



Center for

Air Toxic Metals



Newsletter

A Publication from the Center for Air Toxic Metals at the University of North Dakota Energy & Environmental Research Center

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SCR Effects on Mercury Emissions Appear to Be Coal-Specific

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Have you ever wondered where to find the Ontario Hydro Mercury Speciation Sampling Method? It is available, along with all other EPA sampling methods, on the Internet at <http://www.epa.gov/ttn/emc/prelim.html>. The file description for the Ontario Hydro Method is PRE 3.

The effects of selective catalytic reduction (SCR) systems on mercury speciation appear to be coal-specific, preliminary results of an ongoing study show. The study, jointly sponsored by EPRI, the U.S. Department of Energy (DOE), the U.S. Environmental Protection Agency (EPA), and the EERC, also determined that mercury speciation may be catalyst-specific.

In the United States, many regulatory activities such as newly proposed fine particulate ($PM_{2.5}$) ambient air quality standards, more stringent ambient ozone standards, and restrictions of NO_x aimed at stemming eutrophication of water bodies are resulting in more stringent NO_x emission limits around the country. As a result, a number of utilities are either installing or considering installing SCR systems to reduce NO_x emissions.

While SCRs are a proven technology for NO_x control, limited full-scale measurements in Europe and bench- and pilot-scale tests at the EERC have indicated that the catalyst, normally vanadium—titanium metal oxides, used in SCR systems may promote the formation of oxidized and/or particulate mercury.

Six power plants studied

To further examine the effect that NO_x controls may have on mercury speciation, the EERC performed field sampling at six power plants. In four plants using SCR and NH_3 injection, mercury emissions were sampled and evaluated using the wet-chemistry Ontario Hydro method, as well as near-real-time continuous mercury monitors (CMMs). At these plants, sampling was conducted at the inlet and outlet of the SCR reactor to evaluate the effects of SCR on mercury speciation and emissions. In addition, a fifth plant with a selective noncatalytic reduction (SNCR) unit and a sixth that uses NH_3/SO_3

for ash conditioning were sampled. Additional sampling was performed at each site to include EPA Method 26A to test for chlorides, a selective condensation method to measure SO_3 , and EPA Method 27 to measure NH_3 slip. Fly ash and coal samples were also collected to obtain the mercury balance across the control devices.

Of the four plants using SCR systems, significant oxidation of mercury was shown to occur across the SCR reactor in two of the four. All four plants showed significant nonelemental mercury at the inlet to the particulate control device. The two plants using a flue gas desulfurization (FGD) system showed correspondingly significant mercury removal.

The primary factor affecting mercury speciation appears to be coal and boiler properties. Catalyst space velocity (i.e., residence time) may be a factor as well. Based on these study results, NH_3 injection did not appear to significantly affect mercury speciation for any of the units using SCR, SNCR (urea injection), or flue gas conditioning.

Further field tests planned

Because the laboratory analyses and data interpretation are ongoing, the sponsors of the project consider these results preliminary. While the initial results indicate that SCRs can affect mercury removal in the downstream FGD, these effects appear to be coal-specific and may also be catalyst-specific. Additional field measurements are planned to better understand the effects of coal properties and mercury-catalyst reactions.

For more information, please contact Dennis Laudal, EERC Senior Research Advisor, at (701) 777-5138 or dlaudal@undeerc.org; or John Pavlish, EERC Senior Research Manager, at (701) 777-5268 or jpavlish@undeerc.org.



Director's Message

Mercury 2002

John H. Pavlish
CATM Director

As CATM Director, I would like to welcome you to CATM and take this opportunity to share with you some information on research that is either planned or under way through the CATM program. As you are aware, EPA is currently in the process of developing maximum achievable control technology (MACT) standards to reduce mercury emissions from coal-fired electric utility steam-generating power plants. These standards are scheduled to be drafted by December 2003 and promulgated by December 2004, with full compliance expected by 2007. The exact form of regulation is uncertain at this time, as there is much debate, in particular, on source subcategorization. Also, as EPA continues to develop MACT regulations, Congress is also discussing multipollutant (SO_x , NO_x , and Hg) legislation such as the Jeffords bill and other approaches such as the Bush Clear Skies Initiative. While none of these regulatory strategies has established an exact level of reduction, it is clear that the electric utility industry will be required to achieve significant reductions in the near future. For industry to meet these new regulatory requirements, new technology solutions are needed. Developing new technologies and a better understanding of mercury within these systems, given the regulatory uncertainty, will provide industry the ability to develop appropriate and effective control strategies. Recognizing this need, the CATM program has focused its attention on mercury in the last several years. Through strategic coordination, the program is structured to address both short- and long-term research needs in the areas related to transformation mechanisms, sampling/analysis methods and procedures, control technologies, modeling and databases, and technology commercialization and education. Shown below is a short overview of some of the research efforts that are under way.

Mercury Transformation in Combustion Flue Gases. It has been shown that flue gas and fly ash composition can significantly impact mercury speciation and emissions. A portable bench-scale entrained-flow reactor is being used to evaluate how certain flue gas and fly ash components (HCl, NO, CaO, and Fe_2O_3) affect Hg transformations through combustion and gasification systems.

Development of Mercury Sampling and Analytical Techniques. Understanding the form of mercury is critical to improving our understanding of how mercury behaves in the environment and how control

technologies can be designed to reduce releases to the environment. Previous research under CATM showed that mercuric chloride can be cryogenically trapped from a gas stream and, when coupled with a gas chromatography-mass spectroscopy (GC-MS) system, quantified. Efforts will continue to further develop and validate the trapping and GC-MS techniques for effluent gases from sorbents and combustion flue gases.

Mercury Control Technologies. Without question, innovative and proven technologies are needed to address upcoming regulatory requirements. Ongoing research efforts continue to focus on developing cost-effective mercury control technologies. The near-term focus is on development of sorbent technologies, used either for collection in particulate removal devices or enhanced oxidation for optimum mercury capture in wet scrubbers.

Stability of Mercury in Coal Combustion By-Products. By applying many of the technology options, mercury will be moved from the "gas phase" to the "solid phase" by sorption onto ash and/or sorbents. As an ongoing effort, levels of mercury released to the environment from coal combustion by-products (CCBs) continue to be monitored. Research efforts have expanded to include biologically induced release of mercury to the atmosphere, direct leachability of mercury, and potential ambient temperature release of mercury to the atmosphere from CCBs.

Mercury in Alternative Fuel Sources. Alternative fuel sources such as biomass, oil/tar sands, and oil shale are receiving more attention because of the need to reduce dependence on foreign oil. While most of these alternative fuel sources likely contain a lower mercury concentration than coal on a mass basis, their associated mercury emissions could be comparable on a per unit energy basis. Research is under way to quantify the mercury concentrations and potential emissions of these fuel sources.

Fundamental Study of the Impact of SCR on Mercury Speciation. Previous testing and results by the EERC indicate that mercury oxidation is dependent on coal type and SCR operation. While it is speculated that SO_2/SO_3 and HCl/ Cl_2 concentrations play a pivotal role, it has not been proven. A full-factorial design will be performed to evaluate the independent variables, which include the reactor (none, SCR), presence of acid gases (HCl and SO_2/SO_3), fly ash type, and residence time.

Potential Impact of Selenium on Mercury Exposure. Dietary selenium has the potential to exert a detoxifying influence that counters the damaging effects of methylmercury exposure. Consequently, the health risks of methylmercury exposure may vary in response to individual and regional differences in selenium intake. Research is under way to examine other factors that might influence individual vulnerabilities to methylmercury toxicity and the role selenium may play in lower health risks.

In future editions of the CATM newsletter, I plan to keep you informed as research progresses and key findings unfold. Additionally, I hope you find the articles contained throughout this newsletter interesting and informative.

For more information, please contact John Pavlish, CATM Director, at (701) 777-5268 or jpavlish@undeerc.org.

Predicting Flue Gas Mercury Species

In the winter of 1997–98, EPA published two reports to Congress. *The Mercury Study Report to Congress*, in 1997, identified fossil fuel-fired power plants as the largest source of human-generated mercury emissions in the country. The second report, the *1998 Utility Air Toxics Report to Congress*, examined air toxic emissions from power plants and identified mercury as the toxic of greatest concern. To learn more about mercury emissions from coal-fired units, EPA gathered additional data from power plants. Those data were used to estimate 1999 nationwide and plant-by-plant mercury emissions from coal-fired units. The data confirm that coal-fired power plants are the largest source of human-caused mercury emissions in the United States — about 43 tons of mercury each year. On December 14, 2000, EPA made the decision that it is necessary to control mercury emissions from coal- and oil-fired power plants and plans to issue final regulations by December 15, 2004.

For coal-fired utilities, these impending mercury regulations mean that control strategies must be planned immediately. The efficacy of mercury removal from flue gas is largely dependent upon the species of the mercury that is formed upstream of the control device or system. Mercury emissions take the form of particulate bound, a gaseous elemental form, and gaseous oxidized forms; however, every utility power plant has different fuels with different mercury concentrations and different plant operating parameters. The end result is that the concentrations of specific mercury species cannot be assumed to be the same from plant to plant. Research and development, especially over the past 5 years at the EERC through the CATM program and at other research facilities, have provided excellent information on the physical and chemical factors that govern mercury speciation in combustion flue gas.

In compiling this information, the EERC has made a first attempt at drawing together a conceptual model to aid in determining speciation of mercury in combustion systems. The initial model is based on a compilation of several different cause-and-effect relationships derived from studies in the open literature, as well as recent work performed through CATM on mercury conversion and control. Much of the information in the open literature has been developed in bench-scale settings with carrier gas unrepresentative of actual flue gas from combustion systems. Consequently, attempts made to correlate the data to systems with simulated or actual coal combustion flue gas yield ambiguous results. The model currently under development predicts the amount of mercury oxidized or captured in a combustion system. The oxidized species are more readily removed from systems using current pollution control devices. Initially, it is expected that the model will have many holes and much-needed information will be filled in as the understanding of mercury speciation in combustion systems evolves. The general form of the model follows:

$$Hg^0 = \text{total Hg in the coal} - [Hg^{2+}X_{(g)} + Hg_{(p)}]$$

where

$$Hg^{2+}X_{(g)} = [Hg^0 \text{ converted by fly ash to } Hg^{2+}X_{(g)}] + [Hg^0 \text{ converted to } Hg^{2+}X_{(g)} \text{ by carbon}] + [Hg^0 \text{ converted to } HgCl_{2(g)} \text{ by chloride}] + [Hg^0 \text{ converted by SCR catalyst to } Hg^{2+}X_{(g)}]$$

and

$$Hg_{(p)} = [Hg \text{ carbon sorbed}] + [Hg \text{ fly ash sorbed}]$$

Additionally, information gathered from the EPA's 1999 nationwide plant-by-plant information collection request (ICR) for mercury emission data from coal-fired units will be used to help determine speciation across various types of pollution control equipment when applicable. Some general trends can be seen in the data collected. An example of general trends that can be plotted from the ICR data is shown in Figure 1. This figure shows the elemental mercury at the air heater exit versus the amount of sulfur in the coal. There are distinct differences in the amount of elemental mercury when there is less than 1 lb/MBtu of sulfur as compared to when there is more than 1 lb/MBtu of sulfur in the coal. General trends gathered from the ICR data are being incorporated into the model as appropriate. To extend this analysis, the EERC has developed a neural network (NN) model based on the ICR data. It should be pointed out that the model development is ongoing and the predictions are preliminary at this point. The results obtained after training the NN model have been compared with the observed values of speciated mercury emissions from selected power plants from ICR data. The estimated Hg emissions (oxidized, elemental, and particulate form) and the

continued on page 7

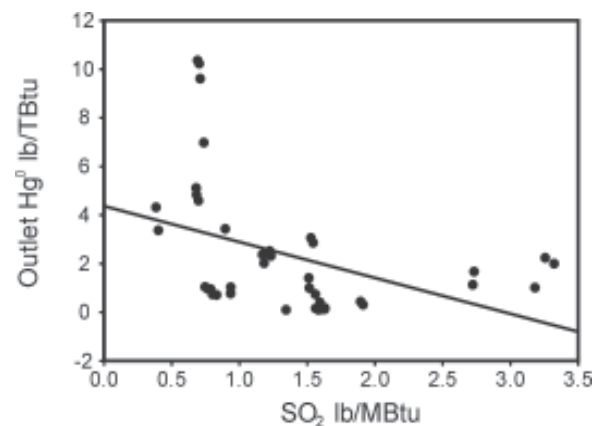


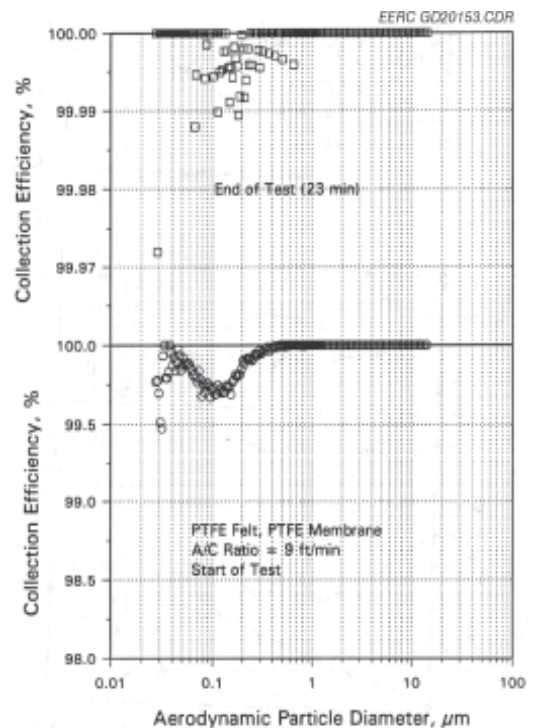
Figure 1. SO_2 lb/MBtu vs. Hg^0 at outlet of airheater derived from the EPA ICR data.

Advanced Technology

Advanced Hybrid™ Moving Forward

A New Concept in Particulate and, Possibly, Mercury Control

The Advanced Hybrid™ filter is rapidly approaching full-scale commercial reality with two full-scale installations scheduled to come on-line this year. The Advanced Hybrid™ is a registered trademark of W.L. Gore & Associates, Inc., the exclusive licensee of what was formerly called the advanced hybrid particulate collector (AHPC). The Advanced Hybrid™ has been under development since 1996, when the first cold-flow concept tests were completed at the EERC. Since then, the concepts have advanced significantly and are currently being evaluated as an approach for mercury control when used with an effective sorbent. Demonstration of the Advanced Hybrid™ for mercury control is being conducted on a 2.5-MW slipstream system at the 450-MW Big Stone Power Plant operated by Otter Tail Power Company.

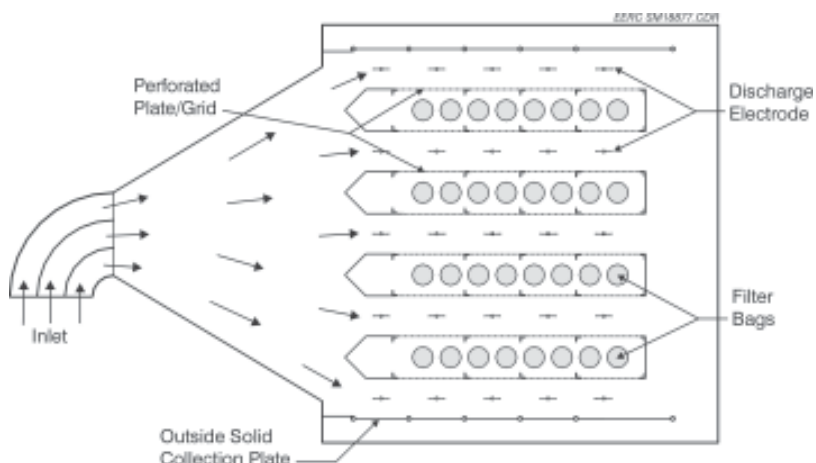


One of the key technical advances leading to the Advanced Hybrid™ concept was development of superior filter media. An extensive evaluation of various filter media that might be suitable for ultrahigh collection was completed in a CATM project in 1995. These results showed that, even at high filtration velocity, GORE-TEX® membrane filter media could achieve over 99.99% collection efficiency of larger as well as submicron particles. However, the higher cost of the Gore filters compared to conventional filter bags and the difficulty of controlling pressure drop at high filtration velocity were hurdles limiting the application of these superior filters. Achieving ultrahigh collection efficiency at high filtration velocity (to keep costs acceptable) and simultaneously maintaining reasonable pressure drop across the device were the major challenges leading to the Advanced Hybrid™ concept.

... appears to have unique advantages for mercury control ...

The availability of a superior filtration media, along with years of experience dealing with the relationships between dust properties and collector performance in both fabric filters and electrostatic precipitators, led to the idea of incorporating both electrostatic collection and filtration in the same vessel. The key advancement was the idea of using electrostatics not only to precollect most of the dust (as in other concepts), but also as a means to significantly enhance bag cleaning. By using alternating rows of bags, discharge electrodes, and collection plates in close proximity, both goals were met.

Extensive data from both the initial 200-acfm testing at the EERC as well as the 9000-acfm (2.5-MW) slipstream test at Big Stone showed that over 99.99% collection efficiency of fine particles was readily achieved. In fact, many of the tests showed that the gas leaving the Advanced Hybrid™ was cleaner (of particulate matter) than the surrounding air drawn into the boiler. Results also demonstrated the Advanced Hybrid™ could operate at high filtration velocity, from 10–14 ft/min at a pressure drop of 6–10 in. W.C. Progress was moving forward at a rapid pace until it was discovered that, under some conditions, minor electrical bag damage could occur.



As a result, extensive theoretical, bench-scale, and pilot-scale investigations were completed to find an approach to prevent bag damage without compromising Advanced Hybrid™ performance. Results showed that the best bag protection and Advanced Hybrid™ performance were achieved by using a perforated plate installed between the discharge electrodes and bags. This perforated-plate design was then installed and extensively tested in the 2.5-MW Advanced Hybrid™ at Big Stone. Results showed that the perforated-plate design solved the bag damage problem and offered even better Advanced Hybrid™ performance than the previous design. All of the Advanced Hybrid™ performance goals were met, including ultrahigh collection efficiency, high air-to-cloth ratio, reasonable pressure drop, and long bag-cleaning intervals leading to long bag life.



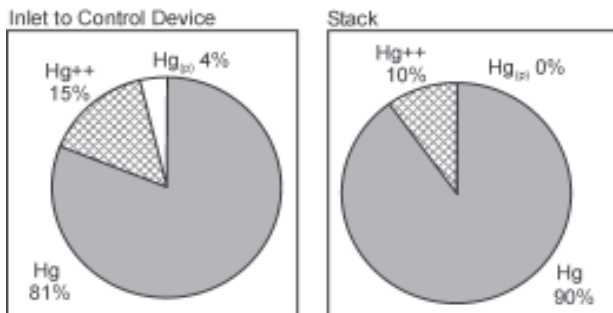
The Advanced Hybrid™ also appears to have unique advantages for mercury control as an excellent gas–solid contactor. The objective of the Advanced Hybrid™ mercury control project is to demonstrate 90% total mercury control in the Advanced Hybrid™ at a lower cost than current mercury control estimates. An initial test with the 2.5-MW Advanced Hybrid™ has already achieved 90% mercury control at low carbon addition rates. Continuing work is focused on developing a better understanding of factors leading to the best control for a variety of conditions. Plans are to demonstrate longer-term mercury control over several months later this year with the 2.5-MW Advanced Hybrid™. Details of the mercury testing will be presented in a future CATM newsletter.

For more information, please contact Stan Miller, EERC Senior Research Manager, at (701) 777-5210 or smiller@undeerc.org; or Mike Jones, EERC Associate Director, Industrial Relations and Technology Commercialization, at (701) 777-5152 or mjones@undeerc.org.

Mercury Control for Lignite-Fired Power Plants Poses a Challenge

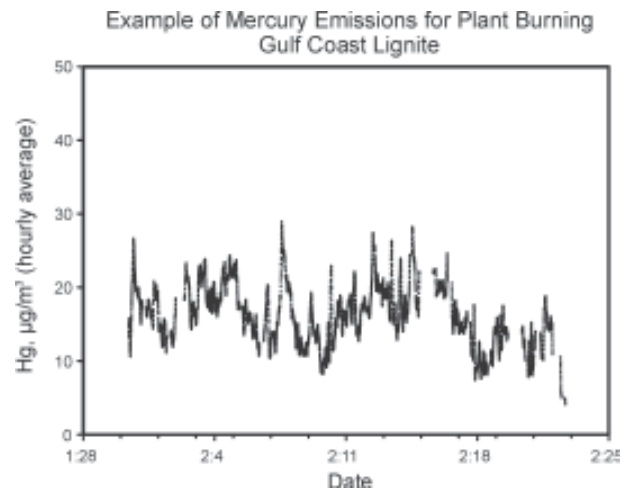
In December of 2000, EPA announced that it was necessary and appropriate to regulate mercury emissions from coal-fired electric utilities. Since then, EPA has been developing maximum achievable control technology (MACT) standards for this source category. Because of varying Hg emissions from 10%–100%, as reported in the ICR data, discussions have occurred regarding subcategorizing the source based on coal type. As documented by the ICR data, different coals in combination with varying plant design configurations do emit different amounts and forms (species) of mercury. Eastern coals, when combusted, typically are much higher in oxidized mercury, allowing more effective capture in scrubbers and with various sorbents. Western coals, including lignites, generally produce much higher levels of elemental mercury, making it harder to remove. Although many of the lignite-fired facilities have some type of scrubber installed, they are not able to take advantage of the technology for mercury control because scrubbers are ineffective for removal of elemental mercury. Consequently, for this source subcategory, other technology options need to be explored. Additionally, based on ICR data, it appears that particulate removable devices such as electrostatic precipitators (ESPs) and fabric filters are also less effective at capturing mercury when high levels of elemental mercury are present. This means that less of the mercury appears to be reactive with the ash; thus less of it is removed across the particulate control devices. From a control perspective, both of these phenomena appear to work against plants firing lignite coals; that is, the elemental mercury concentration is higher compared to other (eastern) coals, and the ash does not appear to be overly reactive with regard to mercury capture. This is more clearly illustrated by the following figure which shows that, for plants burning Fort Union coal, the fraction of elemental mercury is quite high and the fraction of particulate-bound mercury is quite low.

Typical Mercury Emissions and Speciation for Plant Burning Fort Union Lignite



The high variability of mercury emissions from lignite-fired sources will also pose a challenge. Recently, the EERC performed a monthlong mercury-monitoring project funded by EPRI, the host utility, the U.S. Department of Energy (DOE), and CATM at a plant burning a Gulf Coast lignite. An example

of the high degree of variability that was observed at this plant is shown in the following figure. This variability results in an additional challenge with regard to technology options, design, and regulatory compliance issues. It should be noted, however, that while lignites within the United States have many similar chemical and physical characteristics, all lignites do not necessarily contain the same levels of mercury. For example, the Fort Union lignite found mainly in North Dakota has generally lower mercury concentrations as compared to Gulf Coast lignites found in Texas, Louisiana, and Mississippi. As shown above, this difference can also translate into higher and rather large fluctuations in emissions.



Within the last year, the EERC has developed several projects with a number of utilities to address mercury-related concerns and challenges associated with lignite utilization. These projects will provide a better understanding of the variability of mercury emissions (both form and total), as well as assess control technologies that show promise. As an example, the EERC recently initiated a consortium-based 3-year program to develop, test, and demonstrate cost-effective sorbent-based technologies that can be used to reduce mercury emissions from plants burning lignite coal. Sponsors of this program include Saskatchewan Power, Environment Canada, Luscar Ltd., Basin Electric Power Cooperative, Minnkota Power Cooperative, Otter Tail Power Company, and the North Dakota Industrial Commission (NDIC); Minnesota Power, Xcel Energy, and Great River Energy through tailored collaboration with EPRI; and DOE through the EERC's joint venture program.

For more information, please contact John Pavlish, EERC Senior Research Manager, at (701) 777-5268 or jpavlish@undeerc.org; or Mike Holmes, EERC Senior Research Advisor, at (701) 777-5276 or mholmes@undeerc.org.

CATM Welcomes Mike Holmes



The Center for Air Toxic Metals welcomes Mike Holmes as a new addition to the research team. Mike has recently joined the EERC as a Senior Research Advisor and is involved in research in emission control, fuel utilization, process development, and process economic evaluations. He received his M.S. degree in Chemical Engineering from UND in 1986 and B.S. degrees in Chemistry and Mathematics from Mayville State University in 1984. Prior to his position at the EERC, he held the position of Principal Research Engineer at McDermott Technology, Inc. (MTI). At MTI, Mr. Holmes spent 15 years as a process development engineer for advanced energy systems in support of the operating divisions of McDermott International, including Babcock & Wilcox, Jay Ray McDermott Engineering, and Diamond Power Specialty Company.

Mr. Holmes' principal areas of interest and expertise include emission control (air toxics, SO_2 , NO_x , H_2S , and particulate), fuel processing for production of syngas and feed gas for fuel cells, and process development and economics for advanced energy systems. Within the CATM program, Mr. Holmes will focus on mercury transformations and control: two areas that will put his past experience to good use. He was previously active in B&W's development efforts for the control of air toxics from utility power plants. A selected example of Mr. Holmes' previous experience includes project management of Phase III and the end of Phase II of the Advanced Emissions Control Development Program (a 5-year multimillion-dollar program with a primary focus on mercury control). Mike will continue working on development of mercury control strategies as a member of the CATM Program.

For more information, please contact Michael Holmes, EERC Senior Research Advisor, at (701) 777-5276 or mholmes@undeerc.org.

Constance Wixo Hands Off CATM Newsletter Editorial Responsibilities

In the summer of 1994, I was honored and excited to be the editor of the first-ever issue of the *CATM Newsletter*. CATM was in its infancy at the EERC, and from the beginning, I was able to meet and work with many wonderful people all over the United States and the world. Being a part of CATM has been one of the most challenging and rewarding experiences I have had in my career.

Having said that, I am excitedly moving into other areas of challenge at the EERC, and I am very pleased to announce that LaRae Foerster is now the editor of the *CATM Newsletter*. LaRae will do a wonderful job as editor, as can be seen immediately by viewing the inaugural issue of the revamped format for the newsletter.

I hope to keep in touch with many of you through the projects that I will be working on with Steve Benson and others at the EERC in the next few years.

—Constance Wixo

Predicting Flue Gas Mercury Species Continued from Page 3

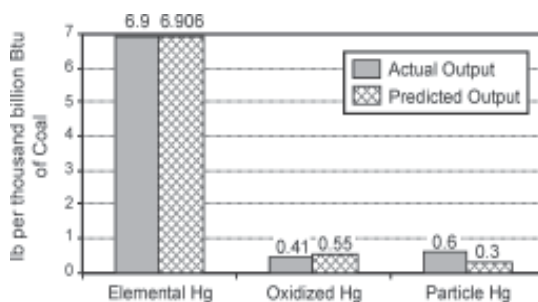


Figure 2. NN model output: predicted and actual emissions of the new plant (untrained data set).

corresponding ICR figures are presented in Figure 2. It can be seen from Figure 2 that the NN model can predict fairly well the speciation of Hg in a combustion system. The inputs used for predicting Hg speciation are mercury concentration in the fuel, heating value of coal, chlorine content, sulfur content, ash content, and temperature. The model then predicts the form of Hg in the combustion system past the air heater and at the inlet to pollution control devices. The EERC plans to make these mercury prediction models available by December 2002.

For more information, please contact Chris Zygarlicke, EERC Senior Research Manager, at (701) 777-5123 or czygarlicke@undeerc.org; Bruce Folkedahl, EERC Research Manager, at (701) 777-5243 or bfolkedahl@undeerc.org; or Bob Jensen, EERC Research Specialist, at (701) 777-5016 or bjensen@undeerc.org.

Air Quality III Conference Slated for September

Air Quality III (AQIII): Mercury, Trace Elements, and Particulate Matter will take place September 9–12, 2002, at the Marriott Crystal Gateway in Arlington, Virginia. The conference is sponsored by the EERC, the Center for Air Toxic Metals (CATM) through the U.S. Environmental Protection Agency (EPA) Office of Research and Development National Center for Environmental Research, the U.S. Department of Energy (DOE) Office of Fossil Energy National Energy Technology Laboratory, and EPRI.

U.S. Senator Byron Dorgan will give a keynote presentation, and U.S. Secretary of Energy Spencer Abraham and EPA Administrator Christine Todd Whitman have also been invited to give keynote addresses. U.S. Senator Kent Conrad will address attendees at the Tuesday evening banquet, and Representative Earl Pomeroy will provide the luncheon address on Wednesday. Speakers include experts on all aspects of air quality, representing government, industry, and the research community worldwide.

AQIII is being recognized by many in the industry as the premier conference on air quality issues. The conference provides a forum in which leaders in science, health, industry, and government come together to discuss issues involving mercury, trace elements, and particulate matter, including policy and regulations, health, measurement, control, transport, atmospheric reactions and chemistry, and modeling. Building on Air Quality II, held in September

2000, AQIII comprises two streams of discussion: one featuring expanded coverage of mercury and the other featuring trace elements and particulate matter. A poster session will be showcased on Wednesday evening.

As critical regulatory issues are being framed and industrial solutions engaged, many organizations have already reserved exhibit space at the conference. As of July 2002, the following exhibitors have registered: Baldwin Environmental, Inc., Croll Reynolds Clean Air Technologies, EERC, EPRI, PS Analytical, Rupprecht & Patashnick, Spectra Gases, Spectrum Systems, Inc., Tekran, Inc., Thermo Electron Corporation, TRC Environmental Corporation, and URG Corporation. Space may still be available. For information, contact Deb Haley at (701) 777-3120 or dhaley@undeerc.org.

The AQIII program and on-line registration can be found at www.undeerc.org.

For more information, please contact Anne Fiala, EERC Administrative Manager, at (701) 777-3119 or afiala@undeerc.org.

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LaRae Foerster, Editor

Phone: (701) 777-5246 Fax: (701) 777-5181

E-mail: lfoerster@undeerc.org

Comments are welcome and may be submitted to the Editor.



University of North Dakota
PO Box 9018
Grand Forks, ND, USA 58202-9018

Phone: (701) 777-5000 Fax: (701) 777-5181
e-mail: jpavlish@undeerc.org
www.undeerc.org

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