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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 on the management of CCBs. Laboratory and field tasks comprised the bulk of the effort, although obtaining a good and representative sample set and method development were also required in order to provide data that would be accurate and relevant to the real-world scenarios experienced at coal-fired power plants.

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 Hg 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 a CCB disposal site was designed and carried out with the goal of addressing the same release mechanisms at CCB management sites.

The primary benefit expected from this work was to support continued environmentally responsible management of CCBs.

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

Goal

The overall goal of this project is to evaluate the impact of mercury and other air toxic elements on the management of CCBs. Specific objectives to accomplish this goal are 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 to be evaluated will be leaching releases, vapor releases to the atmosphere, and biologically induced leaching and vapor releases.

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, arsenic, 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. Anticipated changes in emission regulations, which were subsequently passed on March 15, 2005 (2), 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 mercury emission control. This effort is 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.

Laboratory tasks addressed the following 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 mercury 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. A field task was also conducted to address the same release mechanisms at CCB management sites.

Approach

The project consisted of the seven tasks listed below to address the research needs. The bulk of the research was in Task 5, 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 (3–5).

Work Plan

The work plan for the third year of the project was essentially the same as the previous years (5), with a few minor adjustments to account for situations encountered during the project.

Task 3, sample identification and selection, focused on collecting FGD samples and “paired” sample sets consisting of a true baseline sample without mercury control and a test sample with mercury control.

Laboratory evaluation of air toxic element releases, Task 5, consisted of three subtasks, which were leaching, vapor transport at ambient and elevated temperatures, and microbiological leaching and vapor releases. Leaching evaluations continued with the synthetic groundwater leaching procedure (SGLP) and 30- and 60-day long-term leaching (LTL) procedure in Year 3. A wet FGD sample was added to the ambient-temperature mercury vapor-phase release experiments, which resulted in a slight change of the experimental apparatus explained elsewhere (3).

Progress

Work continued in all tasks in Year 3. However, only the highlights are provided here.

Analytical Method Selection

A topical report was published detailing the analytical methods used in the project entitled “Laboratory Methods for the Evaluation of Potential Release of Mercury from Coal Utilization By-Products” (3). The analytical methods described were applied to Tasks 4–6. Methods development has continued as needed based on the samples evaluated in the tasks.

Leaching

The leaching data obtained through August 2005 were reported in a topical report entitled “Mercury and Air Toxic Element Leaching from Coal Combustion By-Products” (6). The methods used to leach the samples were SGLP, 30- and 60-day LTL, and the toxicity characteristic leaching procedure (TCLP). Not all tests were performed on all samples. The data set is most complete for the element mercury, and the data presented in that report 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 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.

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 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 3 are 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.

Microbiological Releases

The number of evaluations of microbiologically mediated release of mercury and air toxic elements was reduced in Year 3 because complications were encountered. One continuing problem is sulfur releases from FGD materials, which interferes with vapor-phase mercury measurement. An attempt was made to evaluate a paired sample set of fly ash with and without mercury control; however, these samples were found to be highly alkaline, which killed the bacteria added to the samples before the end of the 30-day experiment. The buffer used for previous samples had a low neutralizing capacity for these samples, and the pH of the system exceeded that necessary to help the bacteria thrive.

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. 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 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.

Measurement/Data Acquisition

Because this was 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.

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. Despite more variability than had been hoped for, the data still proved useful.

Status

The 3-year effort has been extended so the project end date is now September 30, 2006. To date the greatest difficulty has been to obtain representative samples of CCBs from full-scale systems that have mercury controls in place. Accomplishments have included the development and selection of methods for use in this project. A report of the methods development and selection activity was published in 2005. The only method that has required some ongoing refinement is the method developed for the evaluation of microbiologically mediated release of mercury and air toxic elements. The difficulties encountered with high-pH samples and high-sulfur (FGD) samples have required modification to the methods and chemicals used to neutralize the samples, which is required to promote microbial growth and activity. A significant number of samples have been evaluated for leaching profiles, elevated-temperature releases of mercury, and ambient-temperature releases of mercury. A report of the leaching work accomplished under this project was prepared and submitted to project sponsors in 2005. Additionally, reports on the elevated-temperature releases and the microbiologically mediated releases are scheduled to be submitted to project sponsors in January 2006. Field testing was performed in 2004, but additional field testing originally scheduled for 2005 was delayed and will be one topic of discussion in a project sponsor and research group conference call to be scheduled early in 2006. EERC researchers will present options for the field work task which are expected to include an additional field test like the one performed in 2004 or an expanded and modified laboratory experiment that may more closely mimic some utilization applications beyond the release experiments already performed and under way. Additional laboratory activities will be performed to complete the data set.

Potential Applications and Benefits

Potential Users and Real-Life Applications

Utility by-product managers and environmental specialists are expected to be the users of the information generated in this project.

Technology Transfer

Results obtained to date in this project have been included in numerous reports and have been presented at appropriate conferences, as indicated below. Dissemination of data and observations will continue throughout the project.

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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 on total mercury content, leaching profiles of mercury and other air toxic elements, and ambient and elevated temperature releases of mercury from CCBs. The work performed under this project was used along with other published research results to develop summary reports to the Utility Solid Waste Activities Group (USWAG) and the CEA. Preliminary data from the microbiologically mediated releases experiments was also used by at least one project sponsor to initiate a disposal plan for CCBs expected to be produced at a coal-fired plant that will be installing mercury emission controls. It is assumed that the decisions that coal-fired power plants may be making based at least in part on the information provided in this project will also help them realize an economic benefit by making informed CCB management decisions before materials are actually placed in disposal settings or marketed.

Environmental and/or Health Benefits

Results to date have shown that most CCBs release low levels of mercury and air toxic elements.

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