

## Center for Air Toxic Metals (CATM) 2003 Research Ideas

The following is a list of compiled research ideas that will be discussed at the annual Research Advisory Council (RAC) meeting on September 9<sup>th</sup>, 2002. Please note the ideas are listed by research topical areas.

### **Research Area 1 – Air Toxic Metals Transformation, Transport, and Sorption Mechanisms**

*Goal:* Develop a fundamental understanding of the mechanisms responsible for the formation of air toxic species within thermal conversion systems for the purpose of designing and operating effective control strategies. The air toxic of primary focus is mercury.

*Current Focus:* Using bench-scale combustion systems and entrained-flow reactors to identify and characterize the kinetic transformation of Hg species in a coal combustion flue gas environment. This involves optimizing Hg<sup>0</sup> chlorination using low-chlorine coal that emits primarily Hg<sup>0</sup> and adjusting HCl, CO, and NO concentrations in combustion flue gas to effectively convert Hg<sup>0</sup> to HgCl<sub>2</sub> and, both measuring and predicting Hg transformation rate as a function of time, temperature, and Hg<sup>0</sup> concentration.

**Overall Priority:**  Low  Low/Med  Med  Med/High  High

#### ***Areas to Consider for Additional/Continuing Research***

1. Gas-Solid (Heterogeneous) Reactions/Interactions. Perform bench-, pilot-, and full-scale research experiments to further elucidate the impacts of flue gas components and fly ash on mercury speciation, with a specific focus on oxidizing Hg<sup>0</sup> to forms more easily removed by control devices. A fundamental understanding of mercury-flue gas-fly ash interactions is needed to accelerate the development of mercury control technologies. Simulated or real flue gases containing low acid gas concentrations (i.e., low chlorine, sulfur, etc. coals) that emit primarily Hg<sup>0</sup> will be used, and oxidation processes using HCl, CO, NO, Fe<sub>2</sub>O<sub>3</sub>, NaOH, and other compounds will be adjusted in combustion flue gas to effectively convert Hg<sup>0</sup> to HgCl<sub>2</sub> or Hg (p).

**Priority:**  Low  Low/Med  Medium  Med/High  High

2. Identify the chemical constituents of tire-derived fuels (TDFs) that promote oxidation of mercury while firing low-rank coals that generally have low chlorine concentrations. The Energy & Environmental Research Center has recently observed that small blends of TDF can significantly alter mercury speciation, leading to more oxidized and particulate-bound mercury. Understanding the role that TDF plays in mercury oxidation when firing low-rank coals may provide insight into oxidation mechanisms.

**Priority:**  Low  Low/Med  Medium  Med/High  High



3. Further explore the chemistry behind why there appears to be poor removal with spray dryer scrubbers and fabric filters under low chlorine conditions. The EERC has a mechanistic model that perhaps explains this phenomenon, but experimental data is needed to confirm.

**Priority:** \_\_\_\_\_ Low \_\_\_\_\_ Low/Med \_\_\_\_\_ Medium \_\_\_\_\_ Med/High \_\_\_\_\_ High

4. Control of Hg Emissions Using Ultraviolet (UV) Light and Ionized Halogens. There is evidence that UV light and halogens (Cl and Br) from sea ice catalyze the oxidation of elemental Hg in the Arctic and Antarctic atmospheres, causing the oxidized form of mercury to deposit on the snow. An investigation of the fundamental mechanism of oxidation needs to be done to validate the hypothesis and to determine the fundamental reaction process and rates, the optimum level of Cl or Br radicals to expedite the reaction, synergisms between the two halogens, and to surmise whether SO<sub>x</sub> and NO<sub>x</sub> may have any detrimental effects on the oxidation reaction in real combustion flue gas. A novel control technology approach might evolve from this fundamental work.

**Priority:** \_\_\_\_\_ Low \_\_\_\_\_ Low/Med \_\_\_\_\_ Medium \_\_\_\_\_ Med/High \_\_\_\_\_ High

5. Mercury Stability in Solid Materials. Specific research efforts should focus on evaluating the effect of biological activity on release of mercury from fly ashes; evaluating the leaching potential of fly ashes from various coal combustion sources; and studying thermal effects due to heating, i.e., solar energy. A 3-year U.S. Department of Energy (DOE) awarded project is being put in place to determine how much mercury is potentially released from coal ash when it is disposed of or used as a raw material in products such as a replacement for cement in concrete. The EERC will manage this project as a collaborative effort between the DOE National Energy Technology Laboratory, Utility Solid Waste Activities Group, Great River Energy, and CATM Affiliates. Since CATM has led the research in this area, it should stay involved and perform research that is complimentary to this program.

**Priority:** \_\_\_\_\_ Low \_\_\_\_\_ Low/Med \_\_\_\_\_ Medium \_\_\_\_\_ Med/High \_\_\_\_\_ High

## **Research Area 2 – Sampling and Analysis of Air Toxic Metals**

*Goal:* Develop and demonstrate advanced analytical and sampling procedures and equipment for air toxic metals.

*Current Focus:* Developing techniques to sample and quantify specific mercury compounds in combustion flue gas.

**Overall Priority:** \_\_\_\_\_ Low \_\_\_\_\_ Low/Med \_\_\_\_\_ Med \_\_\_\_\_ Med/High \_\_\_\_\_ High

### ***Areas to Consider for Additional/Continuing Research***

1. Gas-Phase Mercury.

1a. Continue to explore and develop techniques to definitively identify and quantify mercury compounds in combustion flue gas.

**Priority:** \_\_\_ Low \_\_\_ Low/Med \_\_\_ Medium \_\_\_ Med/High \_\_\_ High

1b. Develop/test a dry-based flue gas-conditioning system for converting oxidized mercury to gaseous elemental mercury. Integrate the dry system with existing continuous mercury monitor (CMM) instrument and test and validate measurements.

**Priority:** \_\_\_ Low \_\_\_ Low/Med \_\_\_ Medium \_\_\_ Med/High \_\_\_ High

2. Particle-Bound Mercury. Evaluate various methods and/or approaches to minimize or eliminate mercury-fly ash interactions during sampling. This could include various probe nozzle designs, particulate separation techniques, and other possible innovative sampling techniques. Developing an effective means of removing ash from flue gas is especially important in cases where highly reactive ash is present.

**Priority:** \_\_\_ Low \_\_\_ Low/Med \_\_\_ Medium \_\_\_ Med/High \_\_\_ High

3. Mercury Radioisotope Tracer. Investigate the use of a mercury radioisotope ( $\text{CH}_3\text{Hg}^{203}$ ) tracer for examining the specific molecular binding affinities of mercury with the protein and lipid components of various tissues. This may provide a technique that would track how mercury interacts at the cellular level and where it ends up.

**Priority:** \_\_\_ Low \_\_\_ Low/Med \_\_\_ Medium \_\_\_ Med/High \_\_\_ High

### **Research Area 3 – Air Toxic Metals Prevention and Control Technologies**

*Goal:* Enhance existing and develop new integrated pollution prevention and control technologies.

*Current Focus:* Advancement of mercury control technology through slipstream, pilot, bench, and laboratory testing to assess and develop various mercury control technology options. Sorbent development efforts are focused on obtaining increased sorbent reactivities and capacities as well as the ability to address coal and site-specific needs. The evaluations are to include measurement of performance with sorbent enhancements, additives, and optimization of operational conditions. Longer-term efforts will focus on improved mercury control in conjunction with  $\text{NO}_x$ ,  $\text{SO}_2$ , and particulate control technologies.

**Overall Priority:** \_\_\_ Low \_\_\_ Low/Med \_\_\_ Med \_\_\_ Med/High \_\_\_ High

#### ***Areas to Consider for Additional/Continuing Research***

1. Evaluate various chlorine (or other) additives for enhancement of sorbent reactivity/effectiveness. Recent pilot and field data suggest that introducing low-cost additives may significantly improve sorbent effectiveness, leading to better sorbent utilization. Additives to the fuel, sorbent, or directly to the flue gas should be considered.

**Priority:** \_\_\_ Low \_\_\_ Low/Med \_\_\_ Medium \_\_\_ Med/High \_\_\_ High

2. Pretreatment of sorbents, such as soaking in water or aqueous chlorine, to improve mercury capture. This is closely related to 1 above but expands the effort by considering simple pretreatment approaches that could significantly enhance mercury capture. A bench-scale system and protocol could be established, which would allow for an evaluation and optimization of pretreatment parameters.

**Priority:**  Low  Low/Med  Medium  Med/High  High

3. Sorbent Development/Testing. Continue to conduct entrained-flow testing using a wide range of sorbents – carbons, fly ash, calcium silicates, iron oxides. Compare entrained-flow results to previous bench-scale bed-type sorbent capacity results.

**Priority:**  Low  Low/Med  Medium  Med/High  High

4. Evaluate the potential of in-situ carbon formation for mercury removal. Results from last year research suggest that this may be possible.

**Priority:**  Low  Low/Med  Medium  Med/High  High

5. Evaluate alternative design configurations for sorbents. The focus is to develop possible schemes, other than simple injection, for interacting sorbents with flue gas. The approach would focus on a method that does not mix the sorbent directly with the bulk amount of fly ash. Thus, only a small amount (if any) of mercury-laden fly ash would have to be disposed of or treated.

**Priority:**  Low  Low/Med  Medium  Med/High  High

6. Test SO<sub>3</sub> addition at very low ppm levels and their impact on sorbent effectiveness.

**Priority:**  Low  Low/Med  Medium  Med/High  High

7. Determine the role/effect of SCR catalyst type/life on mercury oxidation as a function of coal type. Evaluate additives for enhancement of mercury oxidation across SCR systems and subsequent enhanced capture in an electrostatic precipitator, baghouse, or wet scrubber. Key variables to evaluate include the impacts of gas species, impact of adding specific additives, SCR space velocity, age of catalyst, and degree of oxidation. Temperature effects in the range of 300°–700°F should be included.

**Priority:**  Low  Low/Med  Medium  Med/High  High

8. Test promising technologies at power plants using slipstream or scaled-down reactors to evaluate potential of promising technologies with real flue gas.

**Priority:**  Low  Low/Med  Medium  Med/High  High

9. Develop and test sorbents that are effective at removing elemental mercury in dry scrubber applications.

**Priority:** \_\_\_\_\_ Low \_\_\_\_\_ Low/Med \_\_\_\_\_ Medium \_\_\_\_\_ Med/High \_\_\_\_\_ High

10. Evaluate mercury removal options in conjunction with wet ESPs for particulate control.

**Priority:** \_\_\_\_\_ Low \_\_\_\_\_ Low/Med \_\_\_\_\_ Medium \_\_\_\_\_ Med/High \_\_\_\_\_ High

11. Conduct long-term testing to determine the potential for fabric filter blinding, corrosion, and erosion by activated carbon.

**Priority:** \_\_\_\_\_ Low \_\_\_\_\_ Low/Med \_\_\_\_\_ Medium \_\_\_\_\_ Med/High \_\_\_\_\_ High

12. Develop/test additives that can be added to scrubbers that will enhance mercury oxidation (within scrubber) and capture.

**Priority:** \_\_\_\_\_ Low \_\_\_\_\_ Low/Med \_\_\_\_\_ Medium \_\_\_\_\_ Med/High \_\_\_\_\_ High

#### **Research Area 4 – Air Toxic Metals Modeling and Databases**

*Goal:* To predict the speciation and control of mercury based on fuel composition, flue gas composition, temperature, air pollution control device design/operating conditions, and capture media (sorbent, oxidation agent, etc.).

*Current Focus:* Neural network prediction of mercury speciation and control and theoretical modeling of mercury – sorbent interactions. In addition, current modeling capabilities include computational fluid dynamics, kinetic models, thermodynamic models, aerosol formation models, diffusion models, and ash particle formation models.

**Overall Priority:** \_\_\_\_\_ Low \_\_\_\_\_ Low/Med \_\_\_\_\_ Med \_\_\_\_\_ Med/High \_\_\_\_\_ High

#### ***Areas to Consider for Additional/Continuing Research***

1. Enhance artificial neural network modeling to predict mercury speciation and emissions as a function of boiler type, plant configuration, plant operating conditions, and coal quality data. The existing model will be enhanced by using data derived from various field tests as full-scale power plants.

**Priority:** \_\_\_\_\_ Low \_\_\_\_\_ Low/Med \_\_\_\_\_ Medium \_\_\_\_\_ Med/High \_\_\_\_\_ High

1. Conduct mercury speciation modeling across heat transfer devices using a combined computational fluid dynamics (CFD), kinetic, particle/aerosol formation, and thermodynamic model. Opportunities may exist to enhance the oxidation of mercury across heat transfer devices. The interaction of particulate and gas phase species will be considered as well as possible enhancements to heat transfer device design and materials of construction to enhance oxidation.

**Priority:** \_\_\_\_\_ Low \_\_\_\_\_ Low/Med \_\_\_\_\_ Medium \_\_\_\_\_ Med/High \_\_\_\_\_ High

2. Incorporate sorbent dispersion calculations and mass transfer of gas-phase mercury (as well as other gas species) into a simplified computational fluid dynamics model. This

model could be used to evaluate the effect of proper dispersion and various methods of injection.

**Priority:** \_\_\_\_\_ Low \_\_\_\_\_ Low/Med \_\_\_\_\_ Medium \_\_\_\_\_ Med/High \_\_\_\_\_ High

**Research Area 5 – Technology Commercialization, Education, and Information Exchange**

*Goal:* Encourage students to participate in research activities and provide publications and create a forum that will enhance and increase the information exchange between scientists, public health officials, businesses, citizens, industry, and all levels of government.

*Current Focus:* Newsletters, preparation for Air Quality III, working with two University of North Dakota (UND) master’s-level chemical engineers, and working with local schools.

**Overall Priority:** \_\_\_\_\_ Low \_\_\_\_\_ Low/Med \_\_\_\_\_ Med \_\_\_\_\_ Med/High \_\_\_\_\_ High

**Areas to Consider for Additional/Continuing Research**

1. Develop program that will facilitate use of master’s level, doctorate, or postdoctorate students.

**Priority:** \_\_\_\_\_ Low \_\_\_\_\_ Low/Med \_\_\_\_\_ Medium \_\_\_\_\_ Med/High \_\_\_\_\_ High

2. Conferences, i.e., AQ IV

**Priority:** \_\_\_\_\_ Low \_\_\_\_\_ Low/Med \_\_\_\_\_ Medium \_\_\_\_\_ Med/High \_\_\_\_\_ High

3. Newsletters

**Priority:** \_\_\_\_\_ Low \_\_\_\_\_ Low/Med \_\_\_\_\_ Medium \_\_\_\_\_ Med/High \_\_\_\_\_ High

4. CATM Web site

**Priority:** \_\_\_\_\_ Low \_\_\_\_\_ Low/Med \_\_\_\_\_ Medium \_\_\_\_\_ Med/High \_\_\_\_\_ High

**Research Area 6 – Exploratory**

*Goal:* Expand CATM program by exploring issues that are not mainstream or that may arise in the distant future. For example, expand CATM program by exploring issues related to the toxicity of mercury and its interaction with other elements such as selenium in the body.

*Current Focus:* Evaluating the interaction of selenium and mercury in laboratory animals. Evaluating sources of mercury in fuels other than oil and coal.

**Overall Priority:** \_\_\_\_\_ Low \_\_\_\_\_ Low/Med \_\_\_\_\_ Med \_\_\_\_\_ Med/High \_\_\_\_\_ High

***Areas to Consider for Additional/Continuing Research***

1. It is well known that selenium has a "protective effect" against mercury toxicity. It has been demonstrated repeatedly in numerous studies where animals given toxic quantities of mercury survive with fewer symptoms of neurologic damage when selenium has been supplied. The mechanism of the "detoxification" has been associated with direct binding between Hg and Se, forming an adduct which binds to glutathione, the molecule that carries Se and other divalent metal ions across the blood-brain barrier. We have been looking for data on selenium in the Faroe and Seychelle island studies. There is very little information. We have contacted Dr. Clarkson who is in charge of these major studies and he is interested in working with them on the next cohort to determine the selenium status of the women and children. This may be an opportunity to show the potential impacts of selenium on mercury. The problem may be selenium deficiency and not mercury toxicity.

**Priority:** \_\_\_\_\_ Low \_\_\_\_\_ Low/Med \_\_\_\_\_ Medium \_\_\_\_\_ Med/High \_\_\_\_\_ High

2. Gasification of treated wood for power and metal recovery. For the last 50 years there has been an increasing quantity of residential CCA-treated wood headed to our landfills. Rather than think of the millions of tons of hazardous treated wood as a disposal problem, investigations would focus on gasification of treated wood for power, hazardous waste reduction, and precious metal recovery. The concept would be to build distributed cogeneration plants based on gasification technology in proximity to landfills. Energy would be produced either from product-gas conversion or steam-cycle power generation. Copper, chromium, and arsenic from the treated wood could be recovered, and the payback on financial investment of a small gasification plant would be very favorable because of revenue from chemical recovery, especially for copper and chromium. Research would be needed to determine the optimal gasification system and conditions and control systems (high capture efficiency) for economic recovery of metals. The deliverable is a system design and convincing economics for a demonstration.

**Priority:** \_\_\_\_\_ Low \_\_\_\_\_ Low/Med \_\_\_\_\_ Medium \_\_\_\_\_ Med/High \_\_\_\_\_ High

**Research Area 7 – Collaborative Research with Industry**

*Goal:* Encourage participation in and sponsorship of air toxic-related research. Projects require a 50/50 cost-share match not to exceed \$250,000 from CATM.

*Current Focus:* Conducting long-term mercury monitoring and field sites and valuating CMMs to meet long-term monitoring needs.

**Overall Priority:** \_\_\_\_\_ Low \_\_\_\_\_ Low/Med \_\_\_\_\_ Med \_\_\_\_\_ Med/High \_\_\_\_\_ High

***Areas to Consider for Additional/Continuing Research***

1. Continue to perform long-term monitoring at various plants to determine mercury variability and CMM application.

**Priority:** \_\_\_\_\_ Low \_\_\_\_\_ Low/Med \_\_\_\_\_ Medium \_\_\_\_\_ Med/High \_\_\_\_\_ High

2. Participate in full-scale technology testing and demonstration to determine technology performance and cost effectiveness. Program would be structured to require a 50% commercial and 50% CATM cost share arrangement with a coal-fired utility. Baseline mercury speciation and emissions measurements would be determined followed by a series of simulated combustion testing studies done in the lab to determine the most appropriate additive, sorbent, oxidant, catalyst, etc. to develop an effective strategy for mercury control. Control technologies would be tested at bench-, pilot-, slipstream, or full-scale. Funds would be limited to \$250,000 from the CATM program to be matched by a minimum of \$250,000 from industry.

**Priority:** \_\_\_\_\_ Low \_\_\_\_\_ Low/Med \_\_\_\_\_ Medium \_\_\_\_\_ Med/High \_\_\_\_\_ High

3. Testing of potential mercury control technologies. Funds would be set aside to facilitate testing of potential mercury control technologies that are offered by outside technology vendors, or sorbent developers/providers. A cost share match of 50/50 would be required, not to exceed \$250,000 from CATM.

**Priority:** \_\_\_\_\_ Low \_\_\_\_\_ Low/Med \_\_\_\_\_ Medium \_\_\_\_\_ Med/High \_\_\_\_\_ High