





Steven A. Benson, Ph.D.

## CATM Accomplishments for 2000–2001

This is my last official act as the Director of CATM. I have decided to take another position at the EERC, where I will work on various power system initiatives involving the performance of combustion and gasification processes and environmental control systems. This will include many of the issues that I worked on in CATM but will also involve fireside performance, NO<sub>x</sub> reduction, and particulate matter. As I leave the role of director, I would like to announce that John Pavlish will assume the directorship of CATM. John has been involved with CATM as Associate Director for many years, and I am confident that through his leadership and direction, the CATM program will continue to be a success. You will hear more from him in the next *CATM Newsletter*.

CATM is an integral part of the EERC, designed to address science and engineering issues that influence the fate and control of trace elements in thermal systems. CATM consists of five integrated programs areas (PAs), including transformation mechanisms, sampling and analysis, control technologies, modeling and database development, and technology commercialization and education. Some of the key accomplishments in CATM are summarized below.

### ■ PA 1 – Transformation Mechanisms

#### *Fundamental Mechanisms of Mercury (Hg) Species Formation in Power Plants*

- ◆ The effects of cofiring Absaloka and Illinois No. 6 coals with chlorine-rich biomass revealed that high concentrations of alkali metals (~30 wt% on an ash basis) in the alfalfa reacted with the available chlorine to form metal chlorides, thus inhibiting Hg(p) and Hg<sup>2+</sup> formation.
- ◆ Injections of NO<sub>2</sub> into Blacksville (bituminous), Absaloka (subbituminous), and Falkirk (lignite) coal combustion flue gases did not significantly affect Hg speciation.

### ■ PA 2 – Sampling and Analysis

#### *Development of Sampling and Analytical Tools for Oxidized Hg Species*

- ◆ This effort focused on developing an analytical tool to determine the species of Hg<sup>2+</sup> compounds in a flue gas stream

using cryotrapping and mass spectrometry. A method for transferring mercuric chloride from the initial cryotrap to the mass spectrometer was developed.

### ■ PA 3 – Control Technologies

#### *Development of Hg Control Technologies*

- ◆ Tests conducted with and without moisture indicate that moisture plays an important role in the SO<sub>2</sub>–NO<sub>2</sub> interaction that reduces a sorbent's ability to capture and retain Hg.
- ◆ Tests to further evaluate the interactions among Hg<sup>0</sup>, NO<sub>2</sub>, and SO<sub>2</sub> suggest that SO<sub>2</sub> does not produce good Hg capture, while NO<sub>2</sub> produces excellent capture. This suggests that the Hg<sup>0</sup> and NO<sub>2</sub> react heterogeneously to form a mercury–nitrogen compound that is retained by the sorbent.

#### *Characterization of Coal-Derived Hg Sorbents*

- ◆ Two activated carbons (ACs), a high calcium (Norit FGD) and an AC developed at the EERC, were exposed to a simulated flue gas atmosphere with various levels of SO<sub>2</sub>, NO<sub>2</sub>, HCl, Hg<sup>0</sup>, and H<sub>2</sub>O. The exposed sorbents were analyzed using x-ray absorption fine structure (XAFS) and x-ray photoelectron spectroscopy (XPS) to determine the chemistry of S, N, and Hg in the carbons.

- ◆ Under conditions deficient in HCl, the AC sorbent made at the EERC exhibited the ability to capture Hg for a longer period of time without breakthrough than did the Norit lignite-based activated carbon (LAC). The absence of water and HCl also improved the sorbent's capacity to capture Hg. As seen in previous tests, an SO<sub>2</sub>–NO<sub>2</sub> interaction exists, resulting in the desorption of oxidized Hg captured in the sorbent.

#### *Stability of Hg in Combustion By-Products*

- ◆ The project was aimed at determining the mechanisms of Hg release from coal combustion by-products (CCBs) and biomass materials.
- ◆ The results to date indicate no clear evidence that the rate of Hg release is related to the Hg level in the ash. The Hg release from six selected samples

was low—below 200 picograms per 100 grams of CCB for each 90-day equilibration period.

- ◆ UV light was found not to be effective in devolatilizing Hg<sup>0</sup> from the fly ash; however, IR radiant energy resulted in devolatilization of Hg<sup>0</sup> without measurable change in bulk temperature.

### ■ PA 4 – Modeling and Database Development

#### *Application of Database and Models to the Fundamental and Applied Study of Air Toxic Metals*

- ◆ The CATM database was enhanced with the addition of data from U.S. coal-fired power plants utilizing the EPA Information Collection Request (ICR) data. The database now contains over 300,000 analytical measurements.

- ◆ A theoretical model of Hg–sorbent interactions has been developed and is currently being tested. The model is focused on modeling gas-phase mass transfer to the sorbent.

- ◆ A neural network model is being developed to predict plant emissions utilizing data from coal entering and emissions from the plant based on the ICR data.

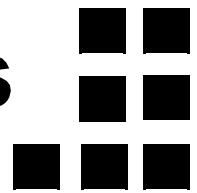
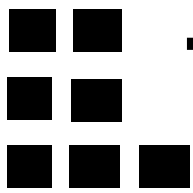
### ■ PA 5 – Technology Commercialization and Education

#### *Technology Commercialization, Education, and Publications*

- ◆ The EERC, through CATM, EPA, and the U.S. Department of Energy, organized and sponsored the Air Quality II: Mercury, Trace Elements, and Particulate Matter Conference (AQII), held September 19–21, 2000, in Tysons Corner, McLean, Virginia. AQII provided over 300 participants from industry, government, academia, and research organizations with strategic information on recent advances.

It has been a pleasure serving as CATM Director, and I have enjoyed the interaction with CATM sponsors and colleagues. I will continue to be involved in projects associated with CATM, so you will see me at meetings. Thank you.

*For more information, contact John Pavlish, CATM Director, at (701) 777-5268 or [jpavlish@undeerc.org](mailto:jpavlish@undeerc.org).*



## Understanding Mercury Sorbent Interactions

The current hypothesis for Hg behavior in a flue gas environment suggests that acid gases ( $\text{SO}_2$ ,  $\text{NO}_2$ , and  $\text{HCl}$ ) and their oxidation products bind with basic sites on a sorbent's surface. Data from a recent project led to further understanding of the mechanisms.

Two activated carbons, high-calcium Norit FGD and a high-sodium carbon made at the EERC, were evaluated to determine their ability to sorb Hg and to determine the surface chemistry of the reacted sorbent particles after exposure to flue gas components. The activated carbons were placed in a fixed bed and subjected to a simulated flue gas atmosphere with mixture levels of  $\text{SO}_2$ ,  $\text{NO}_2$ ,  $\text{HCl}$ ,  $\text{Hg}^0$ , and  $\text{H}_2\text{O}$ . The testing procedure is not meant to mimic the injection of AC into a flue gas stream but simply to gain information about the sorbent's capacity and surface chemistry.

Under simulated flue gas conditions deficient in  $\text{HCl}$ , the AC made at the EERC exhibited the ability to capture Hg for a longer period of time without breakthrough than did the Norit FGD. Thus it improved the capacity for Hg sorption. The absence of water and  $\text{HCl}$  also improved the EERC sorbent's capacity to capture Hg. As seen in previous tests, an  $\text{SO}_2$ - $\text{NO}_2$  interaction was observed that results in the desorption of oxidized Hg captured by the sorbent.

The carbons were characterized by x-ray absorption fine structure (XAFS) to determine the speciation of chlorine, sulfur, and Hg. Most of the sulfur present was of the sulfate form. Sulfur was also present in the elemental and sulfide forms. XAFS also indicated Hg was bound as a chloride or a sulfide/sulfate. The bond energies of these two compounds are too close to differentiate between them.

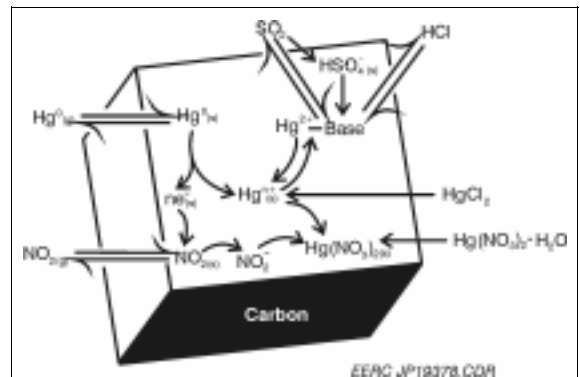
XPS (x-ray photoelectron spectroscopy) analysis was used to determine the form and abundance of Cl, S, and N on the surface of the ACs. A survey scan revealed the presence of C, N, O, Na, Mg, Al, Si, P,

S, Cl, Ca, and Fe on the ACs. More detailed high-resolution scans indicated predominantly sulfate sulfur and organic chlorine and chloride. Nitrogen was present as an ammonium salt and a nitride. Analysis of an unexposed sample indicated no Cl and mostly sulfate sulfur. The analysis of an unexposed sample also indicated sulfur absorbed from the flue gas is sulfate. A future study will have several tests involving a sorbent deficient in silicon. The absence of silicon will allow for XPS analysis of Hg on the sorbent.

FT-IR (Fourier transform infrared spectroscopy) analysis was completed on the eight exposed samples. The FT-IR analysis could only indicate the presence of sulfate and possibly nitrate. The FT-IR technique was not able to provide any additional information.

Chlorine seems to be very important in the Hg sorption process. When  $\text{HCl}$  is not in the flue gas, breakthrough of Hg occurs earlier. In the presence of  $\text{HCl}$  in the flue gas, the Cl disappears from the AC after breakthrough.

It is speculated that several sorption events occur during the exposure of carbon sorbents to flue gas components. Part of the Hg binding mechanism likely involves the oxidation of  $\text{SO}_2$ . When  $\text{NO}_2$  is omitted from the flue gas, less sulfate was accumulated. The effect of  $\text{H}_2\text{O}$  also indicates that the oxidation mechanism involves water, likely in the formation of the sulfite intermediate.  $\text{HCl}$  did not appear to have an effect on the sulfate formation reaction in the case of either carbon. One explanation is that the volatility of  $\text{HCl}$  is much greater than the  $\text{H}_2\text{SO}_4$ .  $\text{HCl}$  may compete effectively with  $\text{SO}_2$  for the active sites, but as time progresses, the formation of sulfate changes the relative volatility of the acids.



Schematic of Hg binding mechanism.

Protons would then transfer to chloride and  $\text{HCl}$  escape in the gas phase.

Results from a recent project confirm that there is competition for these basic sites and that at breakthrough, the sites must be saturated with sulfate, since no more Cl can bind. Consequently, the  $\text{Hg(II)}$  is also unable to bind to the stabilizing basic sites at this time and is released as volatile  $\text{Hg(II)}$  forms.

Since very little data exist for Hg compounds, the identity of all the volatile Hg species remains unknown. The figure shown above is a representation of the possible Hg binding mechanism that is being further investigated and developed through the CATM program.

This project was cofunded by the Consortium for Premium Carbon Products from Coal (CPCPC) of the Pennsylvania State University and CATM.

**For more information, please contact Steve Benson, EERC Senior Research Manager, at (701) 777-5177 or sbenson@undeerc.org; Jason Laumb, EERC Research Engineer, at (701) 777-5114 or jlaumb@undeerc.org; or Ed Olson, EERC Senior Research Advisor, at (701) 777-5155 or eolson@undeerc.org.**

# Scott Renninger Named New RAC Chair

CATM has named Scott Renninger the new Chair of its Research Advisory Council (RAC). Scott currently serves as a senior project manager for the Environmental Projects Division at the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) colocated in Morgantown, West Virginia, and Pittsburgh, Pennsylvania. He leads several multimillion dollar cooperative agreements within DOE's Hg control technology development program.

Throughout the years, DOE and the EERC have teamed on numerous projects to further the development of effective Hg control technologies. Beginning in 1995, DOE initiated the Advanced Emissions Control Technology Program (Mega-PRDA Program) to develop, test, and evaluate approaches to controlling Hg emissions from coal-fired utility boilers. Highlights from this and other DOE Hg-related projects are summarized below:

ADA Technologies, Inc. (ADA), tested its "Mercur-RE Process" for removing Hg from coal-burning boilers.

DOE teamed with Public Service Company of Colorado (PSCO), EPRI, and ADA to perform pilot- and full-scale evaluations to compare the effectiveness of carbon injection to Hg sorption on native fly ash.

DOE and EPRI funded a Radian International Corporation project focused on catalytic oxidation of vapor-phase elemental Hg, enhanced removal of particulate-bound hazardous air pollutants (HAPs) by electrostatic charging of liquid drops, and enhanced removal of Hg with additives in the flue gas desulfurization (FGD) process liquor.

A team of researchers led by Physical Sciences, Inc. (PSI), developed a quasi-empirical model called the Toxics Partitioning Engineering Model (ToPEM) to predict the formation and partitioning of trace element emissions.

PSI was awarded a Phase II SBIR (Small Business Innovation Research) project to develop a zeolite sorbent and demonstrate its effectiveness.

DOE and the Ohio Coal Development Office funded a Babcock & Wilcox (B&W) project aimed at development of practical, cost-effective strategies for reducing HAP emissions from coal-fired electric utility plants. The 3-phase project was conducted at the Clean Environment Development Facility (CEDF) in Alliance, Ohio.

Argonne National Laboratory (ANL) tested a new concept to enhance gaseous Hg removal in wet scrubber environments.

Under a recent solicitation to test and further develop technologies for control of Hg, DOE is partnering with coal-fired utilities to perform large-scale field testing as described below:

B&W, through McDermott Technology, Inc., is demonstrating a cost-effective Hg removal system at two coal-fired power plants equipped with wet scrubbers. The technology involves adding small amounts of a liquid reagent to the scrubbing solution to attain a target of 90% Hg removal at a cost of one-half to one-fourth of the cost of current activated carbon Hg removal methods.

ADA is developing a portable system that injects a dry sorbent such as fly ash or activated carbon. A cool-water mist is sprayed into the flue gas to cool it to the temperature range in which the dry sorbent is most effective. Because cooling the flue

gas can increase the formation of corrosive SO<sub>3</sub>, ADA's technology includes a reagent injection system to control the buildup of SO<sub>3</sub>, if necessary.



*Scott Renninger, CATM  
Research Advisory Council Chair*

From the list of Hg projects described above, it is clear that DOE is committed to developing cost-effective control technologies for the utility industry. Scott's experience with Hg and his involvement in DOE's Hg programs will enable him to serve effectively as the new RAC Chair.

**For additional information, please contact Scott Renninger at (304) 285-4790 or [srenni@netl.doe.gov](mailto:srenni@netl.doe.gov), or John Pavlish, CATM Director, at (701) 777-5268 or at [jpavlish@undeerc.org](mailto:jpavlish@undeerc.org).**

*(EPA Decision, continued from front page)*

limited field data suggest that it may also be effective at oxidizing Hg only with high-chlorine coals.

In summary, the available data indicate that existing pollution control methods are not effective in controlling the emissions of Hg<sup>0</sup> from low-chlorine western coals. Given that, the EERC is initiating a research project specifically targeted at developing and field-testing control technologies that are effective for plants burning western coals.

EERC researchers have been at the forefront of advancing the understanding of Hg chemistry, measurement, transformations, solid-gas interactions, and development of control technologies for many years. While progress has been made in developing technologies to remove Hg from plants firing western coals, many challenges still remain.

**If you would like to learn more about or participate in this project, please contact John Pavlish, CATM Director, at (701) 777-5268 or at [jpavlish@undeerc.org](mailto:jpavlish@undeerc.org).**

# CATM Performs Regression Analysis of ICR Data – Part I

**T**he 1990 Clean Air Act Amendments set a course for dealing with hazardous air pollutants (HAPs). There are 188 HAPs, 11 of which are trace elements and associated compounds, including antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, Hg, nickel, and selenium. In 1993, the EERC established the Center for Air Toxic Metals (CATM) under the sponsorship of the U.S. Environmental Protection Agency (EPA) to work cooperatively with industry and government to develop sound scientific information on air toxic metals. The goal of CATM is to understand the chemical behavior of trace metals in fuels and energy systems in order to provide a valid basis for measuring and controlling air toxic emissions and for evaluating their fate and impact on the environment.

In support of this goal, CATM has developed and maintains a large database including detailed information on analysis (sample type and analytical method), engineering (system type, design, and operating parameters), and materials (sample type and origin). The database is fully relational and can retrieve all samples that meet any given criteria.

Because of concern over Hg emissions, EPA issued an ICR on select coal-fired electric utilities in the United States. The purpose of the request was to determine if there is a need to regulate Hg emissions from these facilities. The ICR consisted of three phases. Phase I involved collecting information on each coal-fired power plant

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## Air Quality III Set for Fall 2002

The Air Quality III: Mercury, Trace Elements, and Particulate Matter Conference is currently being organized to be held in the Washington, D.C., area in the fall of 2002. The format for AQIII will be similar to that of AQII, with one stream focused on Hg issues and a second stream focusing on trace elements and particulate matter.

The EERC, along with the U.S. Environmental Protection Agency (EPA), through the EERC's CATM, the U.S. Department of Energy National Energy Technology Laboratory, and EPRI organized and cosponsored AQII to provide participants with strategic information regarding advances made in Hg and particulate matter research.

AQII was held September 19–21, 2000, in McLean, Virginia, with over 300 attendees from 42 states and 7 countries. The demographic breakdown showed approximately 50% of the attendees

represented industry, 25% represented government organizations, and the remaining 25% represented research and academia. The attendees provided extremely positive feedback, including the following:

- ◆ *"Impressive group of presenters and exhibitors."*
- ◆ *"This conference is a 'must attend' for all researchers, policy-makers, and regulators. Far and away the best all-round conference with respect to mercury and PM<sub>2.5</sub> issues."*
- ◆ *"Excellent, well-organized conference with breadth of knowledgeable speakers and vendors—I'll be back for 'AQIII'."*
- ◆ *"...a well-rounded, informative program on the science, technology, and policy of some of today's most pressing air quality issues..."*
- ◆ *"The scientific information coupled with regulators' and industries' perspective was*

*not only good, but is necessary for continued economic growth and maintaining our environment."*

- ◆ *"Really one of the best conferences I've ever attended, and I've attended all of them."*

The conference provided an opportunity for attendees to discuss key interrelationships between policy, science, and emerging issues that lead to acceptable programs and policies to protect human health, the environment, and economic growth. AQIII will continue these discussions. Look for a flyer with more detailed information and location coming to you later this year, and mark your calendars!

**For additional information, please contact John Pavlish, CATM Director, at (701) 777-5268 or at [jpavlish@undeerc.org](mailto:jpavlish@undeerc.org) or Deb Haley at (701) 777-3120 or at [dhaley@undeerc.org](mailto:dhaley@undeerc.org).**

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