

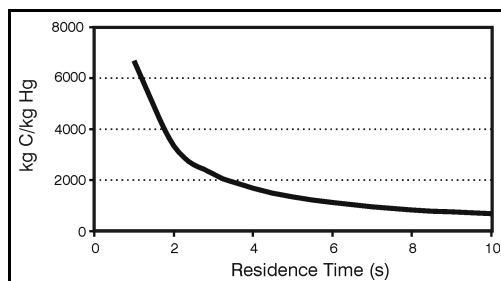


Activated Carbon Injection for Mercury Control in Coal-Fired Boilers

Among the air toxic metals addressed in the 1990 Clean Air Act Amendments, mercury (Hg) is of special concern because of its persistence and bioaccumulation as methylmercury in the environment and the high neurodevelopment toxicity evidenced by catastrophic health impacts of high-level Hg exposures in Minamata, Japan, and Iraq between 1950 and 1970. Since the late 1960s, states have taken effective actions to reduce many uses of Hg and to decrease Hg release into the environment from industry (e.g., chloralkali plants), consumer products (batteries and switches), and some combustion sources. Federal regulations affecting Hg emissions from municipal and medical waste incinerators were issued by EPA between 1995 and 1997. Coal combustion is now estimated to be the largest source of anthropogenic Hg release in the United States, accounting for 46% (33% for utility boilers and 13% for commercial/ industrial boilers) of the total. EPA's schedule for addressing the need for Hg control for coal-fired utility boilers includes an information collection request to utilities in January 1999 (concluding May 2000), a review by the National Academy of Science followed by regulatory determination in December 2000, and issuance of final Hg control rules, if warranted, by December 2004.

One of the most promising methods for controlling Hg emissions from coal combustion involves injection of activated carbon upstream of either an ESP or baghouse, since virtually all coal-fired boilers are equipped with one of these two particulate control devices. Sorbent injection would be relatively easy to retrofit and would be applicable to both industrial and utility boilers. Sorbent injection research, funded

by the U.S. Department of Energy (DOE) and EPRI and presented in EPA's *Mercury Study Report to Congress*, indicates carbon-to-mercury ratios between 9500:1 and 100,000:1. A low sorbent injection rate would have a negligible impact on boiler system performance and ash utilization, whereas a high injection rate could have a significant impact. The required ratio may depend on many different variables, including the concentrations of Hg and acid gases (e.g., SO₂, NO₂, and HCl) in the combustion gas, Hg speciation as Hg⁰ or Hg²⁺, temperature, fly ash properties, and the particle size, composition, reactivity, and capacity of the sorbent.



Carbon Requirements for 95% Removal at a 4-µm Particle Size.

One of the key questions to be answered in evaluating sorbent injection is whether capture is limited by the diffusion of the Hg from the bulk gas to the sorbent particles or by the capacity of the sorbent particle. The limiting effect of diffusion is minimized by dispersing a very large number of very small particles in the combustion gas and by allowing sufficient time for diffusion to take place from the gas to the particles. However, as the size of the particle becomes smaller, its capacity to absorb Hg is reduced to the point where this becomes the controlling factor.

A mathematical model was developed to evaluate the limiting effects that diffusion and sorbent capacity have on Hg capture in relation to the size of sorbent particles and their residence time in the combustion gas. This research was coordinated through the EERC's CATM program and was completed in May 2000 by R. Brintnell as a thesis for a Master of Science degree in Chemical Engineering at the University of North Dakota. The model calculates the fraction of Hg that would diffuse from a discrete gas volume surrounding a sorbent particle to the surface of that particle. The model assumes that the flow of combustion gas is laminar so that the particle remains fixed within its corresponding gas volume and that the Hg diffusing to the surface is immediately adsorbed on the particle so that the concentration in the gas at the surface is zero.

Good agreement was obtained between analytical and numerical solutions for these assumptions based on Fick's law of diffusion, which predicts that the rate of diffusion is directly proportional to the concentration gradient in the gas volume. As a larger number of particles are introduced and the discrete volume surrounding each particle is reduced, a larger fraction of Hg is removed by diffusion. Thus the diffusion model can be used to establish the number of particles and the corresponding amount of carbon of a specified size that would be needed to reduce the initial Hg concentration by any specified percentage (e.g., by 95%). The Hg absorption capacity of this amount of carbon can then be checked to determine whether diffusion is indeed the controlling factor. A larger amount of carbon would be

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Steven A. Benson, Ph.D.

CATM Directions for 2000–2001

By December 2000, EPA, under court order, must make a determination on whether to regulate mercury (Hg) (and other metals) emissions from electric utilities. Assuming regulations are forthcoming, EPA is scheduled to propose regulations by December 2003 and promulgate them by December 2004, with full compliance expected from utilities by 2007. The urgency to develop effective control technologies for elemental and oxidized Hg in flue gas has never been so great. In response to this sense of urgency, the CATM program for 2000–2001 is largely aimed at Hg control and measurement technologies. Six of the seven projects are focused on Hg. Project 6 is focused on trace elements associated with oil-fired systems. The following projects have been approved, and work will begin in June 2000.

■ **Project 1 – Fundamental Mechanisms of Mercury Species Formation in Power Plants**

Controlling and predicting Hg emissions from coal-fired power plants can be accomplished by improving the fundamental understanding of the mechanisms involved in Hg–flue gas–fly ash interactions that result in Hg oxidation (i.e., formation of inorganic mercuric compounds, $Hg^{2+}X[s,g]$, where X is $Cl_2[g]$, $SO_4[s]$, $O[s,g]$, etc.) and Hg sorption on ash particles, i.e., formation of particulate Hg ($Hg[p]$). The research will discern and model the mechanisms by which gaseous elemental Hg ($Hg^0[g]$) transforms to $Hg^{2+}X(s,g)$ and $Hg(p)$ in the postcombustion environment of a boiler.

■ **Project 2 – Development of Sampling and Analytical Tools for Oxidized Mercury Species**

Bench-scale investigations of Hg sorbents operating in a gas stream containing elemental Hg and both NO_2 and SO_2 showed that breakthrough of Hg occurred in about an hour, compared with breakthrough times of several hours for the same sorbents in other gas mixtures. The Hg form emitted from the sorbent into the gas stream was an oxidized species whose identity was established as mercuric nitrate monohydrate by trapping in a cold solvent

and subsequent gas chromatography–mass spectrometry (GC–MS) analysis. This trapping and identification of a specific vapor-phase oxidized Hg species is a novel breakthrough in Hg research and will be further exploited in this project. The work will further develop the cryotrapping technique for additional species. To provide high-confidence identification and quantitation of the Hg species, a method will be developed for introducing the cryotrapped species into an ion trap mass spectrometer with a mass spectrometry–mass spectrometry (MS–MS) function.

■ **Project 3 – Development of Mercury Control Technologies**

Cost-effective Hg control for coal-fired boilers is a primary research need identified in the EPA *Mercury Study Report to Congress*. This EERC project addresses that primary need, as well as more specific needs stated in the report. This project is intended to test promising cost-effective sorbents and catalysts that have high reactivities to provide rapid in-duct Hg capture or oxidation when injected upstream of an air pollution control device.

■ **Project 4 – Computer-Based Tools**

The primary goal of this project is to develop computer-based tools that will aid in predicting Hg transformation mechanisms and speciation as a function of fuel quality and system operating conditions. This information can be used to improve measurement and control of Hg emissions from thermal sources. The secondary goal is to continue to incorporate new data into the EERC CATM database. These computer-based tools will be made available to researchers and others interested in Hg and other trace element transformations and control.

■ **Project 5 – Mercury Stability in the Environment**

This project is a continuation of the work conducted at the EERC to evaluate the stability of Hg in combustion by-products and in ash disposal sites, with an emphasis on coal combustion by-products (CCBs). Changes in Hg mobility that may be induced by microbial activity will be investi-

gated by using techniques to measure the release of Hg from CCBs. Experiments will be conducted where the CCB material is mixed with a diverse microbial inoculant known to contain the required microorganisms. After simple nutrients are added to encourage growth, the experimental mixture will be incubated. Any increases in gas-phase Hg and leachable Hg will be measured.

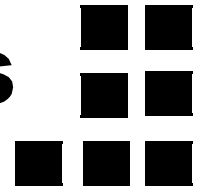
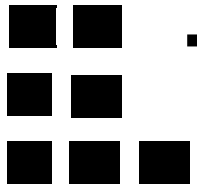
■ **Project 6 – Nickel, Chromium, and Arsenic Speciation of Ambient Particulate Matter in the Vicinity of Oil-Fired Utility Boilers**

This project is aimed at identifying and quantifying the Ni, Cr, and As species composing ambient particulate matter (PM) in the vicinity of two oil-fired utility boilers. Uncertainties in the chemical speciation of Ni, Cr, and As in ambient PM associated with oil-fired boilers greatly affect inhalation health risk estimates, primarily because of the great variability in cancer potencies for different chemical species. For example, nickel subsulfide (Ni_3S_2) and hexavalent chromium (Cr^{6+}) compounds are considered the most carcinogenic Ni and Cr species on the basis of available human epidemiology and animal studies.

■ **Related Project – Characterization of Coal-Derived Mercury Sorbents**

This project, cofunded by the Consortium for Premium Carbon Products from Coal (CPCPC) at the Pennsylvania State University and the CATM Affiliates Program, is aimed at determining the mechanisms of interaction of SO_2 and NO_2 with selected activated carbon sorbents. The work will focus on exposing the sorbents to various flue gas compositions containing SO_2 and NO_2 with and without Hg^0 vapor. The surfaces of the reacted sorbents will be characterized using several analytical methods, including x-ray absorption fine structure, x-ray photoelectron spectroscopy, and diffuse reflectance infrared spectroscopy, to determine the nitrogen, sulfur, and oxygen species.

For more information, contact Steve Benson, CATM Director, at (701) 777-5177 or sbenson@undeerc.org.



Hydrothermal Treatment: An Affordable Option for Mercury and Sulfur Removal

One of the major problems facing the coal industry and the industries that utilize coal for energy is the lack of cost-effective methods for removal of sulfur (S) and selected hazardous air pollutants (HAPs) from coal. With the threat of the imposition of caps on HAP emissions, especially mercury (Hg), and the current emission requirement of <1.2 lb of SO₂/MMBtu, the need for an economically feasible treatment that will enable the use of high-S coal supplies becomes increasingly important. To date, no economically feasible process for substantially reducing the Hg content (greater than 75% removal) or

Air Quality II Conference Scheduled for September 19–21, 2000

The first Air Quality conference held in December 1998 reviewed the state of science and policy on the pollutants Hg, trace elements, and particulate matter in the environment in relation to their impacts on health and ecosystems, emission prevention and control, measurement methods, and atmospheric reactions and modeling.

The Conference on Air Quality II: Mercury, Trace Elements, and Particulate Matter will provide participants with strategic information regarding advancements made in the topic areas introduced at the first Air Quality conference and will include items such as the Hg Information Collection Request (ICR), Toxic Release Inventory (TRI) data, and PM_{2.5} supersite selection.

This conference will provide an opportunity for leading representatives from

industry, government, research institutions, and academia to discuss these issues.

The conference will open with a Plenary Session with several keynote speakers providing an overview of the conference topics, followed by two streams (Mercury and Particulate Matter) of technical sessions that will include over 50 oral presentations. A poster session and social will take place the first evening of the conference, with an estimated 30 poster presentations anticipated. A banquet will be held the second evening, and the conference will conclude with a panel session focusing on environmental policy.

Chairs and speakers are currently being finalized, and a conference program listing all chairs, speakers, presentations, and conference details is planned to be mailed out in June.

The conference will be held at the McLean Hilton, and the registration fee for the conference is \$595 until August 15, 2000. More information regarding conference details can be found at www.undeerc.org.

For additional information, please contact Steve Benson, CATM Director, at (701) 777-5177 or at sbenson@undeerc.org; John Pavlish, CATM Associate Director, at (701) 777-5268 or at jpavlish@undeerc.org; William Stelz, EPA Project Officer for CATM, at (202) 564-6834 or at stelz.william@epa.gov; Scott Renninger at (304) 285-4790 or at srenni@netl.doe.gov, or Paul Chu, Toxic Substances Manager, EPRI, at (650) 855-2812 or at pchu@epri.com.

(Hydrothermal Treatment, continued from page 3)

capture these costs and savings has been performed, with the results summarized in the following table. A 500-MW pc-fired plant firing Illinois No. 6 coal with a 65% capacity factor and heat rate of 9710 Btu/kWh was used as the basis. Cleaning levels of 50% ash, 70% S, 80% Hg, and a Btu enhancement of 31% were assumed.

The results show that the fuel cost of using the hydrothermally treated coal is higher than that for the raw coal, even with the lower tonnage required for the treated coal. However, when credit is taken for operational and maintenance savings due to the lower ash level, SO₂ credits generated, and reduction in waste disposal costs, the use of the hydrothermally treated coal becomes the economically attractive alternative. Under this scenario, the break-even cost of hydrothermal treatment is approximately \$17/ton. If a price of \$200/ton of SO₂ removed is assumed, the break-even point is approximately \$22/ton.

Hydrothermal treatment of high-S bituminous coal can produce a product of superior quality to both the currently marketed bituminous coals and the imported PRB coals. The benefits of using the hydrothermally treated coal offer substantial savings to a

Cost for Cleaned Coal Summary – Illinois No. 6			
Cleaned Coal Cost per MMBtu:		\$1.39	\$1.56
Cleaned Coal Premium			
	per ton clean coal	\$15	\$20
	per MMBtu clean coal	\$ 0.51	\$ 0.68
Annual Clean Coal Cost		\$34,512,000	\$39,444,000
Annual Raw Coal Cost		\$25,835,000	\$25,835,000
Coal Differential Cost		\$ 8,677,000	\$13,608,000
Annual Savings Attributed to Clean Coal			
Transportation Differential per ton of Coal	\$2.42	\$739,000	\$739,000
Operating Cost Differential per ton of Ash	\$0.63	\$ 51,000	\$ 51,000
Maintenance Cost Differential per ton of Ash	\$1.54	\$126,000	\$126,000
Efficiency Cost Differential per ton of Ash	\$2.62	\$215,000	\$215,000
Annual Value of SO ₂ Credits Generated	\$135	\$9,411,000	\$9,411,000
Annual Savings Due to Reduced Waste Disposal	\$10	\$822,000	\$822,000
Actual Cost for Switch to Clean Coal.....		(\$2,687,000)	\$2,244,000
Cost for Hg Control per pound of Hg Removed.....		(\$10,827)	\$9,012

utility, which should provide the economic incentive to buy the higher-priced cleaned coal. Industrial users, who many times have fewer resources to spend on capital improvements for pollution control, should also realize advantages from using the hydrothermally treated coal. Therefore, hydrothermal treatment should benefit both the utility and industrial users of coal. More importantly, mining companies will

have the capability of offering a reasonably priced Hg- and S-compliant coal.

For more information, please contact Michael Mann, EERC Senior Research Advisor, at (701) 777-5193 or at mmann@undeerc.org; or Ronald Timpe, EERC Research Manager, at (701) 777-5219 or at rtimpe@undeerc.org.

Mercury and VOC Control Using Fiber-Based Bioreactors

A novel technology for prevention and control of hazardous air pollutants (HAPs) was investigated by researchers at the EERC and the Chemistry and Chemical Engineering Departments of UND involving the application of microorganisms in a fiber-based trickle-bed bioreactor to remove trace metals and volatile organics from contaminated gas/air. The bioreactors are novel in that they use a polymer fiber support for the microorganisms, which improves the efficiency of removal and reduces the quantity of cell mass required per given volume of contaminated air. This work is an extension of previous work focused on the use of live bacteria and algae for the removal of heavy metals from contaminated waters.

Efficient long-term adsorption requires a high concentration of bacteria in the bioreactor. In existing commercial biofilters, the amount of biomass is inherently low

compared to the bulk of an inert support, because excess biomass causes excessive pressure drop. However, recently, fiber supports were suggested for immobilization of bacteria in bioreactors. Fiber-based bioreactors may retain much larger amounts of live bacteria compared with the granule-based bioreactors. For instance, polyaramide fibers exhibit an adsorption of up to 1700 mg of live biomass per g of fiber when compared with 1 to 20 mg/g for granular sorbents.

Biological methods of air purification based upon the ability of certain bacteria to degrade toxic organic compounds to produce carbon dioxide and water may be considered an alternative to the traditional methods. The ability of many microorganisms to adsorb metals onto their cell surface has been observed in water purification studies. These metals become a permanent part of the cell structure and are, therefore, not desorbed to rerelease

the metal pollutant. The metals accumulate in the cell biomass and require periodic harvesting of the biomass; i.e., the removed metal-laden biomass can be treated for recovery of the metal. The purpose of this study was to demonstrate that metal adsorption could also occur from the gas phase.

The results of this study demonstrate the feasibility of using live bacteria to remove Hg from air, with Hg removal efficiencies as high as 63% achieved under nonoptimized conditions (see figure on back page). Mercury removal efficiency remained constant throughout the duration of the experiments, which were run continuously for 10 days. Ethanol and ethyl acetate removal was 100%, while removal rates for styrene and toluene were lower (90% and 50%, respectively). Therefore, the presence of Hg was not detrimental to the

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(Activated Carbon, continued from front page)

required to the extent that either capacity or the rate of absorption at the surface is controlling.

Computations based on this model were performed for residence times of 1 to 10 seconds and for uniform particle sizes between 1 and 10 μm , as shown in the figures on page 1 and below. The effect of

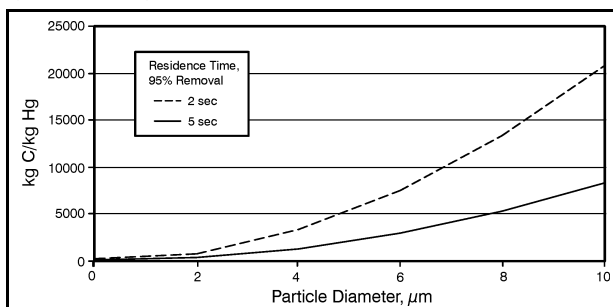
uniform particle size. For example, 95% control would be achieved at a highly favorable sorbent-to-carbon ratio of about 1000:1 for 2- μm particles and a residence time of 2 seconds—and the capacity of the carbon would be sufficient, in this case, to absorb the Hg. However, the capacity would become insufficient at either smaller sizes or longer residence times, indicating that capacity would be the controlling factor

in this region. Also, the calculated carbon-to-mercury ratio as controlled by diffusion increases sharply at larger particle sizes, to a ratio of approximately 20,000 at 10 μm . Variations in the diffusivity of Hg with temperature between 120° and 180°C had little effect on the carbon-to-mercury ratio calculated for smaller particle diameters but a slightly greater effect at

range of particle sizes represented by a lognormal distribution with a geometric standard deviation of 2. The required carbon-to-mercury ratio for this size distribution increased by a factor of 6 over that for monosize sorbent particles at a mean size of 2 μm and by a factor of 32 at a mean size of 1 μm . This indicates that the coarse fraction of the size distribution adds very significantly to the mass add rate but contributes little to the adsorption as controlled by diffusion. Therefore, an effective sorbent should be both finely ground and have a narrow size distribution.

An extension of this model should be developed to estimate diffusional control under turbulent flow conditions where the sorbent particles move relative to the flue gas. The effect of sorbent size distribution, capacity, and surface reactivity needs to be validated experimentally.

For more information, please contact Everett Sondreal, EERC Principal Research Advisor, at (701) 777-5235 or at esondreal@undeerc.org; or John Pavlish, CATM Associate Director, at (701) 777-5268 or at jpavlish@undeerc.org.



Carbon Requirement as a Function of Particle Diameter.

particle size at 95% control is shown in the above figure for residence times of 2 and 5 seconds. These results indicate that diffusional resistance would not be limiting at reasonable injection rates for a very finely ground carbon sorbent having a

larger sizes. Substantially larger amounts of carbon are indicated to be required for a sorbent with a size distribution that includes an appreciable coarse fraction. Computations were performed for a sorbent having a

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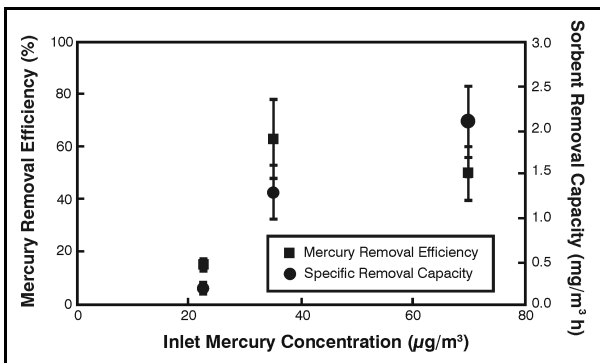
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(Bioreactors, continued from previous page)

bacterial ability to metabolize volatile organic compounds (VOCs), indicating that combined Hg and VOC removal is possible using this type of system.

The work on biofilters is directed mainly at providing pollution prevention options for small- and medium-sized businesses and has broad applications in industries

such as metal fabrication and welding, steel foundries, and smelting operations and in some chemical processes such as chlorine production, fiberglass formulation, and others. While the project focused on mercury removal, other pollutants that would be affected by these processes include lead, arsenic, selenium, cadmium, chlorine, fluorine, sulfur, and volatile organics.



Mercury Removal Using Biofilters.

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Mercury Emissions from Oil

The EERC, through the CATM program, has initiated a project aimed at identifying the issues related to the initial concentration and fate of Hg from oil-fired systems.

Similar to coal, the Hg content of oil has been shown to vary significantly with source. Hg contents in crude oil and various oil products have been reported to vary by several orders of magnitude. This project will perform analyses on a limited set of domestic and international crude oils, research analytical techniques, and perform a literature review of all data related to Hg in oil.

For further information, please contact Tom Erickson, EERC Associate Director, at (701) 777-5153 or at terickson@undeerc.org.

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