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

Year 1 Annual Report

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

ABSTRACT

This effort is focused on the evaluation of coal combustion by-products (CCBs) for their potential to release mercury and other air toxic elements under different controlled laboratory conditions and investigate the release of these same air toxic elements in select disposal and utilization field settings to understand the impact of various emission control technologies. Information collected during Year 1 was evaluated and interpreted together with past Energy & Environmental Research Center data and similar data from other studies. Results were used to determine if mercury release from CCBs, both as currently produced and produced with mercury and other emission controls in place, is a realistic environmental issue.

The 3-year project was designed to develop baseline information on release mechanisms of select elements in both conventional CCBs and modified or experimental CCBs. In Year 1, the modified or experimental CCBs were selected to represent CCBs from systems that have improved emission controls. Controlling these emissions has a high potential to change the chemical characteristics and environmental performance of CCBs.

The development of reliable methods to determine the release of mercury from CCBs provided a means of evaluating the environmental risk associated with CCB management practices. Using appropriate methods to develop a data set of currently produced CCBs and CCBs produced under experimental/simulated conditions provided a baseline for the CCB industry to understand the impact of various emission control technologies.

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

EXECUTIVE SUMMARY

This 3-year project was designed to develop baseline information on release mechanisms of select elements in both conventional coal combustion by-products (CCBs) and CCBs generated from laboratory-, bench-, and full-scale mercury emission control technologies.

Over the duration of the planned effort, the study of three mechanisms of release of mercury and air toxic elements from CCBs were proposed. These are 1) direct leachability, 2) vapor release of mercury at ambient and elevated temperatures, and 3) biologically mediated leachability and vapor release of Hg and other air toxic elements.

In Year 1, the project activities focused on:

- Assembling literature to facilitate sample and methods selection.
- Identifying and obtaining appropriate CCBs for laboratory evaluations.
- Continuing the development of methods to evaluate mercury and air toxic releases from CCBs.
- Determining the release of mercury under different conditions for the three mechanisms identified.

The literature search task resulted in the assembly of over 350 documents on topics related to the technical issues of this project. In Year 1, 87 samples were obtained from various sources. Several of the assembled samples met the criteria outlined at the project kickoff meeting and were used in laboratory experiments.

Methods to evaluate mercury and air toxic element releases were initially developed under other Energy & Environmental Research Center efforts, but in Year 1 of this project, work was performed to select methods for leachability studies and improve the methods for evaluation of vapor-phase transport of mercury, especially for ambient temperature vapor-phase and microbiologically mediated releases. Improved methods were applied to several samples. Results indicated very limited mercury release from CCBs from direct leachability. Release of mercury on exposure to high temperatures was significant, but none of the CCBs tested released mercury at less than 225°C. At temperatures up to 700°C, samples did not generally release all mercury present in the sample. The most difficult laboratory experiments to conduct were those for ambient temperature and microbiologically mediate mercury releases. A limited number of samples were evaluated for these release mechanisms. Ambient temperature experiments provided a range of results indicating that some CCBs act as a mercury sink while others can release very low quantities of mercury. Results provided some evidence to indicate that organomercury species can be formed through biotic action.

Additional laboratory work will continue in Year 2, and field experiments will be initiated.

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

1.0 PROJECT SUMMARY

This effort is focused on the evaluation of coal combustion by-products (CCBs) for their potential to release mercury and other air toxic elements under different controlled laboratory conditions and investigate the release of these same air toxic elements in select disposal and utilization field settings to understand the impact of various emission control technologies. Information collected during Year 1 was evaluated and interpreted together with past Energy & Environmental Research Center (EERC) data and similar data from other studies. Results were used to determine if mercury release from CCBs, both as currently produced and produced with mercury and other emission controls in place, is a realistic environmental issue.

The 3-year project was designed to develop baseline information on release mechanisms of select elements in both conventional CCBs and modified or experimental CCBs. In Year 1, the modified or experimental CCBs were selected to represent CCBs from systems that have improved emission controls. Controlling these emissions has a high potential to change the chemical characteristics and environmental performance of CCBs.

The development of reliable methods to determine the release of mercury from CCBs provided a means of evaluating the environmental risk associated with CCB management practices. Using appropriate methods to develop a data set of currently produced CCBs and CCBs produced under experimental/simulated conditions provided a baseline for the CCB industry to understand the impact of various emission control technologies.

2.0 OBJECTIVES

The goal of this effort was to evaluate the impact of mercury and other air toxic elements on the management of CCBs. Supporting objectives were to 1) determine the release potential of selected air toxic elements, including mercury and arsenic, 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 specific mechanisms of air toxic element releases evaluated include leaching releases, vapor releases to the atmosphere, and biologically induced leaching and vapor releases.

3.0 BACKGROUND/APPROACH

Mercury and other air toxic elements can be present in fly ash, bottom ash, boiler slag, and flue gas desulfurization (FGD) material. Emission control technologies have a significant potential to impact the Hg and other air toxic element concentrations present in fly ash and FGD materials.

Significant changes in the chemical composition, physical properties, and morphology of by-products may occur as a result of the application of new emission controls. This project was designed to evaluate CCBs from all coal types (bituminous, subbituminous, and lignite) and a limited number of coal blends.

The presence of Hg, As, and other air toxic elements in CCBs poses a potential environmental problem depending on their stability under disposal and utilization conditions, a concern raised by state regulatory agencies (1) and citizen groups (2). Anticipated changes in emission regulations may impact the elements and concentrations of elements incorporated into or sorbed onto CCBs, and it is important to understand the fundamental behavior of these elements in CCBs in order to manage them in an environmentally sound manner. Data also need to be developed on by-products from advanced emission control technologies, such as those under development for Hg emission control. Year 1 efforts increased the database of leaching characteristics of conventional fly ash samples and ash produced from systems with various existing and potential emission controls in place and will continue in Years 2 and 3.

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) biologically induced leachability and vapor release of Hg and other air toxic elements from CCBs. These tasks address fundamental issues critical to determining the release of these constituents over the life cycle of CCBs in a variety of management scenarios. In coming years, a field task will address the same release mechanisms at CCB management sites.

The EERC is currently investigating leaching, ambient and near-ambient temperature Hg release from CCBs, thermal release of Hg from CCBs at temperatures from ambient to 700°C, and the effects of microbial action on the release of Hg and organomercury compounds from CCBs (3, 4). The EERC has been conducting leaching studies on CCBs and other materials for over 20 years (5–7). Ambient, near-ambient, and thermal release of Hg studies have been ongoing for approximately 3 years. Studies to evaluate the impact of biological activity on leaching and vapor transport have also been initiated at the EERC (4). During the course of this research, methods for leaching and thermal desorption have been developed.

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. Several issues have been raised by the U.S. Environmental Protection Agency's (EPA's) Office of Research and Development (ORD) and Office of Solid Waste (OSW) related to the best means of evaluating the leaching potential of CCBs. In this project, leaching methodologies were reviewed. In Years 2 and 3 of this effort, recommendations will be made and coordinated with EPA, based on the appropriateness of existing methodologies. The existing leaching data set is not representative of the broad cross section of fly ash and FGD material currently produced in the United States.

Thermal release, particularly of Hg, is important from the perspective of long-term use, storage, or disposal of CCBs. Although the concentration of Hg in CCBs is relatively low, the large volumes of CCBs produced annually cause concern about potential mercury releases. Ambient, near-

ambient, and elevated-temperature studies of Hg release resulted in the development of an apparatus to determine mercury release in real time from CCBs.

Previous EERC experiments (4) indicate that Hg is released from CCBs at ambient and near-ambient temperature. These preliminary laboratory data warrant further investigation. Vapor transport experiments evaluated Hg release from a bed of CCBs at ambient and near-ambient temperatures and constant airflow through the bed. The design of these experiments is critical to give laboratory results that can be compared to field experiments at CCB management sites.

The wide distribution and variety of microorganisms in the environment indicate that microbiological release of Hg and other air toxic elements needs to be investigated. A wide variety of specific microbe interactions can affect key elements associated with CCBs, including oxidation–reduction and alkylation–dealkylation reactions. The microbial cycling of other air toxic metals follows a similar pattern to that seen with mercury. In order for microbes to be metabolically active, a few constraints must be satisfied. In some CCB management options, these criteria are unlikely to be met, but for options where they can be met, laboratory experiments simulated appropriate scenarios.

4.0 METHODS

4.1 Literature Search

The existing EERC database of documentation on the subjects of mercury and other air toxic elements on CCBs, the mobility of those elements from CCBs, and new control technologies were augmented by a focused literature search during the initiation of this effort. The majority of this task was completed in Year 1, but literature monitoring as well as contact with the U.S. Department of Energy (DOE), EPA, and other groups involved in research and regulatory activities related to this effort will continue throughout the project. An annotated bibliography of references was assembled and will be updated over the duration of the project.

4.2 Analytical Methods Selection

As noted in several forums in recent years, the methodologies used to evaluate CCBs must be relevant to the material and the management of CCBs where possible. Under this task, EERC researchers continued to participate in discussions and efforts to identify appropriate methodology. EERC researchers reviewed methods currently being used at the EERC and elsewhere to determine the best possible methods for this effort. The appropriateness of individual leaching procedures is frequently debated, and selection of leaching procedures for this effort will be a key activity under this task.

4.3 Sample Identification and Selection

Samples for use in this project were identified through government, industry, and marketing contacts. CCBs were selected from systems with conventional emission control technologies and advanced emission control technologies. Examples of samples from conventional technologies are wet and dry FGD materials, ammoniated ash from systems using selective catalytic reduction, selective noncatalytic reduction, and "high"-mercury fly ash. The high-mercury fly ash samples came from systems producing fly ash with higher-than-average carbon content or, in some cases, those from fabric filter collection systems. 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 technologies. Fly ash samples containing activated carbon injected for mercury sorption were included in the samples. Selected samples represent bituminous, subbituminous, and lignite fuels. Samples include 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. A summary of samples obtained and evaluations performed on these samples is included in Appendix A.

Review of previous work, the EPA report on the management of CCBs, Information Collection Request data, and input from industrial partners facilitated sample identification and selection. EERC researchers, DOE, EPA, and industrial partners were asked to aid in the selection and collection of CCBs from advanced emission control technologies.

4.4 Chemical and Physical Characterization

Characterization of selected samples included determination of the bulk chemical composition of major, minor, and trace constituents. Samples were evaluated for pH. The characterization data were assembled into an existing database at the EERC. This task provided information to facilitate prioritization of the air toxic elements for the laboratory and field efforts to be completed in Years 2 and 3 of this project.

4.5 Laboratory Evaluation of Air Toxic Element Releases

Assembled samples were used in laboratory experiments focusing on specific release mechanisms of mercury and other air toxic elements. Primary release mechanisms are leaching, vaporization, and biologically stimulated leaching and vaporization. Air toxic elements including mercury, arsenic, and selenium were evaluated for release through leaching. Vapor release experiments based on previous work and a fundamental understanding of mercury chemistry focused on mercury. Chemical characterization, industry input, and environmental and regulatory concerns were used to develop a prioritized list of air toxic elements on which to focus this effort.

4.5.1 Leaching

A wide variety of leaching protocols, including batch and column leaching procedures, were used to evaluate CCBs for leaching potential and profiles. Leaching procedures to be used in this task were selected based on a critical review of existing procedures and regulatory requirements as noted in the analytical methods selection.

Since mercury and other air toxic elements in CCBs have been shown to be released and transported through leaching, the full suite of elements were determined in leachates.

4.5.2 Vapor Transport

The vapor transport experiments focused on mercury. The release of mercury from CCB samples was investigated at ambient and near-ambient temperatures to simulate disposal and many utilization options for CCBs. Long-term ambient and near-ambient temperature desorption were quantified. Air or another suitable gas flowed through pressurized containers containing up to 150 grams of CCBs. As the gas flowed through the CCB, any mercury released from the CCB was collected on a gold-coated quartz trap. After 90 days, the gold-coated quartz traps were desorbed at 500°C, analyzed using atomic fluorescence (AF), and reattached to the apparatus. In this manner, a long-term, integrated picture of mercury release was obtained.

A similar effort was undertaken for elevated temperatures to simulate some manufacturing scenarios for CCB utilization. Thermal devolatilization of mercury and mercury compounds were investigated at temperatures between ambient and 700°C. A small CCB sample was placed in a tube furnace and heated at a linear ramp from ambient to 700°C. Mercury release was measured in real time.

4.5.3 Microbiological Release

Tests for biological mobilization of metals were performed using a select group of CCBs. The methodology, under development at the EERC, requires 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 element-free gas and monitored for the release of elements from the mixture. Freshly collected sediment from a local brackish wetland was used as the inoculum. This inoculum will contain a variety of microbes including both aerobic and anaerobic bacteria.

During the experiments, mixtures were mechanically agitated at room temperature and sparged with clean gas. Aerobic and anaerobic conditions were used in this task. Under aerobic conditions, the electron acceptor was oxygen. Under the anaerobic conditions, the electron acceptor was the appropriate salts present in the CCB (e.g., iron and sulfate). Mercury released from the sample was trapped on two outlet gas traps, a gold-coated quartz trap and a carbon trap.

These samples will generally be incubated for 30 days; it is expected that 30 days will be sufficient to consume the glucose added, so significant additional activity is not expected after that time. At the termination of incubation, the traps will be analyzed for Hg, as in the vapor transport

task, and the CCBs or CCB–soil mixtures will be subjected to leaching procedures to determine if the aqueous mobility of the metals has been affected.

4.6 Field Investigations

Field investigations will be initiated in Year 2 of the project.

4.7 Data Reduction and Interpretation

Data generated during Year 1 were compiled. In Years 2 and 3, the data will be assembled into a database and presented to project sponsors.

4.8 Technology Transfer

Technology transfer activities for Year 1 focused on discussing similar efforts with other entities, discussing various leaching methods, and networking with people to obtain CCB samples. Project researchers attended three national CCB meetings and presented on various mercury related topics.

5.0 QUALITY ASSURANCE/QUALITY CONTROL

The EERC is committed to delivering consistent and high-quality research that meets our clients' needs and expectations. In order to ensure that the goals of this project are realized, an organizationwide quality management system (QMS) authorized and supported by EERC managers is in effect and governs all programs within the organization. The EERC established and formalized a QMS and quality control (QC) procedures in August 1988. The EERC *Quality Manual* defines the requirements and the organizational responsibilities for each major element of the QMS and references the supporting documents needed to provide a comprehensive program. Compliance with this manual and its supporting documents assures that the EERC adequately fulfills governmental and private clients' requirements relating to quality and compliance with applicable regulations, codes, and protocols.

This project is required to follow the *Quality Manual*, project-specific quality assurance (QA) procedures, and all revisions. The EERC QA Manager implements and oversees all aspects of QA/QC for all research, development, and demonstration projects and will review the QA/QC components of this project. The Project Manager is responsible for ensuring that project-specific QA/QC protocols are followed.

All laboratory procedures and instrument calibrations follow nationally recognized or approved standards and methods put forth by EPA, American Society for Testing and Materials (ASTM), National Institute for Standards and Technology, and other agencies. Each laboratory manager is responsible for ensuring that the applicable QA/QC procedures in this project are implemented.

5.1 Quality Objectives

The quality objectives of this effort support continued environmentally responsible management and appropriate federal regulation of CCBs. Results of the 3-year project 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 the utilization of CCBs. If the environmental performance changes, the project will facilitate an understanding of appropriate management options and provide direction for any future regulatory assessment of CCBs.

5.2 Measurement/Data Acquisition

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. The Analytical Research Laboratory, where most of the work was done, is EPA-approved through the state of North Dakota. As part of the test plan, both replicate and blank experiments were performed to ensure the quality of the results.

5.3 Assessment and Validation

The standard analysis techniques used in the project indicate acceptable performance criteria. The repeatability of the data was within the expected $\pm 20\%$, 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.

The thermal desorption curves of HgO and $HgCl_2$ released peaks at temperatures repeatable to within 10%. Again, this is a technique in development, and further improvements are expected.

6.0 ACCOMPLISHMENTS/RESULTS

6.1 Literature Search

A literature search was performed, resulting in over 300 documents from which to draw background and supporting information as well as methodology for this project. The documents comprise primarily documents already in-house, and most of the documents are journal articles. Other document types include but are not limited to papers and presentations from meetings and conferences, reports, and test methods. The majority of documents relate to mercury. Also included are documents relating to leaching and trace elements, with an emphasis placed on arsenic, chromium, and selenium. The documents can also be grouped into the following categories: fate of elements during the combustion of coal, fate of elements (mercury in particular) in the environment, analytical methods used to determine quantity and/or speciation of elements, and leaching procedures. The primary materials studied in the documents include CCBs, soil, air, and water. Ten

of the documents relate specifically to information about CCBs resulting from the use of mercury control technologies. Evaluations of the materials include leaching, vapor transport, ASTM C618, and foam index test.

Because a large volume of information was assembled, the literature will likely be housed in an electronic database in the coming years.

6.2 Analytical Methods Selection

Analytical methods were selected based on previous work at the EERC and by other groups. For leaching, it was decided to use the EERC-developed method called the synthetic groundwater leaching procedure (SGLP) along with long-term leaching (LTL). Leaching methods to be evaluated will be expanded in the following years. The analytical method used for mercury analysis was double gold amalgamation AF spectroscopy along with some cold-vapor atomic absorption (AA) spectroscopy. Double gold amalgamation AF was used to analyze both the gold-coated quartz traps from the long-term ambient temperature release experiments and the Carbotrap™ and gold-coated quartz traps from the microbiologically mediated mercury release experiments. AA was used for the determination of mercury in real time from the thermal release experiments. Organic mercury species formed in the microbiologically mediated release experiments are being determined using solid-phase microextraction followed by separation using gas chromatography (GC) with detection by AF spectroscopy. Bulk oxides in CCBs were determined using x-ray fluorescence. Trace mercury was determined using a DMA-80 (direct mercury analyzer). Trace elements other than mercury will be determined using furnace AA and inductively coupled argon plasma spectroscopy. Other parameters such as pH are being determined using standard laboratory equipment and techniques.

6.3 Sample Identification and Selection

Eighty-seven samples were obtained from various sources during the first year of this effort. Confidentiality of sample identity was discussed with sample submitters, and where requested, confidentiality agreements were signed. Samples included primarily coal fly ash samples and FGD samples produced from bituminous coal, subbituminous coal, lignite, and a very limited number of coal blends. Most samples were generated in pulverized coal-fired units. Most samples were collected from facilities with electrostatic precipitators. Sixteen samples were from testing of mercury control technologies, primarily the use of activated carbon.

6.4 Chemical and Physical Characterization

Total mercury content of the samples ranged from <0.01 to 0.6 μg/g. Chemical and physical characterization included bulk chemical composition of major, minor, and trace constituents. Samples were also evaluated for loss on ignition, and identification of carbon forms was initiated. The preliminary characterization data were entered into an existing database at the EERC to facilitate data interpretation.

6.5 Laboratory Evaluation of Air Toxic Element Releases

Assembled samples were used in the following laboratory experiments focusing on specific release mechanisms of mercury and other air toxic elements.

6.5.1 Leaching

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. Several issues related to the best means of evaluating the leaching potential of CCBs have been raised by EPA ORD and OSW. In fact, EPA held a meeting in early 2002 during which EPA representatives and others proposed an extensive series of leaching protocols for CCB leaching characterization. EERC researchers reviewed the proposed methods and held discussions with scientists at the DOE National Energy Technology Laboratory (NETL). DOE NETL provided an alternate proposed method, and the EERC proposed that the SGLP with the LTL option be used. Both the proposed NETL and EERC methods included a long-term component, although the NETL long-term component is a simulated long-term evaluation. The EERC agreed to participate in a testing program that will include the EERC SGLP with a long-term component, the NETL leaching method, and the EPA-proposed leaching procedure. This effort is under development with DOE NETL. At this time, EPA has not agreed to participate.

EERC researchers presented their thoughts on the requirements of an appropriate leaching characterization evaluation for CCBs in a paper entitled "A Leaching of CCBs: Observations from over 25 Years of Research" at the 2003 International Ash Utilization Symposium held in October 2003 in Lexington, Kentucky (8). The paper was presented with the intent to elevate awareness of the issues related to selection of leaching procedures.

6.5.2 Vapor Transport

Experiments were conducted to determine if thermal desorption can determine mercury speciation. The following subtasks further describe this task.

6.5.2.1 Long-Term Ambient Release

Six ash samples were previously evaluated in duplicate for the release of mercury over 263- and 264-day periods in Tests 1 and 2, respectively, through the Center for Air Toxic Materials® (CATM®) (2, 6). However, blank values for the samples were an unresolved issue. In Test 1, separate empty bottles were used in an attempt to have a blank value to subtract from all sample results. An improved method was used in Test 2. Each sample bottle was emptied of ash and gas was allowed to continue to flow, collecting mercury for an additional 180 days. These two 90-day periods were used to derive a separate blank for each sample container. The apparatus (see Figure 1) was similar to that described for the microbiologically mediated release of mercury and is described in detail by Pfughoeft-Hassett et al. (7)

After mercury vapor was collected for the two 90-day time intervals, the tubes were desorbed by heating the analytical gold-coated quartz trap to approximately 500°C, and the mass of released mercury was determined using AF.

The measured mercury released from blank bottles was higher than from the sample bottles in Test 1, and confirmation of this was desired before it was suggested that the ash samples appeared to be sorbing mercury rather than emitting mercury. Higher blank values were also seen in the method used for Test 2. If one calculates and compares the emission rate in pg/day for the blank of each sample container and the containers with ash in them from Test 2, it becomes apparent that the ash samples appear to be sorbing mercury. These values are presented in Table 1 as averages of the duplicate samples.

Table 1. Comparison of Emission Rates Between the Empty Bottles and the Bottles Containing Ash in Test 2, pg/day

Sample	Bottles with Ash	Bottles Without Ash	Difference
99-188	2.237	2.161	−0.076
99-189	0.077	1.127	1.05
99-692	0.081	2.454	2.373
99-693	0.077	4.328	4.251
99-722	0.696	7.165	6.469
99-724	0.411	4.436	4.025

Long-term ambient temperature desorption experiments have indicated that five of the six CCBs analyzed acted as mercury sinks, although these samples were previously reported as having released small amounts of mercury vapor. The previously reported value of a maximum of 0.26 grams of mercury release from 200,000 tons of ash (2, 4) actually becomes a negative number in light of these new data. This does not necessarily mean that no mercury was being released from the CCBs, but that in our experiments, eleven of the containers appeared to release more mercury after emptied of ash than while containing ash. The total mercury content of these ashes has not correlated to the apparent amount of mercury released or sorbed.

Twelve additional ash samples are currently being tested for long-term ambient temperature release of mercury. This set of experiments will be completed in approximately 250 days. As these samples are being tested, an additional set of at least twelve additional samples will be started.

6.5.2.2 Thermal Desorption at Elevated Temperatures

A schematic for the controlled thermal desorption of mercury and mercury compounds was assembled and is shown schematically in Figure 2. The apparatus was constructed using an AA spectrophotometer for mercury detection and included a small tube furnace and temperature controller for thermal desorption. A Hewlett Packard 3395 integrator was used for data collection. Detection of thermally desorbed mercury and mercury compounds from approximately 1-gram samples was done in an electrically heated quartz cell operated at 800°C. The use of a heated cell allowed detection of mercury compounds by thermally decomposing compounds to form elemental mercury, which can be detected by AA. Gas flow was 20 cm^3/min of nitrogen. The temperature controller was ramped from ambient temperature to 700°C at a rate of 25°C per minute. The AA was

calibrated for the amount of mercury thermally desorbed from some of the CCBs tested. This was done by injecting a known amount of mercury from air saturated with elemental mercury onto a gold-coated quartz trap and thermally desorbing the mercury in the same manner as samples.

Thermal desorption curves were developed for 50 CCB samples (see Appendix A). The ash samples included those from the combustion of lignite, subbituminous, and bituminous coals, pilot and full-scale samples, fly ash and fly ash–FGD mixtures, and with or without mercury control technologies in place. Some of the 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.

A large variety of CCBs have been analyzed for the thermal release of mercury. Most of the thermal curves generated were straightforward, containing only one or two major desorption peaks. Examples are shown in Figures 3 and 4. However, background noise or other interferences were encountered occasionally. For example, high-carbon ash samples seemed to generate more background noise, which the deuterium background correction lamp did not mitigate. High-sulfur

CCBs also produced an irregular baseline and unidentifiable peaks; however, the use of the deuterium lamp background correction reduced the interfering background.

Mercury compounds were also analyzed. HgO and $HgCl_2$ were added directly to pulverized quartz powder to simulate an inert matrix. Upon thermal desorption, 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.

Upon 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 Sample 99-186, the CCBs spiked with $HgCl_2$ eluted peaks at temperatures lower than the plain CCB. Spiking samples with HgO yielded variable decomposition temperatures. Thermal desorption curves were rather difficult to interpret since there is no way, at present, using this apparatus, to determine exactly what is happening during the thermal treatment. There are several possible scenarios:

1. Mercury and mercury compounds, as sorbed, are being released, unchanged, during the thermal desorption procedure.

2. 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.

3. Mercury or mercury compounds are chemically reacting with the CCB components then thermally desorbed according to the first or second scenario as described above.

Unfortunately, this delayed desorption was not completely reproducible, making “peak matching” with desorption curves of the mercury compounds without ash difficult and problematic.

Calibration of the AA with elemental mercury 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 one to quantify the amount of mercury desorbed from the CCBs. However, concentration results from the CCBs were not reproducible.

6.5.3 Microbiological Release

Three CCBs were tested for the microbiologically mediated release of mercury and are listed in Table 2. One ash sample is from a full-scale demonstration of a mercury control technology.

The apparatus was constructed as shown in Figure 5. A 250-mL Erlenmeyer flask was fitted with an impinger inlet/outlet tube with the inlet center shorted 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

Table 2. CCB Sample Description and Total Mercury Content

Sample	Coal/Ash Description	Additional Information	Hg, μg/g
99-188	Powder River Basin subbituminous fly ash + FGD Material	Neutralized	0.131
01-002	Eastern bituminous fly ash		0.234
03-060	Subbituminous fly ash	*Advanced Hybrid*™ filter technology	NT[a]

[a] Not tested.

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. This was 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 CCB with buffer (starved), and three contained the CCB with buffer and glucose (fed). A 50- or 80-gram aliquot of CCB was placed in the flasks and 94 or 100 mL of a phosphate buffer (with or without glucose, as appropriate) was added to create a neutral pH. The CCB and buffer amounts varied because of the CCB density. The ash-containing flasks also had 100 μL of mixed bacterial culture added. The source of bacteria was a mixed bacterial inoculum from a brackish wetland.

Mercury vapor was collected for approximately 30 days. 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 AF. 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 collection the mercury vapor on a gold-coated quartz trap, which was analyzed as described above.

Bacterial counts were performed upon completion of the 30-day period. A 1-mL aliquot of solution was taken from each flask. The aqueous supernate was serially diluted in 0.1% sodium pyrophosphate buffer (pH 7.0) 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.

Improvements to the experimental setup are being made in the current CCB (03-060) investigation. An initial bacterial count is being performed to provide a baseline comparison value. The gold-coated quartz collection traps are being analyzed once a week in an attempt to see a trend of elemental mercury release. The reusable traps are placed back on the system after analysis, and mercury is collected again.

The biological activity experiments were conducted in triplicate primarily because the mass of mercury collected on the gold-coated quartz and Carbotrap™ collection traps can only be tested one time. If the amount of mercury captured on the trap over the duration of the experiment was too high for the settings used when testing on the AF instrument, the value was incomplete or lost.

Results to date have been confusing; however, general trends have emerged. 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 has also generally followed that trend. The elemental mercury vapor captured on the gold-coated quartz traps has been higher than that seen in the long-term ambient-temperature vapor-release experiments. The flasks containing buffer only have been treated as blanks.

The results from the experiment using CCB 99-188, a subbituminous fly ash neutralized prior to the experiment, are shown in Table 3. AF instrument problems resulted in incomplete results for the elemental mercury captured on some of the gold-coated quartz traps because of the 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 shows more bacteria in the flasks in which the bacteria were fed glucose in both the anaerobic and aerobic conditions.

Table 3. Results of Microbiologically Released Mercury from CCB 99-188

Anaerobic	Gold Trap Hg, ng	Gold Trap Hg, ng/g	Carbotrap™ Hg, ng	Carbotrap™ Hg, ng/g	Bacterial Count/mL

Blank	3.92		0.3		930
Blank	3.98		0.19		ND[a]
Fed	63.1	1.26	0.72	0.014	>24,000,000
Fed	45.6[b]	0.91[b]	2.32	0.046	>24,000,000
Fed	69.2	1.38	4.14[c]	0.083[c]	>24,000,000
Starved	NA[d]	NA[d]	1.83	0.037	240,000
Starved	47.7[b]	0.95[b]	5.62	0.112	93,000
Starved	66.3	1.33	2.07	0.041	43,000
Aerobic					
Blank	2.37		0.08		ND
Blank	1.65		0.06		ND
Fed	31.5	0.63	1.06	0.021	>24,000,000
Fed	61.3	1.23	0.86	0.017	>24,000,000
Fed	33.2	0.66	1.93	0.039	>24,000,000
Starved	45	0.90	0.66	0.013	240,000
Starved	42.2	0.84	0.50	0.01	240,000
Starved	44.9	0.9	0.89	0.018	93,000

[a] Not detected.
[b] Value is believed to be low because of testing conditions.
[c] Value may be high because of testing conditions.
[d] Value was not obtained because mass of mercury was too high for testing conditions.

The results from the experiment using CCB 01-002, an eastern bituminous fly ash, are shown in Table 4. 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 CCB 99-188, pg/g versus ng/g. 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.

Initial results from CCB 03-060, a subbituminous fly ash resulting from the full-scale use of *Advanced Hybrid™* filter technology, are shown in Table 5. These initial 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 high blank values from the buffer solutions still need to be resolved.

Table 4. Results of Microbiologically Released Mercury from CCB 01-002

Anaerobic	Gold Trap Hg, pg	Gold Trap Hg, pg/g	Carbotrap™ Hg, pg	Carbotrap™ Hg, pg/g	Bacterial Count/mL
Blank	1280		95.47		NT[a]
Blank	2303		203		NT
Fed	155	3.1	13.45	0.27	ND[b]
Fed	177.3	3.55	14.12	0.28	ND
Fed	376.9	7.54	12.66	0.25	ND
Starved	66.49	1.33	13.16	0.26	ND
Starved	45[c]	0.9	22.29	0.45	ND
Starved	56.28	1.13	19.9	0.4	ND
Aerobic					
Blank	1096		36.16		NT
Blank	1160		44.52		NT
Fed	405.71	8.11	13.76	0.28	>24,000,000
Fed	1758	35.2	52[c]	1.04	>24,000,000
Fed	136.1	2.72	13.16	0.26	>24,000,000
Starved	48[c]	0.96	5.876	0.12	43,000
Starved	79.39	1.59	13.59	0.27	24,000
Starved	30.48	0.61	4.739	0.1	150,000

[a] Not tested.
[b] Not detected.
[c] Lower sensitivity.

6.6 Field Investigations

Task 6 is planned as a Year 2 activity although preliminary discussions of potential field sites were held.

6.7 Data Reduction and Interpretation

Data reduction and interpretation were initiated in Year 1 by placing data into a database management system; however, it is too early to draw conclusions from the data available.

6.8 Technology Transfer

Ms. Debra Pflughoeft-Hassett, Project Manager, attended the DOE NETL Mercury Control Research & Development Program Review Meeting in Pittsburgh on August 12–13, 2003. Ms. Pflughoeft-Hassett presented information on mercury impacts on by-products. Discussions were held with other groups performing similar efforts and with potential suppliers of samples.

Table 5. Initial Gold-Coated Quartz Collection Trap Results of Microbiologically Released Mercury from CCB 03-060 after 28 Days

Anaerobic	Hg, pg	Hg, pg/g
Blank	581.4	NA[a]
Blank	257	NA
Fed	143.7	1.80
Fed	206.4	2.58
Fed	48.98	0.612
Starved	55.74	0.697
Starved	41.99	0.525
Starved	117.2	1.47
Aerobic		
Blank	102.8	NA
Blank	69.39	NA
Fed	3262	40.8
Fed	1557	19.5
Fed	3132	13.2
Starved	50.86	0.636
Starved	43.22	0.540
Starved	65.07	0.813

[a] Not applicable.

Project Researcher, Mr. David Hassett, acted as a coordinator for a session entitled "Mercury and Coal Utilization By-Products" at the Air Quality IV (AQIV) International Conference on Mercury, Trace Elements, and Particulate Matter held September 22–24, 2003, in Arlington, Virginia. Mr. Hassett and Ms. Loreal Heebink coauthored a paper and a poster presentation at AQIV.

Mr. David Hassett and Ms. Loreal Heebink attended the International Ash Utilization Symposium in Lexington, Kentucky, October 20–22, 2003. Mercury-related papers entitled "Long-Term Mercury Release from CCBs" and "Mercury Release from FGD" were presented. Discussions were also held with Ms. Mae Gustin, University of Nevada, on methodology for evaluation of vapor releases of mercury as part of the filed activities planned for Year 2.

7.0 FUTURE RESEARCH NEEDS

7.1 Year 2 Tasks

7.1.1 Literature Search

The existing EERC database of documentation on the subjects of mercury and other air toxic elements on CCBs, the mobility of those elements from CCBs, and new control technologies will continue to be augmented by assembling additional literature as it becomes available in Year 2. A first draft of the annotated bibliography will be prepared and distributed.

7.1.2 Analytical Methods Selection

This task was completed in Year 1 of the project; however, in Year 2 of the project, the presentation of the selected techniques will be presented along with data from Years 1 and 2. Further, if needed, the selected methods will be modified to accommodate any field samples that are collected during Years 2 and 3.

7.1.3 Sample Identification and Selection

Additional samples for use in this project will be identified through government, industry, and marketing contacts in Year 2. While many samples were obtained in Year 1, it will be necessary in Year 2 to collect samples associated with field sites and provide sample types that were unavailable in Year 1. The objective of this task is to select CCBs from systems with conventional and advanced emission control technologies.

7.1.4 Chemical and Physical Characterization

In Year 2, this task will focus on samples obtained in Year 2, especially those associated with field sites. Characterization of selected samples will include determination of the bulk chemical composition of major, minor, and trace constituents. Samples will also be evaluated for particle size, morphology, pH, and general reactivity based on heat of hydration and cementation. The characterization data will be assembled into an existing database at the EERC and made available to DOE and industrial sponsors.

7.1.5 Laboratory Evaluation of Air Toxic Element Releases

Assembled samples will be used in laboratory experiments focusing on specific release mechanisms of mercury and other air toxic elements. Primary release mechanisms are leaching, vaporization, and biologically stimulated leaching and vaporization. Air toxic elements will be evaluated including mercury, arsenic, and selenium for release through leaching. Vapor release experiments, based on previous work and a fundamental understanding of mercury chemistry, will focus on mercury. The chemical characterization, industry input, and environmental and regulatory concerns will be used to develop a prioritized list of air toxic elements on which to focus this effort. The list developed for this project is mercury, arsenic, selenium, cadmium, lead, nickel, and chromium.

7.1.5.1 Leaching

Since mercury and other air toxic elements in CCBs have been shown to be released and transported through leaching, the full suite of elements will be determined in leachates. The oxidation state of select elements including chromium will be determined in some leachates.

In addition to leachates of as-received CCB samples, selected biologically activated CCBs generated from other laboratory experiments will be leached.

7.1.5.2 Vapor Transport

The vapor transport experiments will continue to focus on mercury. The release of mercury from CCB samples will be investigated at ambient and near-ambient temperatures to simulate disposal and many utilization options for CCBs. Long-term ambient temperature desorption will be quantified.

A similar effort will be undertaken for elevated temperatures to simulate some manufacturing scenarios for CCB utilization. Thermal devolatilization of mercury and mercury compounds will be investigated at temperatures between ambient and 700°C. A small CCB sample will be placed in a tube furnace and heated at a linear ramp from ambient to 700°C. Mercury release will be measured in real time.

7.1.5.3 Microbiological Release

Tests for biological mobilization of metals will be performed using a select group of CCBs and mixtures of CCBs with topsoil. The methodology under development at the EERC requires the CCB or CCB–soil mixture to be buffered to near neutral with phosphate buffer. The sample will then be 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 element-free gas and monitored for the release of elements from the mixture. Freshly collected sediment from a local brackish wetland will be used as the inoculum. This inoculum will contain a variety of microbes including both aerobic and anaerobic bacteria.

7.1.6 Field Investigations

This task will focus on developing information to determine how laboratory results can be used effectively to determine potential releases of air toxic elements from CCBs in real-world management settings. Field investigations will be initiated in Year 2 of the project. EERC researchers will work with industry to identify field opportunities for this effort. No actual management activities will be performed under this effort; however, CCBs from field activities will be collected, and associated field sites will be evaluated for potential field sample collection. Field sampling will include air samples to determine mercury vaporization from CCBs, groundwater and surface water, and solids including CCBs and sediments, depending on the management activity. Examples of CCB management practices to be included in field investigations are 1) wet/dry disposal sites (with leachate collection, if possible); 2) mine placement; 3) soil amendments; and 4) manufacturing, such as FGD gypsum wallboard, aggregate, and building products. EERC

researchers will propose to include concrete at the upcoming project annual meeting. Industrial partners will facilitate the selection of field applications and aid in identifying field sites.

7.1.7 Data Reduction and Interpretation

All data collected through the end of Year 2 will be compiled into a database and interpreted together with past EERC data and similar data from other studies. Results will be used to determine if mercury and other air toxic element releases from CCBs, both as currently produced and with mercury and other emission controls in place, are a realistic environmental issue.

7.1.8 Technology Transfer

Technology transfer activities will continue throughout the duration of the project.

7.2 Year 3 Tasks

7.2.1 Literature Search

The existing EERC database of documentation on the subjects of mercury and other air toxic elements on CCBs, the mobility of those elements from CCBs, and new control technologies will be augmented by a focused literature search during the initiation of this effort. The majority of this task will be completed in Years 1 and 2, but literature monitoring as well as contact with DOE, EPA, and other groups involved in research and regulatory activities related to this effort will continue throughout the project. An annotated bibliography of references will be finalized in Year 3.

7.2.2 Analytical Methods Selection

It is anticipated that this task will be completed in Year 2.

7.2.3 Sample Identification and Selection

It is anticipated that this task will be completed in Year 2.

7.2.4 Chemical and Physical Characterization

Characterization of selected samples will be completed in Year 3. All characterization data will be assembled into an existing database at the EERC and made available to DOE and industrial sponsors.

7.2.5 Laboratory Evaluation of Air Toxic Element Releases

7.2.5.1 Leaching

Leaching experiments will continue as needed to complete the leaching release data for the project samples. Work on methodology and associated discussions with DOE NETL and EPA will also continue as needed.

7.2.5.2 Vapor Transport

The vapor transport experiments will continue as needed to complete the vapor release data for the project samples.

7.2.5.3 Microbiological Release

Tests for the biological mobilization of metals will continue as needed to complete the leaching and vapor release data for the project samples and mixtures of project samples with soil.

7.2.6 Field Investigations

Field investigations will be completed during Year 3.

7.2.7 Data Reduction and Interpretation

All data collected will be compiled into a database and interpreted together with past EERC data and similar data from other studies. Results will be used to determine if mercury and other air toxic element releases from CCBs, both as currently produced and with mercury and other emission controls in place, is a realistic environmental issue.

7.2.8 Technology Transfer

Technology transfer activities will continue throughout the duration of the project.

7.3 Equipment

CATM funds were not used to purchase equipment (supplies greater than $5000) during Year 1; however, additional equipment is needed to perform future work based on results in Year 1. Equipment proposed for Years 2 and 3 will be funded by DOE NETL and EERC.

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APPENDIX A

PROJECT SAMPLES AND PROCEDURES COMPLETED