

2006 HIGHLIGHTS

The following are project highlights of research performed through CATM during the last year.

MERCURY TRANSFORMATIONS IN COAL COMBUSTION FLUE GAS

Research within this area is imperative for development and validation of improved mercury emission measurement, monitoring, and control technologies. This year's research sought to capture multiple interactions among mercury species, other flue gas components, fly ash and unburned carbon (UBC), and injection of sorbents and/or additives into coal combustion flue gas. The main focus was on mercury-related issues, including transformation mechanisms of mercury within coal flue gas, but emphasis was also placed on understanding the impact that applying mercury control techniques had on other hazardous air pollutants (HAPs) in flue gas and other coal combustion by-products (CCBs).

To study mercury-flue gas chemistry in a high-temperature, halogen-enriched flue gas environment, an existing entrained-flow reactor (EFR) at the EERC was upgraded so that experiments could be performed in the temperature range from 400° to 800°C to evaluate the kinetics of mercury transformations in a high-temperature environment. Mercury kinetic tests were conducted in January 2007 during the 1-week pilot-scale combustion test sponsored by CATM Program Area 3 using both bituminous and subbituminous coal, with calcium chloride addition into the combustion zone. Data analysis is under way.

In order to understand the role UBC content in coal fly ash plays on Hg⁰ oxidation and adsorption, two relatively carbon-rich fly ashes have been collected and tested for their ability to capture mercury: one from bituminous coal and one from subbituminous coal. The carbon-bearing subbituminous fly ashes were effective in capturing Hg, whereas in the bituminous fly ash, they were not. Both coal fly ashes were sieved to concentrate the larger UBC particles. Particle characterization seems to indicate that the degree of Hg adsorption and Hg⁰ oxidation

depends significantly on the morphology, microstructure, and/or chemical composition of UBC particles.

Tests of impregnated standard activated carbon (AC) and a fly ash with a sulfur compound solution were conducted on the EERC bench-scale thin-bed reactor to determine whether Hg⁰ capture results from interactions with sulfur forms alone or in synergy with AC. The impregnated fly ash showed little capacity for elemental mercury, and the impregnated AC showed breakthrough similar to the untreated carbon, indicating no capacity benefits as a result of impregnation using the sulfur compound. The kinetic experiments indicate that a sulfur species formed on the carbon surface has an inhibitory effect on the mercury oxidation that is overcome by HCl when it is present.

THE FATE OF ARSENIC IN WASTE-TO-ENERGY (WTE) FACILITIES

Arsenic-treated wood used in residential and industrial applications will be a disposal issue for the next 25 to 50 years. WTE facilities present the greatest opportunity for mass disposal of treated wood products. Based on this identified opportunity, the EERC conducted a study to determine the fate of copper, chromium, and arsenic from treated wood under the conditions found in a WTE facility, showing that combustion of arsenic-treated wood in a WTE facility is a technically feasible alternative for disposal. Flue gas emissions are not expected to exceed federal regulatory limits with implementation of maximum achievable control technologies at WTE facilities; however, high arsenic levels may cause combustion ash to be classified as hazardous waste.

SAMPLING AND ANALYTICAL METHODS

In this task, a project was initiated to develop an accurate and reproducible method for analyzing biological samples of very low mass for the determination of Hg, Se, and other elements in biological matrices. A literature review was done to identify applicable sample preparation and analytical techniques.

Microdigestion procedures and analytical techniques, including inductively coupled plasma mass spectroscopy (ICP-MS) and cold-vapor atomic absorption spectroscopy (CVAAS) are being investigated for modification and will be compared with suitable biological standard reference materials.

EPA Method 26A, a wet-chemistry method to measure Cl_2 and HCl emissions, determines average total chlorine concentration over an extended period of time but cannot differentiate continuous changes in Cl_2 and HCl concentrations, which is essential for understanding time-dependent reactions, such as fluctuations in Hg chlorination caused by kinetic and equilibrium processes. Using actual coal combustion flue gas, the EERC demonstrated that gaseous HCl and Cl_2 could be selectively sampled and analyzed using infrared (IR) spectroscopy (Thermo Electron Model 15C HCl analyzer) with modifications. Work will now proceed to the development of a prototype continuous Cl_2 monitor.

Activities in this task will supplement data generated in an ongoing related CATM project entitled "Measurement of Halogens." It is the goal of the project to develop a sensitive, reliable, and reasonably priced method at the EERC with existing equipment that is as sensitive as instrumental neutron activation analysis (INAA) (1–10 ppm Br and Cl determination in coals), but can provide better distinction between Br and Cl. The challenge is to develop a preparation procedure that significantly increases the sample size, while minimizing possible instrumental interferences. Initial results show very low detection of Br in alkaline solutions by ICP-MS. Work will continue to determine lower limits of quantitation for Br and Cl with two identified methods.

A task of this project is also evaluating dry sorbent traps, which are presently unacceptable for Appendix K of the Clean Air Mercury Rule (CAMR) because, under certain sampling conditions, particularly for long sampling times in a high SO_2/SO_3 flue gas environment, the method is not reliable on low spike recoveries and mercury breakthrough. This project is evaluating ways to improve the spiking system,

overcome certain interferrants like SO_2/SO_3 , as well develop a sorbent-additive that will capture and retain Hg in the traps.

CATM researchers continue to improve laser spectroscopic techniques for determining mercury. Previous tests have shown this method as feasible for measuring mercury in flue gas; however, when NO_2 or SO_2 are present, they interfere with mercury measurement because they have broad absorptions in the UV. Techniques such as modulating the lamp wavelength and separating the mercury using gold amalgamation are being investigated with varying degrees of success to allow measurement in air versus argon.

The last task is developing a sampling protocol for arsenic (arsine gas), selenium (hydrogen selenide), and mercury (Hg^0) in a reducing gas environment, such as in gasification. This includes both development of a sample-conditioning protocol that will convert the desired species into a form suitable for continuous emission monitor (CEM) measurement as well as possible modifications to the system to find a solution for some of the caustic solutions. Results will be compared to those obtained by EPA Method 29 for trace metals.

MEASUREMENT OF HALOGENS

This ongoing project is using existing methods and developing improved methods for evaluating the effects of Cl and Br on the conversion of Hg^0 to inorganic and organic Hg compounds with coal combustion flue gas and statistically evaluating the results for interelemental correlations. Work has been focused on modifying and simplifying EPA Method 26A to allow for better detection of Cl and Br and discerning between them. Testing is still under way and provides data for the preceding project.

DEVELOPMENT OF AN OXIDIZED MERCURY- SPIKING SYSTEM

CATM researchers are completing a project to design an Hg^{2+} -spiking system that can be used in field continuous mercury monitor (CMM) installations—CMM manufacturers,

researchers, and power plants can benefit from such a quality assurance/quality control (QA/QC) tool. This catalysis-based system will use elemental mercury and chlorine to form reactive gaseous HgCl_2 . Parametric testing showed the portable prototype system is capable of producing a stream of over 98% oxidized mercury. During operation, measurements with the Nippon CMM indicated more than 95% of the mercury entering the reactor is oxidized to a form that is transported out of the system. This prototype can be used with compressed air or nitrogen for the dilution gas and nitrogen gas for the permeation sources. This system has been operated continuously for more than 2 weeks without significant changes in output ($\pm 2\%$ of output over a 24-hour period).

DEVELOPMENT OF CONTROL TECHNOLOGIES

CATM research activities continue to focus on the development and testing of control technologies, especially for mercury. Several bench-scale tests have been performed to evaluate potential sorbents for mercury control—both those prepared at the EERC and those provided by external vendors. Tests were completed to support CATM sorbent development research, with additional tests to be performed as new sorbents are identified. Testing continues to evaluate the effect of SO_3 on sorbent performance. Tests in a full-factorial design have been completed to determine the effects of SO_3 on sorbent reactivity and capacity for oxidized mercury control. Results were compiled to facilitate a greater understanding of the mechanisms between the sorbent and flue gas occurring on the surface of the carbon. Future work will further evaluate the effects of SO_3 concentration and fixed-bed temperature, as well as moisture and acid gas concentrations, on mercury sorbent performance. A future CATM project will look at the effects of SO_3 on the capture of Hg and HgCl_2 by brominated carbon sorbents. In order to evaluate mechanisms for Hg–flue gas interactions, several approaches for creating highly dispersed mercury sorbents have been investigated and tested at the bench scale. Next-generation proprietary nanoparticle sorbents are currently being synthesized and will be tested in 2007.

CATM testing continues to evaluate alternatives to better utilize sorbents, including ACs. Field testing of the EERC proprietary sorbent enhancement technology has been successful. The information and experience obtained during the field test will facilitate future optimization of the on-site sorbent enhancement technology. The EERC and the Babcock & Wilcox Company (B&W) are now teaming together in the process of designing and fabricating a commercial enhancement unit capable of treating coal-fired power plant up to 600 MW.

CATM researchers also continue the evaluation of ways to improve the cobenefit effects of selective catalytic reduction (SCR) with flue gas desulfurization (FGD) systems. The upgrade on the bench-scale SCR unit has been completed. The next step will be incorporating the mercury oxidant delivery system with the bench-scale SCR. Tests have been planned to evaluate the performance of a number of mercury oxidants on mercury oxidation across the SCR.

Pilot-scale testing planned for January 2007 will provide an opportunity to use actual flue gas for various tests involving other areas of CATM research.

MODELING MERCURY SPECIATION IN COAL COMBUSTION SYSTEMS AND INTERACTIONS ON ACTIVATED CARBON

A quantum mechanical approach was employed in the study of mercury interactions with flue gas components on AC surfaces. The complexity of such interactions makes it difficult to obtain quantitative thermodynamic data and reaction rates experimentally. However, a recently developed structural/mechanistic model developed under CATM offers the possibility to perform such calculations which yield energy minima for reactants, intermediates, and products. From these calculations, information about the relative thermodynamic stabilities and optimum conditions of the species involved can be obtained. Information about barriers to reactions is vital in the determination of reaction rates and rate constants and can also be obtained from these calculations after fully characterizing the transition state species in the

reaction path. This thermochemical information at the determined optimum conditions together with rates can allow one to adjust certain experimental parameters in the most cost-effective manner while maintaining high throughput capacity.

Initial results based on free energy and enthalpy data for the elementary reactions on the AC surface seem to indicate that predominantly aromatic compounds will suffer a larger energy penalty in oxidizing elemental mercury at room temperature than their aliphatic counterparts. The insertion step of Hg^0 on the graphene edge surface is not thermodynamically favorable at 298.15 K. On the other hand, surface activation by acidic flue gas components and the capture of Cl ions by the chemisorbed mercury adducts is feasible, and this yields organomercury chlorine compounds, which eventually release the captured Hg as HgCl_2 at breakthrough.

INVESTIGATION OF MERCURY AND CARBON-BASED SORBENT REACTION MECHANISMS

Research in this project was conducted through a consortium focused on improving the mercury capture efficiency of carbon-based sorbents in flue gases typical of firing lignite and other low-chlorine, low-sulfur fuels and focused on establishing a better understanding of mercury-sorbent reaction mechanisms, with the goal of improving mercury capture. The project aimed to develop better sorbents to control mercury emissions in subbituminous- and lignite coal-fired power plants equipped with fabric filters, electrostatic precipitators, and wet and dry scrubbers through investigation of surface reaction mechanisms by which carbon sorbents oxidize and capture mercury. The research plan examined flue gas-mercury interactions on carbon sorbents, sorbent surface chemistry, effects of surface modifications to the carbon structure on kinetics and capture, and evaluation of the efficiency of ACs prepared with surface modifications in low-chlorine fuel combustion applications. In previous years, the research in this project focused on examining the role of HCl in promoting the oxidation of elemental mercury on the carbon surface; the effort this year focused on the mechanism of SO_2 oxidation as a competing reaction on the carbon surface. Testing showed the promotion effect of HCl on

the oxidation of SO_2 is consistent with the promotion effect on the oxidation of mercury, suggesting that the carbon catalysis mechanisms are similar. Various methods were used to elucidate the surface of the carbon and the effectiveness of modifications to the surface.

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

The stability of mercury and other air toxic elements associated with CCBs has become a prominent question as the coal-fired utility industry works to develop and test mercury emission controls that may consequently increase the mercury and air toxic element concentrations associated with CCBs. In order to address the potential for release of selenium and arsenic from CCBs, sorbents, and combinations adequately, one key release mechanism that must be evaluated is elevated-temperature vapor release. The overall goal of this project is to develop a method to quantify the real-time evolution of selenium and arsenic from fly ash at elevated temperatures. The development of a method to thermally desorb selenium and selenium compounds has been the focus of evaluation this year.

MERCURY'S INTERACTION WITH SELENIUM

Using animal models developed in previous years, this project is an integrated study to better understand how Se affects Hg accumulation and how high Hg exposure harms Se physiology. Because bioaccumulation of Hg occurs in plants that are also known to bioaccumulate Se, this research will provide insights into the ways that Se status influences MeHg toxicity at the cellular level and assess the influence of Se on Hg accumulation in Hg hyperaccumulator plants while evaluating applications for remote sensing using spectral reflectance. CATM research with insects demonstrated that organic and inorganic dietary Se are equally effective in preventing toxic effects of high Hg exposures; food chain experiments are being completed to examine the influence of dietary Se in the normal range of intakes on absorption and retention of dietary MeHg present at low concentrations reflecting natural exposures. Also, cell cultures grown with graduated concentrations of Se that are subjected

to MeHg and inorganic Hg added at incremental concentrations ranging from none to toxic levels are being used by CATM researchers to conduct Se dose-, form-, and time-dependent studies. These studies evaluate MeHg toxicity using sensitive markers of cell health and death, including rates of MeHg demethylation. Additionally, programmed cell death (apoptosis) in MeHg exposed brain tissues is being assessed. Finally, CATM researchers are studying the interactions of dietary Hg and Se and possible connections between trace metals and heart disease through the examination of heart tissues of human patients with dilated cardiomyopathy, a pathology reportedly associated with high Hg accumulations.

PHYSIOLOGICALLY BASED PHARMACOKINETIC MODEL OF MERCURY– SELENIUM INTERACTIONS

This project is being conducted using the data generated from a separate but complementary animal research project entitled “Investigating the Importance of Hg–Se Interactions.” A previously developed physiologically based pharmacokinetic (PBPK) model of mercury distributions is being extended into a new, more comprehensive mathematical model called the Physiologically Oriented Integration of Nutrients and Toxins (POINT) model. This model reflects the influence of methylmercury and its metabolites on selenium availability in various tissue compartments. Animal exposure experiments conducted in this project have been done, and the POINT model has been used to evaluate and interpret the results of the complementary rat study. Results confirm earlier CATM findings, but allow a more in-depth analysis of Hg and Se interactions. Preliminary results indicate that toxic levels of dietary mercury affect Se distribution to the brain and limit Se availability, impairing enzyme activities that protect against oxidative damage from free radicals produced as a result of normal metabolic activities. The model will also be applied to human data to examine historically noted correlations and predict risk in human populations. The POINT model considers time–dose correlations of dietary Hg consumption in the context of the Se physiology that appears to be the molecular target of Hg toxicity. Therefore, this is the first

study to comprehensively examine the underlying interactions between Hg exposure and the protective effects of dietary Se status in establishing associated risk.

MERCURY METABOLISM AND SELENIUM PHYSIOLOGY STUDIES

The research activities for this project are ongoing from previous years. Selenium has long been known to be a mercury antagonist, but results of this project support the hypothesis that mercury is a selenium antagonist. This distinction appears to define the primary mechanism of mercury toxicity and is of pivotal importance in quantifying the risks associated with mercury exposure. Continued analysis of results from dietary rat studies demonstrates that low-selenium diets resulted in sensitivity to mercury exposure. Meanwhile, rats fed selenium-rich diets showed no adverse effects from consumption of otherwise toxic levels of mercury. Because selenium is an essential nutrient that is particularly important in brain function, the signs and symptoms of mercury toxicity appear to occur as a consequence of mercury-dependent selenium sequestration and the resulting loss of physiological functions normally supported by selenium.

MERCURY–SELENIUM INTERACTIONS IN AQUATIC ECOSYSTEMS

Activities in this project are also ongoing from the previous year and investigated the affinity of selenium for mercury and selenium’s influence on mercury retention in aquatic ecosystems. Continued analysis confirms that the effect appears to occur intracellularly, resulting in formation of an insoluble HgSe complex, which limits the biological availability of both elements. Physiological experiments using rapid-growing, short-lived insects were conducted, which continue to show selenium-dependent protection against mercury toxicity in insects and appear to reflect findings showing selenium-dependent enzyme cellular activities in all other animal species.

MOLECULAR INTERACTIONS OF TOXIC METALS

This project investigates the molecular interactions between mercury and selenium and explores a potentially novel molecular mechanism involving nickel subsulfide interaction with DNA (deoxyribonucleic acid). These studies compare and contrast direct, indirect, and consequent molecular mechanisms of toxicity. Distinctions between molecular mechanisms of various toxic substances determine how they inflict physiological damage. This provides a new perspective on the molecular mechanism of mercury toxicity, which appears to act through a consequent mechanism, rather than through inducing direct or indirect molecular damage within exposed cells.

TECHNOLOGY COMMERCIALIZATION, EDUCATION, AND PUBLICATION

To facilitate the transfer of technical information produced by CATM, several communication vehicles are used, including participation in both domestic and international conferences, symposia, workshops, and other educational programs, and annual meetings; quarterly reports on topical issues related to mercury through a collaborative project funded by CATM Affiliates, U.S. Department of Energy, and the Canadian Electricity Association; and the publication of a newsletter that is also available electronically. In addition, the CATM Director and staff provide input into various public forums during the year to assist in the development of venues of technology transfer that may not be directly funded by CATM.

The CATM Web page has been maintained throughout the year and can be accessed at www.undeerc.org/catm. Copies of the *CATM Newsletter* and topical reports to CEA are available and can be accessed via the CATM Web page for download and distribution.

CATM continues to be instrumental in various venues for disseminating information to the public and specifically to stakeholders affected by toxic metal issues. This included presentations at the MEGA symposium, the 8th International Conference on Mercury as a Global Pollutant, the Western Fuels Symposium, and distribution via the CATM Web site, CATM newsletter, participation on a mercury experts committee, and informal exchanges at regional workshops. CATM researchers also continued specific training of future and current researchers and utility personnel, including focused cutting-edge training on all aspects of CMMs. This training was delivered in late 2005, May 2006, and will be periodically presented as long as there is an interest among stakeholders.

