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

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## *Project Description*

As coal-fired power plant emission control technologies change, it is anticipated that mercury and air toxic elements will have a greater potential to be associated with and/or concentrated on solid by-products. This project was designed and has been carried out to determine the stability and levels of selected air toxic elements that may be released to the environment from coal combustion by-products (CCBs) under typical management scenarios. This focused effort selected and developed methodologies, determined the levels of releases, determined release mechanisms, and allowed the estimation of the impact of mercury and other air toxic elements (arsenic, cadmium, chromium, lead, nickel, and selenium) on the management of CCBs.

Laboratory tasks addressed three types of release mechanisms: 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 mercury and other air toxic elements from CCBs. The laboratory tasks addressed fundamental issues critical to determining the release of these constituents over the life cycle of CCBs in a variety of management scenarios. Evaluation of mercury releases at laboratory-simulated field sites was designed and carried out with the goal of addressing the same release mechanisms at CCB management sites.

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.

The effort is sponsored by the U.S. Department of Energy National Energy Technology Laboratory (DOE NETL), the CATM Affiliates Program, Cinergy, the Electric Power Research Institute, Great River Energy, the North Dakota Lignite Research Council, and the Utility Solid Waste Activities Group (USWAG).

### *Goal*

The overall goal of this project was to evaluate the impact of mercury and other air toxic elements on the management of CCBs. Specific objectives to accomplish this goal 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.

### *Rationale*

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 mercury 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 EERC project was designed to evaluate CCBs from all coal types (bituminous, subbituminous, and lignite) and a limited number of coal blends.

The presence of mercury and other air toxic elements in CCBs poses a potential environmental problem depending on the stability of these elements under disposal and utilization conditions, a concern raised by state regulatory agencies (1) and citizen groups. As a result of changes in emission regulations, changes may result that impact the elements and concentrations of elements incorporated into or sorbed onto CCBs. For this reason, this project was undertaken to facilitate the understanding of 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 mercury emission control. This effort focused on increasing the database of elemental releases from conventional fly ash samples and ash produced from systems with various existing and potential emission controls in place.

### *Approach*

The project consisted of the seven tasks listed below to address the research needs. The bulk of the research was in Tasks 5 and 6, with the other tasks supporting the goal of the project.

Task 1. Literature search
Task 2. Analytical methods selection
Task 3. Sample identification and selection
Task 4. Chemical and physical characterization
Task 5. Laboratory evaluation of air toxic element releases
Task 6. Field investigations
Task 7. Data reduction and interpretation

#### Experimental Apparatus

The laboratory subtasks and the field investigation task each used an experimental apparatus to evaluate air toxic element releases. Each of these is described in detail elsewhere (2–6).

### Work Plan

The work plan for Year 4 focused on Task 5: Laboratory evaluation of air toxic element releases and Task 6: Field investigations. Task 5 consisted of three subtasks: 1) leaching, 2) vapor transport at ambient and elevated temperatures, 3) and microbiological leaching and vapor releases. The field task was modified to evaluate mercury releases from CCB–soil mixtures in the laboratory.

## *Progress*

Highlights of progress are provided here.

### Leaching

Leaching of samples continued using the synthetic groundwater leaching procedure (SGLP) and 30- and 60-day long-term leaching (LTL) methods. Not all tests were performed on all samples. The data set supported previous preliminary conclusions for the element mercury:

- Total mercury content of samples generated both with and without mercury emission controls present and leachate concentrations did not correlate.

- 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 0.01-µg/L reporting limit.

- 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 (arsenic, cadmium, chromium, lead, nickel, and selenium), 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 the air toxic elements studied, except selenium. Activated carbon appears to sorb selenium as it does mercury. Fly ash samples with activated carbon injection (ACI) have higher total selenium concentrations than the paired fly ash sample without ACI.

- Generally, higher total concentrations of air toxic elements do not correlate to higher leachate concentrations.

- All air toxic elements showed reduced, increased, or variable leaching concentrations with increased time using SGLP and LTL tests. Based on previous EERC work, these leaching profiles are expected to be sample-dependent.

### Ambient-Temperature Vapor-Phase Mercury Release

Numerous samples have been evaluated for the release of mercury vapor at ambient temperature over the duration of the project. Samples included in the evaluation in Year 4 were fly ash with and without mercury control including paired fly ash sample sets and FGD materials including paired fly

ash + FGD–spray dryer absorber (SDA) sample sets, FGD gypsum, and FGD filtercake. The main observations to date are as follows:

- Results obtained from experiments to evaluate long-term ambient-temperature release of mercury from CCBs ranged from a net release to a net sorption of mercury.
- Replicate tests frequently yield highly variable results, but the extremely low levels both of sorption and release of mercury indicate that this release mechanism has very low potential to impact the loading of mercury in the atmosphere.
- The limited FGD material samples investigated do not follow the same trend as fly ash samples. Preliminary results indicate a higher rate of mercury vapor release.

The reporting of results was changed slightly in Year 4 to indicate the mercury vapor release as a percentage of the total mercury present. Table 1 shows an example from a set of Fort Union lignite fly ash samples consisting of a baseline sample and various ACI samples with low and high ash contents.

**Table 1. Long-Term Ambient-Temperature Mercury Experiment Results Example**

| ID No. | Total Hg, µg/g | Average Total Sorbed or Released Hg over 97 Days, µg/g | Average % Sorption or Release over 97 Days | Average Years to Release 100% of Hg |
|---|---|---|---|---|
| Baseline | 0.104 | −0.0000000139 | −0.0000134 | NA[a] |
| Low Ash-1 | 39.0 | 0.0000000402 | 0.000000103 | 259,393,862 |
| High Ash-1 | 12.7 | 0.0000000253 | 0.000000199 | 134,078,921 |
| Low ash-2 | 35.9 | −0.0000000179 | −0.0000000498 | NA |
| High ash-2 | 12.6 | −0.000000120 | −0.000000950 | NA |
| Low ash-3 | 44.5 | −0.0000000759 | −0.000000170 | NA |
| Low ash-4 | 64.5 | −0.000000105 | −0.000000162 | NA |

[a] Not applicable.

**Microbiological Leaching and Vapor Releases**

An additional experiment was accomplished using four eastern bituminous fly ash samples with pH values that were favorable to bacterial growth. The experiment indicated a greater release of elemental mercury and organomercury vapor under aerobic conditions than under anaerobic conditions. This is consistent with other eastern bituminous fly ash samples evaluated under this project.

The leachates generated were also analyzed. Arsenic, lead, and mercury leachate concentrations and leachate pH values were higher in the aerobic samples; whereas, chromium, nickel, and selenium leachate concentrations were lower. Cadmium leachate concentrations were similar.

Because of difficulties experienced in the microbiological experiments over the duration of the project, a CCB–soil mixture experiment was performed to evaluate microbiologically mediated mercury releases from CCBs. This initial experiment is summarized under the field investigation task for this project.

### Field Investigation

The second field investigation of the project was shifted to the laboratory to focus on determination of release of methylated or organomercury species using mixtures of CCBs and soil. An experimental apparatus similar to that used in the long-term ambient-temperature mercury release experiments was used. A 20% addition of CCBs was combined with the soil and collection traps containing Supelco Carbotrap™ to capture organomercury compounds was added to the system. The apparatus is described in more detail elsewhere (6). Six fly ash–soil mixtures, one FGD material–soil mixture, and a soil alone were investigated under aerobic conditions. The fly ash samples included eastern bituminous, subbituminous, and Fort Union lignite samples with and without mercury control technology testing. The observations to date include the following:

- Elemental and organomercury vapor releases were extremely low, reported as subpicograms of mercury/g mixture/day.
- The rate of elemental mercury vapor release was higher than what was noted in the fly ash-only samples in the long-term ambient-temperature mercury release experiments. The rate of elemental mercury vapor release generally decreased from Period 1 to Period 2 testing with the exception of two fly ash–soil mixtures, which contained fly ash from mercury control technology testing.
- The release rate of organomercury vapor decreased for all mixtures from Period 1 to Period 2.

## *Quality Assurance/Quality Control*

### Quality Objectives

The quality objectives of this effort support continued environmentally responsible management of CCBs and appropriate federal regulation of CCBs. The quality objective was to select and/or modify experimental methods that would be most appropriate for the material types.

### Measurement/Data Acquisition

Because this was primarily a laboratory project to evaluate mercury and air toxic element 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. For release experiments, standard techniques were generally not available, so experimental protocols were developed as part of the project and documented in a topical report.

### Assessment and Validation

The standard analysis techniques used in the project indicate acceptable performance criteria. The repeatability of the data was generally within the expected ±20%. Any deviations were noted, and experiments and/or analyses were repeated to identify the source of the discrepancy. Release experiments were evaluated throughout the project for appropriateness for the materials of interest. Evaluation criteria included assessment of interferences and repeatability.

***Status***

This 4-year effort has been completed. Laboratory activities continued in 2006 to complete the data set. Reports on the microbiologically mediated mercury and air toxic element releases and elevated-temperature vapor-phase mercury releases were published in 2006. A modified laboratory experiment was developed to evaluate mercury releases from soil–CCB mixtures in lieu of additional field work. Data interpretation was challenging throughout the project because of incomplete sample identification, limited availability of paired baseline and mercury emission control test sample sets, variations in sorbents, and the presence of sorbent-enhancing agents that may or may not have been identified. The extensive data produced on fly ash both without and with sorbents has allowed conclusions to be drawn regarding the stability of mercury associated with the fly ash. Additional work outside this project will be required in order to better assess the stability of mercury associated with FGD materials and the halogen stability in fly ash and FGD materials. Additional work will also be needed to better understand the impact of microbial activity on the stability of mercury associated with fly ash, sorbents, and FGD materials. The comprehensive final project report will be available in 2007.

***Potential Applications and Benefits***

Under this project, several methods were developed that are expected to be applied by research and industry groups to evaluate specific CCBs. The stability of mercury associated with CCBs could impact the use of CCBs in many existing commercial applications, and the methods developed in this project are expected to aid in addressing that issue. The data set, especially the data from fly ash–AC (activated carbon) is expected to be beneficial to the CCB industry in evaluating management options for CCBs when mercury emission controls are installed on individual units/plants.

Results of the multiyear 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 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.

**Potential Users and Real-Life Applications**

Utility by-product managers, CCB marketers, and environmental specialists are expected to be the users of the information generated in this project, and the information is expected to facilitate decisions about management options. Data assembled in this report provide an indication of levels of mercury and other air toxic elements that will be present in fly ash and FGD following installation of mercury emission controls as well as the potential for those to mobilize under disposal and utilization scenarios.

**Technology Transfer**

Results obtained to date in this project have been included in numerous reports and have been presented at appropriate conferences as follows:

- Hassett, D.J. HOT TOPIC: Mercury and Its Impact on CCBs. Presented at the Coal Ash Professionals Training Course, April 19–21, 2006, Memphis, TN.

- Hassett, D.J. Mercury and Coal Combustion By-Products; In *Proceedings of the International Conference on Coal Ash;* Pretoria, South Africa, Oct 2–4, 2006.

- Hassett, D.J.; Heebink, L.V.; Zacher, E.J.; Pflughoeft-Hassett, D.F. Mercury and Air Toxic Element Impacts on CCB Disposal and Utilization. Presented at the Coal Ash Resources Research Consortium® (CARRC®) Midyear Meeting, Washburn, ND, Aug 29, 2006.

- Hassett, D.J.; Pflughoeft-Hassett, D.F.; Heebink, L.V.; Buckley, T.D.; Zacher, E.J. *Elevated-Temperature Vapor-Phase Mercury Measurement from Coal Combustion By-Products*; Topical Report for the U.S. Department of Energy National Energy Technology Laboratory; Energy & Environmental Research Center: Grand Forks, ND, Feb 2006.

- Heebink, L.V.; Pflughoeft-Hassett, D.F.; Hassett, D.J.; Buckley, T.D.; Zacher, E.J. Laboratory Assessment of the Impact of Carbon-Based Sorbents on the Management of Fort Union Lignite CCBs. In *Proceedings of the 20th Symposium on Western Fuels;* Denver, CO, Oct 24–26, 2006.

- Pflughoeft-Hassett, D.F.; Hassett, D.H.; Heebink, L.V.; Buckley, T.D. The Current State of the Science Related to the Rerelease of Mercury from Coal Combustion By-Products. *Ash at Work* **2006,** *Winter/Spring.*

- Pflughoeft-Hassett, D.F.; Hassett, D.J.; Gallagher, J.R.; Heebink, L.V.; Zacher, E.J.; Jung, R.; Buckley, T.D. *Microbiologically Mediated Mercury and Air Toxic Element Rereleases from Coal Combustion By-Product*s; Topical Report for the U.S. Department of Energy National Energy Technology Laboratory; Energy & Environmental Research Center: Grand Forks, ND, Feb 2006.

**Technical and Economic Benefits**

Technical benefits have already been realized from this project both by project sponsors and by other members of the utility industry and the regulatory community through the dissemination of results. CCB management rarely plays a significant role in the economic evaluation of implementation of new emission technologies or fuels under consideration for coal-based power plants; however, the stability of mercury on fly ash demonstrated in this project indicates that current disposal practices are appropriate for the fly ash that will generated in mercury emission control systems utilizing AC. This supports the continued regulation of CCBs under Resource Conservation and Recovery Act (RCRA) Subtitle D for solid wastes and alleviates concern that RCRA Subtitle C (for hazardous wastes) regulations could be considered for CCBs generated with mercury control technologies.

**Environmental and/or Health Benefits**

Results to date have shown that the stability of mercury associated with CCBs is very high. Other air toxic elements exhibit stability similar to that in fly ash and FGD material produced without mercury emission controls present. These findings indicate that current CCB disposal practices are adequately protective of the environment and human health. It further indicates that CCBs produced from systems with mercury emission controls are expected to exhibit environmental performance similar to those produced without mercury emission controls present. Applications where the CCB is subjected to temperatures greater than 200°C are a likely exception, but in these cases, the project data indicate that mercury release is correlated to total mercury concentration.

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