MEASURING MERCURY RELEASES FROM CCBS

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INTRODUCTION

The University of North Dakota Energy & Environmental Research Center (EERC) initiated research on the evaluation of the mercury content of and releases from coal combustion by-products (CCBs) in 1997. Since 2003, EERC efforts have been conducted under a U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL)- and industry-sponsored effort with the goals of 1) formalizing laboratory techniques to measure mercury releases, 2) developing a database of mercury release data, and 3) interpreting the data relative to the management options for CCBs. During the course of this research, the EERC has encountered numerous challenges.

BACKGROUND

For the majority of existing coal-fired power plants, the lowest-cost leading technology to comply with mercury emission regulations is the injection of powdered activated carbon (PAC) into the flue gas prior to the particulate control device(s). However, new technologies and sorbents are under investigation by DOE, the Electric Power Research Institute (EPRI), the EERC, and others. The second most promising technology is wet calcium-based flue gas desulfurization (FGD) systems.

Fly ash and FGD materials are most likely to have increased mercury concentrations depending on the mercury emission control strategies selected. In the work performed at the EERC, data on the release of mercury from fly ash both with and without unburned or activated carbon present have been compiled using laboratory techniques that yield reproducible results with minor experimental and analytical issues. However, FGD materials, which vary both in physical properties and chemical composition, depending upon the system from which they are produced, have offered up significant experimental and analytical challenges. Similar challenges are expected for products containing FGD materials, such as wallboard. Another issue that has yet to be well addressed is the development and acceptance of appropriate experimental protocols to measure mercury release from CCB-containing products for environmental and health risk information.

DISCUSSION

The EERC has used several laboratory experiments to measure mercury releases from FGD materials. The laboratory protocols used to successfully evaluate releases of mercury from fly ash included:

- Batch leaching.
- Ambient-temperature release.

- Elevated-temperature release measured in real time by atomic absorption.
- Microbiologically mediated vapor-phase releases in batch experiments with specialized traps for organomercury.

When these protocols were applied to FGD materials, the physical properties of the FGD materials and the high sulfur content impacted the performance of some of the methods used.

Leaching

Figure 1 summarizes EERC leaching data for FGD materials. One paired sample set of FGD material without and with mercury control is shown. In addition, samples of FGD gypsum collected at a bituminous-fired facility with selective catalytic reduction (SCR) on and off are also shown. These samples were not considered "paired" samples because they were collected several months apart. The variability of mercury in coal over time has been noted in other studies and may be an explanation for the lower total mercury in the sample with SCR on as compared to the one with SCR off. These samples point out the potential for erroneous conclusions if samples *without* mercury control are compared one-to-one to samples ***with*** mercury control, unless these samples are a true baseline sample and a paired sample ***with*** mercury control. Further, the leachability of mercury from these limited FGD material samples indicates that the concentrations of leachable mercury from FGD materials does not correlate to total mercury content, is very low, and is comparable to that observed for fly ash samples both without and with activated carbon (AC) present.

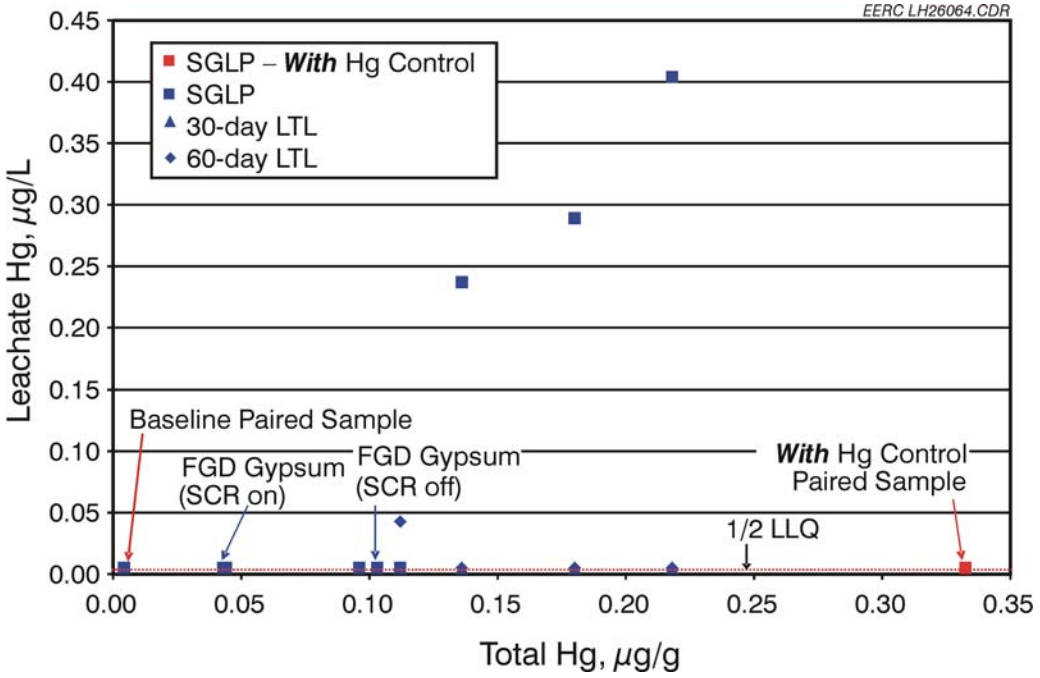

Figure 1. Total mercury vs. short- and long-term leachable mercury for FGD material samples.

Vapor-Phase Releases

Ambient-temperature releases of mercury from FGD materials were measured by placing samples in containers, introducing mercury-free air into the container, and trapping mercury on analytical traps at the exit. The amount of water present with some FGD materials impacted the experimental design compared to the one used for fly ash in that the air had to be collected from above the sample level within the container. When evaluating fly ash, the air was sampled from the fly ash near the bottom of the sample container. Moisture also had an impact on the measured release of fly ash, and it was observed that as moisture evaporated over time, the mercury release was reduced. Figure 2 shows data collected on one FGD sample. A reduction in the moisture was observed and as the test progressed and a black substance formed. The black substance has yet to be identified, but is potentially an example of one issue that can impact mercury measurement on FGD materials. FGD samples are generally at a near-neutral pH and provide an excellent medium for mold and microbial growth which may impact the total mercury release and rate of release. The sampling, handling, and storage of FGD material samples may have an impact on the mercury releases measured.

When evaluating mercury releases from FGD material samples at elevated temperatures, the EERC found that real-time analysis of the mercury releases was not possible because of coincidental release of sulfur which interfered with the atomic absorption measurement of mercury.

In evaluating vapor-phase mercury releases under microbiologically mediated conditions, it was observed that sulfur releases interfered with the protocol used successfully with many fly ash

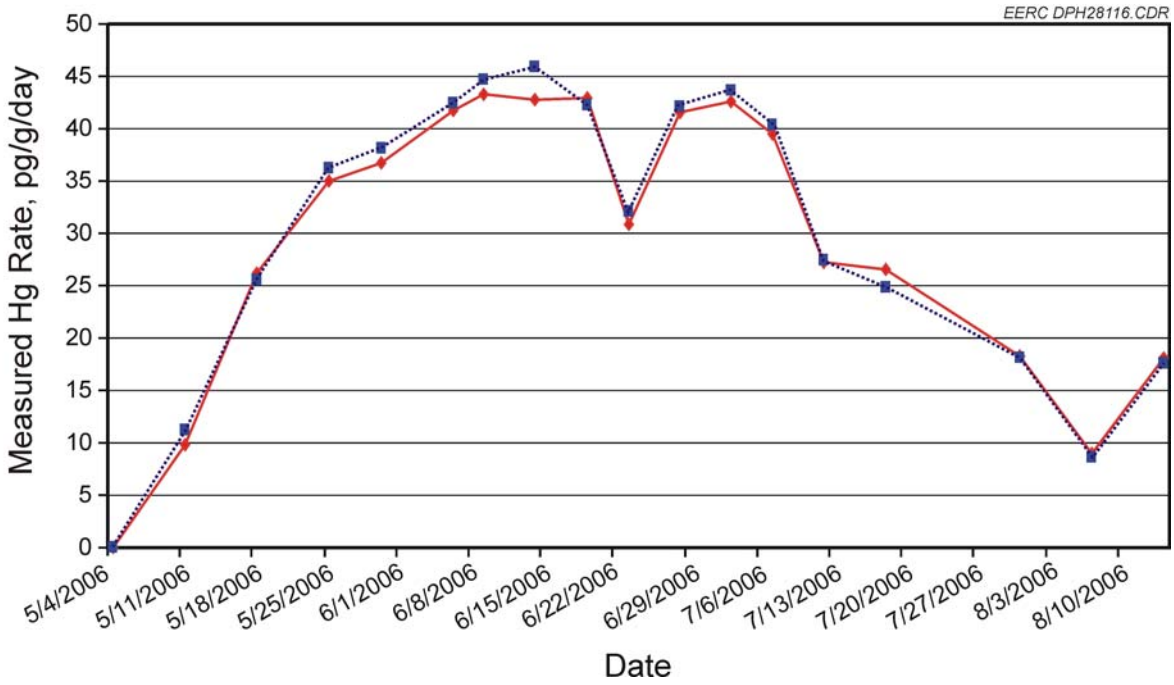

Figure 2. Mercury releases from a wet FGD material over a 3-month period.

samples. Sulfur was released as H_2S and collected on the analytical traps, making them unusable. H_2S release from wet FGD material samples was noted by several groups even when being stored. Not only do the H_2S emissions interfere with the analytical traps used by the EERC, the H_2S may be indicative of changes in the FGD material that may impact the actual release potential of the mercury. The EERC changed its procedure to measure microbiologically mediated mercury releases from CCBs, and that methodology is described elsewhere (1).

SUMMARY

The measurement of mercury releases from CCBs requires careful experimental design and analytical technique which will continue to be modified to meet these challenges. Communication among researchers and industrial groups is needed to facilitate development of appropriate methodologies and interpretation of results. The EERC and several groups have ongoing discussions to facilitate a better understanding of these challenges. Continued research and testing is expected to be performed by these groups on an individual and collaborative basis.

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