.0815	04-036	0.265	0.111
04-036	0.516	0.139	04-036	0.374	0.0723

* Not tested.

Table 18. Microbiological Leached Total Trace Element Results, µg/L

Anaerobic								Aerobic							
ID No.	As	Cd	Cr	Pb	Hg	Ni	Se	ID No.	As	Cd	Cr	Pb	Hg	Ni	Se
03-082	56	0.36	15	<2.0	0.034	22	23	03-082	14	0.35	13	<2.0	0.018	28	26
03-082	7.9	0.32	14	<2.0	0.041	16	3.8	03-082	19	0.35	15	<2.0	0.014	39	34
03-082	96	0.31	16	<2.0	0.036	18	22	03-082	26	0.34	13	<2.0	0.037	22	30
04-035	NT*	NT	NT	NT	NT	NT	NT	04-035	NT	NT	NT	NT	NT	NT	NT
04-036	NT	NT	NT	NT	NT	NT	NT	04-036	NT	NT	NT	NT	NT	NT	NT

* Not tested.

Table 19. Microbiological Buffer Total Trace Element Results, µg/L

Element	As	Cd	Cr	Pb	Hg	Ni	Se
Concentration	<2.0	0.41	18	<2.0	<0.01	<2.0	<2.0

Anaerobic

Samples 04-035 and 04-036 exhibited no growth in either the broth or plates. Sample 03-082 did show growth in PTYG broth. A bright yellow color to the media in the test tubes indicated the presence of sulfur-reducing bacteria, especially one flask of Sample 03-082. Cell density was not determined in this sample, and the plates for this sample's dilution exhibited no growth.

Aerobic

Samples 04-035 and 04-036 exhibited no growth on either broth or plates.

Sample 03-082 plate counts indicated cell density in excess of 25 million cells per mL in the original sample. When the MPN was performed on the dilution samples in PTYG broth, they indicated cell densities in agreement with the plate counts.

Figure 3. Summary of microbiological results.

It is likely that for the samples (04-035 and 04-036) that did not exhibit growth, it was due largely to pH fluctuations occurring during the fly ash slurry portion of the experiment. Results of leachate mercury and air toxic element concentrations are found in Table 18. The leachate from Samples 04-035 and 04-036 was not tested because of the excessive pH levels. The microbiological buffer was tested for the same elements (Table 19). Mercury mobilization can be correlated with growth of microorganisms.

Microbiologically Mediated Release of Mercury from CCBs – Experiment 6

A sixth experiment was initiated to evaluate four samples (Table 20) under aerobic and anaerobic glucose-fed conditions in triplicate. The latest method was modified slightly. An 18-g (instead of 20-g) sample, a 135-mL (instead of 150-mL) buffer solution, and a 100-µL aliquot of a sulfate-reducing bacteria culture were used for evaluation. The sample and buffer aliquots were

Table 20. Samples Included in Microbiological Release Experiment 6

ID No.	Coal Type	Sample Type	Mercury Control	Total Hg, µg/g
04-035	Lignite	Fly ash	No	0.160
04-036	Lignite	Fly ash	Yes	0.287
05-001	Lignite	Fly ash	No	0.004
05-003	Lignite	Fly ash	Yes	0.565

reduced to allow for more sulfuric acid, but the ratio of sample to buffer solution was maintained. A sample-dependent amount of sulfuric acid was added over an extended period of time instead of within 1 day. The bacteria were added after the addition of the buffer and acid to allow the systems to neutralize. The system was stirred intermittently over the duration of the experiment.

The samples evaluated consisted of two paired sample sets, collected before and during mercury control testing. Samples 04-035 and 04-036 were repeated from the previous experiment because the pH had risen above the acceptable pH range for bacterial survival by the end of the previous experiment.

Acid addition over an extended period was attempted to maintain an acceptable pH level over the duration of the last 30-day experiment. However, the pH of an aerobic sample measured 10.5 at the 20-day mark, which was significantly above the acceptable range of 6.5–8.5 for bacterial survival. The pH of all samples exceeded 10.5, which killed the bacteria. A pH adjustment of all samples was attempted for reinoculation of bacteria but was unsuccessful, and this experiment was aborted because the samples could not be pH-adjusted to an appropriate range to support microbial activity.

OBSERVATIONS AND CONCLUSIONS

As noted throughout this report, the laboratory development of the method used and its application to a variety of samples offered significant challenges. Major challenges were:

- High blank values from the buffer solutions.
- Generation of hydrogen sulfide from high-sulfur samples, resulting in poisoning of the analytical traps.
- Difficulty in maintaining a neutral pH, and associated microbial growth, in samples with an initially high pH.
- Growth of fungi in addition to bacterial growth in some samples.
- Difficulty in maintaining constant gas flow to a large number of sample containers, which was solved by use of GC capillary tubing.
- Difficulty in keeping samples suspended.

Several general conclusions can be drawn from the work presented in this report.

The formation of organomercury compounds was evident in all of the microbiologically mediated experiments. Unexpectedly, the greatest releases were found under aerobic conditions. This has been tentatively related to fungal action but has not yet been verified. It has been observed, however, that organomercury formation appears to be directly related to the amount of fungi present in the flasks at the end of the experiments. It had been expected that sulfate-reducing bacteria, known to be present in our innoculum and in FGD material samples, would be the primary source of methylation.

Sulfate-reducing bacteria in sulfur-rich samples such as FGD material tended to form large amounts of hydrogen sulfide in the anaerobic flasks. This hydrogen sulfide production required putting traps on the flasks in order to keep the hydrogen sulfide and its odor out of the lab. The hydrogen sulfide also made analyses impossible because of the formation of colloidal sulfur soon after the samples were harvested. Additionally, hydrogen sulfide collected in the Carbotrap™ tubes, came off as elemental sulfur and precluded analyses of these traps in our normal manner. This analytical problem is under investigation, but no solution has yet been developed.

A further modification to our protocol will involve using a distillation step in the determination of organomercury in aqueous samples. This will eliminate matrix effects in the derivitization step used just prior to analysis by gas chromatography.

Highly alkaline ash samples generated from lignite have proven particularly difficult to maintain at near neutrality. Experiments performed in the absence of bacteria provide us with a neutralization capacity for acid addition, but in microbiological experiments, these neutralized solutions quickly rise to above pH 10.5, thus killing the bacteria. We have been using dilute sulfuric acid for neutralization and believe that after neutralization, a sulfate coating has deposited around individual particles. After bacteria are introduced, we believe that the bacterial action may be removing the protective sulfate coating from alkaline particles thus releasing additional alkalinity. At this time, this is our only working hypothesis and solutions based on this hypothesis are under investigation.

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APPENDIX A

MICROBIOLOGICAL SAMPLE SET

pH = pH too low.
IS = Insufficient sample.
LP/SOW = Low priority, analysis was not part of the proposed statement of work.
LP/ID = Low priority, insufficient sample identification information.
NA = Not applicable.

ID No.	Sample Type	Coal Type	Hg Control	Hg (µg/g)	pH	LOI	Hg Total	Total Trace	SGLP	30-day LTL	60-day LTL	Thermal Curve	Long-Term Ambient	Microbiological	Carbon Forms
99-188	Fly ash + FGD–SDA	Subbituminous	No	0.112	12.34	2.07%	Completed	Completed	Completed	Completed	Completed	Underway	Completed	Completed	LP/SOW
01-002	Fly ash	Eastern bituminous	No	0.187	4.03	6.05%	Completed						Completed	Completed	LP/SOW
03-060	Fly ash	Subbituminous	Yes	1.86	11.32	2.28%	Completed	Completed	Completed	Completed	Completed	Underway	Completed	Completed	Completed
03-079	Fly ash	Lignite	No	0.785	11.72	2.54%	Completed	Completed	Completed	Completed	Completed	Underway	IS	Completed	Completed
03-082	FGD filtercake	Eastern bituminous	No	0.218	7.47	4.20%	Completed	Completed	Completed	Completed	Completed	Pending	Underway	Completed	NA
04-035	Fly ash	Lignite	No	0.159	12.68	2.24%	Completed	Completed	Completed	Completed	Completed	Completed	Underway	Pending	LP/SOW
04-036	Fly ash	Lignite	Yes	0.287	12.64	2.16%	Completed	Completed	Completed	Completed	Completed	Completed	Underway	Pending	LP/SOW
04-043	Fly ash	Lignite	No	0.689	11.48	Pending	Completed	Pending	Pending	Pending	Pending	Pending	IS	Completed	LP/SOW
05-001	Fly ash	Lignite	No	< 0.005	12.84	0.90%	Completed	Completed	Underway	Pending	Pending	Underway	Pending	Pending	LP/SOW
05-003	Fly ash	Lignite	Yes	0.565	12.85	1.04%	Completed	Completed	Underway	Pending	Pending	Underway	Pending	Pending	LP/SOW

APPENDIX S

MICROBIOLOGICALLY MEDIATED LEACHING AND VAPOR-PHASE TRANSPORT TASK SAMPLE SET

ID No.	Sample Type	Hg Control Configuration	Coal Type	Hg (µg/g)	10–15-Min pH, Avg.	24-Hr pH	Avg. LOI, %
99-188	FGD-SDA		PRB Subbituminous	0.112	12.38	12.22	2.07%
01-002	Fly Ash		Eastern Bituminous	0.187	3.90	NT	6.05%
03-006	Fly Ash		Eastern Bituminous	0.194	4.71	6.78	5.24%
03-007	Fly Ash		Eastern Bituminous	0.141	4.27	5.52	4.48%
03-060	Fly Ash + Activated Carbon	Pre-Primary PCD	PRB Subbituminous	1.86	11.32	11.90	2.37%
03-079	Fly Ash		Fort Union Lignite	0.785	11.77	11.62	2.54%
03-082	FGD Filtercake		Eastern Bituminous	0.233	7.83	7.85	4.86%
04-003	Fly Ash		Eastern Bituminous	0.685	9.35	8.54	8.45%
04-035	Fly Ash		Fort Union Lignite	0.159	12.73	12.74	2.46%
04-036	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI Pre-Primary PCD	Fort Union Lignite	0.287	12.72	12.77	2.33%
04-043	Fly Ash		Gulf Coast Lignite	0.689	11.65	11.28	NT
05-001	Fly Ash		Fort Union Lignite	<0.01	12.67	12.51	0.90%
05-003	Fly Ash + Enhancing Agent + Activated Carbon	Enhancing Agent on Coal, ACI before SDA	Fort Union Lignite	0.565	12.62	12.29	1.04%
05-018	Fly Ash		Eastern Bituminous	0.123	7.49	8.49	3.01%

APPENDIX T

FIELD INVESTIGATIONS TASK SAMPLE SET AND FUNDAMENTAL CHARACTERIZATION DATA

ID No.	Field Task	Sample Type Notes	Hg (µg/g)	10–15-Min pH	Overnight pH	24-Hr pH	Moisture Content, %	LOI, %
04-055	1	Fly ash	<0.01	9.36	9.13		15.0%	5.73%
04-056	1	Wet FGD material + mill rejects	0.188	8.62	8.51		21.3%	3.31%
04-057	1	Wet FGD material + mill rejects	0.207	8.68	8.53		19.3%	2.18%
04-058	1	Background Soil from Natural Grasslands	0.050	8.57	8.40		12.6%	6.88%
04-059	1	Bottom ash/mill rejects + wet FGD material	0.044	8.77	9.29		7.02%	1.99%
04-060	1	Wet FGD material	0.299	8.55	8.27		23.3%	2.49%
04-061	1	Bottom ash/mill rejects + wet FGD material	<0.01	9.08	9.72		16.2%	12.9%
04-062	1	Bottom ash/mill rejects + wet FGD material	<0.01	9.78	10.33		28.8%	7.73%
04-063	1	Stabilized wet FGD material (with fly ash)	0.080	8.94	9.14		15.0%	3.40%
04-064	1	Stabilized wet FGD material (with fly ash)	0.250	8.72	8.63		23.5%	2.68%
04-065	1	Stabilized wet FGD material (with fly ash)	0.011	10.33	10.81		10.1%	3.68%
06-014	2	soil-peat moss mix	0.067	7.42		7.48	38.5%	44.2%

APPENDIX U

ALTERNATE FIELD TASK DATA

Table U-3. CCB–Soil Experiment Organomercury Results Compared to Soil

ID No.	Replicate	Period	Calculated CCB–Soil Mixture Hg Total (µg/g)	No. Days in Testing Period	OrganoHg Release Rate in Testing Period Compared to Soil (pg/g/day)	% OrganoHg Released Over Testing Period (From Calculated Total Hg) Compared to Soil	Years to Release 100% Calculated CCB–Soil Mixture Hg at Measured Rate Compared to Soil	Above or Below Soil Release over Testing Period	Experiment Duration, Days	Cumulative OrganoHg Release Rate in Testing Period Compared to Soil (pg/g/day)	Cumulative % OrganoHg Released Over Testing Period (From Calculated Total Hg) Compared to Soil	Years to Release 100% Calculated CCB–Soil Mixture Hg at Measured Rate Compared to Soil	Above or Below Soil Release over Experiment
03-060	1	1	0.426	19	-0.0047	-0.000021%	-249,006	Below					
03-060	1	2	0.426	22	-0.0008	-0.000004%	-1,437,004	Below					
03-060	1	3	0.426	49	-0.0190	-0.000219%	-61,439	Below					
03-060	1	4	0.426	77	-0.0005	-0.000009%	-2,263,313	Below	167	-0.0063	-0.000248%	-184,590	Below
03-060	2	1	0.425	19	-0.0038	-0.000017%	-306,627	Below					
03-060	2	2	0.425	22	-0.0007	-0.000004%	-1,675,948	Below					
03-060	2	3	0.425	49	-0.0200	-0.000230%	-58,307	Below					
03-060	2	4	0.425	77	-0.0008	-0.000015%	-1,422,466	Below	167	-0.0066	-0.000261%	-175,583	Below
04-003	1	1	0.190	19	-0.0038	-0.000038%	-136,582	Below					
04-003	1	2	0.190	22	-0.0001	-0.000001%	-4,499,912	Below					
04-003	1	3	0.190	49	-0.0095	-0.000243%	-55,157	Below					
04-003	1	4	0.190	78	0.0393	0.00161%	13,273	Above	168	0.0151	0.00134%	34,465	Above
04-003	2	1	0.190	19	-0.0037	-0.000037%	-142,075	Below					
04-003	2	2	0.190	22	0.0003	0.000004%	1,665,484	Above					
04-003	2	3	0.190	49	0.0006	0.000015%	923,520	Above					
04-003	2	4	0.190	79	0.0239	0.000990%	21,857	Above	169	0.0110	0.000977%	47,396	Above
04-029	1	1	0.106	15	0.0003	0.000005%	884,116	Above					
04-029	1	2	0.106	25	-0.0002	-0.000006%	-1,232,013	Below					
04-029	1	3	0.106	50	-0.0159	-0.000753%	-18,201	Below					
04-029	1	4	0.106	79	0.0029	0.000215%	100,622	Above	169	-0.0033	-0.000531%	-87,154	Below
04-029	2	1	0.106	15	-0.0004	-0.000006%	-720,231	Below					
04-029	2	2	0.106	26	0.0019	0.000047%	150,686	Above					
04-029	2	3	0.106	49	-0.0160	-0.000744%	-18,046	Below					
04-029	2	4	0.106	79	0.0031	0.000233%	92,817	Above	169	-0.0030	-0.000481%	-96,166	Below
04-054	1	1	3.60	19	-0.0039	-0.000002%	-2,551,068	Below					
04-054	1	2	3.60	22	-0.0001	0.000000%	-146,858,672	Below					
04-054	1	3	3.60	49	-0.0136	-0.000019%	-723,001	Below					
04-054	1	4	3.60	81	0.0037	0.000008%	2,645,740	Above	171	-0.0026	-0.000012%	-3,804,226	Below
04-054	2	1	3.60	19	-0.0043	-0.000002%	-2,313,976	Below					
04-054	2	2	3.60	22	-0.0002	0.000000%	-50,784,241	Below					
04-054	2	3	3.60	49	-0.0147	-0.000020%	-671,982	Below					
04-054	2	4	3.60	81	0.0008	0.000002%	12,857,511	Above	171	-0.0044	-0.000021%	-2,266,176	Below
05-009	1	1	0.060	19	-0.0033	-0.000105%	-49,631	Below					
05-009	1	2	0.060	23	0.0002	0.000008%	811,862	Above					
05-009	1	3	0.060	48	-0.0190	-0.00152%	-8,632	Below					
05-009	1	4	0.060	78	0.0093	0.00121%	17,649	Above	168	-0.0015	-0.000418%	-110,120	Below
05-009	2	1	0.060	19	-0.0033	-0.000105%	-49,790	Below					
05-009	2	2	0.060	23	0.0002	0.000006%	1,001,620	Above					
05-009	2	3	0.060	48	0.0047	0.000376%	34,951	Above					
05-009	2	4	0.060	78	0.0254	0.00331%	6,456	Above	168	0.0127	0.00358%	12,858	Above
05-025	1	1	2.58	19	0.0034	0.000003%	2,060,761	Above					
05-025	1	2	2.58	21	0.0057	0.000005%	1,239,898	Above					
05-025	1	3	2.58	50	-0.0092	-0.000018%	-771,837	Below					
05-025	1	4	2.58	82	0.0125	0.000040%	565,151	Above	172	0.0044	0.000030%	1,588,470	Above
05-025	2	1	2.58	19	-0.0038	-0.000003%	-1,843,196	Below					

ID No.	Replicate	Period	Calculated CCB–Soil Mixture Hg Total (µg/g)	No. Days in Testing Period	OrganoHg Release Rate in Testing Period Compared to Soil (pg/g/day)	% OrganoHg Released Over Testing Period (From Calculated Total Hg) Compared to Soil	Years to Release 100% Calculated CCB–Soil Mixture Hg at Measured Rate Compared to Soil	Above or Below Soil Release over Testing Period	Experiment Duration, Days	Cumulative OrganoHg Release Rate in Testing Period Compared to Soil (pg/g/day)	Cumulative % OrganoHg Released Over Testing Period (From Calculated Total Hg) Compared to Soil	Years to Release 100% Calculated CCB–Soil Mixture Hg at Measured Rate Compared to Soil	Above or Below Soil Release over Experiment
05-025	2	2	2.58	21	0.0004	0.000000%	16,069,573	Above					
05-025	2	3	2.58	50	-0.0053	-0.000010%	-1,344,485	Below					
05-025	2	4	2.58	82	0.0004	0.000001%	17,531,901	Above	172	-0.0016	-0.000011%	-4,332,263	Below
05-038	1	1	0.074	15	-0.0022	-0.000044%	-92,695	Below					
05-038	1	2	0.074	25	-0.0002	-0.000005%	-1,350,142	Below					
05-038	1	3	0.074	49	-0.0170	-0.00113%	-11,913	Below					
05-038	1	4	0.074	79	-0.0005	-0.000059%	-369,850	Below	168	-0.0055	-0.00124%	-37,037	Below
06-014	1	1	0.067	15									
06-014	1	2	0.067	25									
06-014	1	3	0.067	49									
06-014	1	4	0.067	78					167				