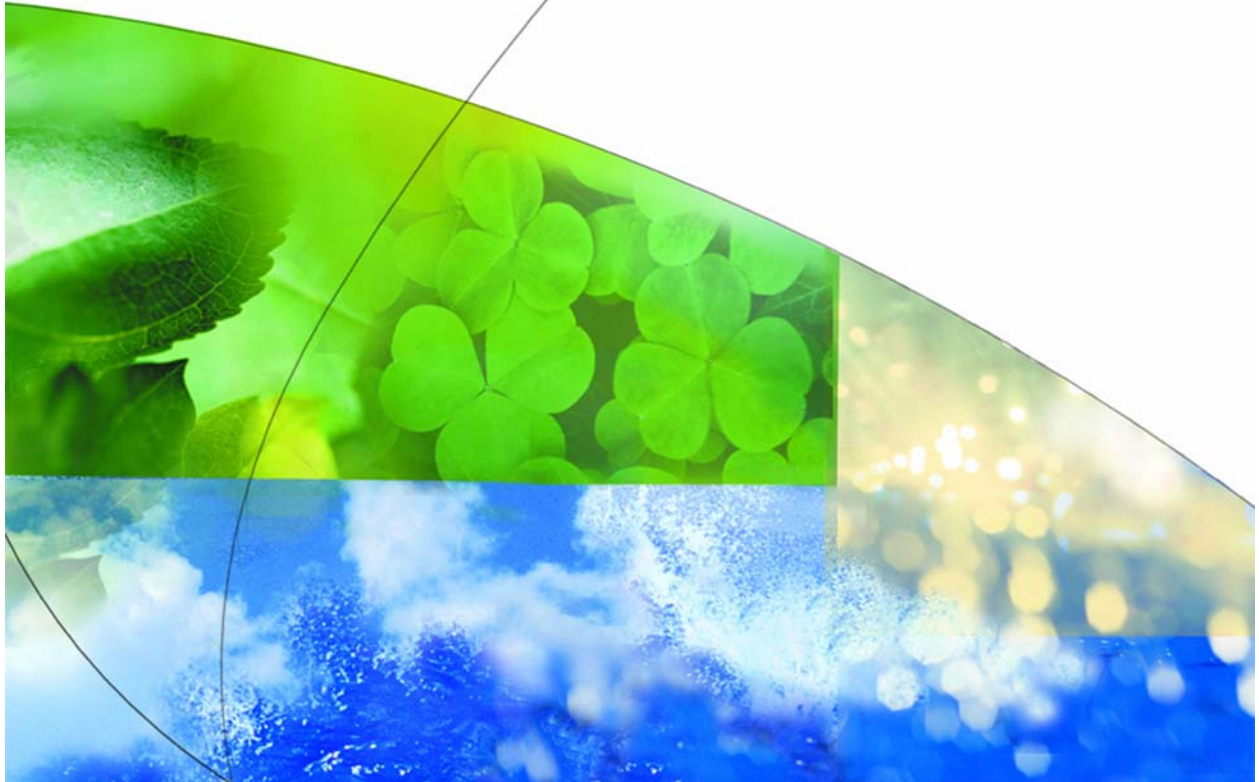


MERCURY INFORMATION **CLEARINGHOUSE**



Quarter 3 – Advanced and Developmental Mercury Control Technologies

July 2004



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QUARTER 3 – ADVANCED AND DEVELOPMENTAL MERCURY CONTROL TECHNOLOGIES

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REPORT AVAILABILITY

This report is available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650 and the CEA mercury program Web site (www.ceamercuryprogram.ca).

TABLE OF CONTENTS

LIST OF FIGURES	ii
EXECUTIVE SUMMARY	iii
INTRODUCTION	1
MERCURY POLICY	3
QUARTER 3 FOCUS: ADVANCED AND DEVELOPMENTAL MERCURY CONTROL TECHNOLOGIES	5
Evaluation Criteria	6
K-Fuel or K-Fuel Plus	6
Company Profile	6
K-Fuel Process	7
Combustion Modification and in Situ Generation of Sorbents	9
Process and System to Reduce Mercury Emission Combustion Modification	9
Thief Process for the Removal of Mercury from Flue Gas	10
Method for Removal of Vapor-Phase Contaminants from a Gas Stream by in Situ Activation of Carbon-Based Sorbents	11
New Sorbent Developments	13
Amended Silicates	13
Bromine-Impregnated Activated Carbon	15
Direct Bromine Injection	16
Advantages	17
Status and Development Issues	17
MerCAP	17
Advantages	18
Status and Development Issues	18
W.L. Gore & Associates, Inc.,-Promoted Felt Filter Bag Inserts	19
Advantages	20
Status and Development Issues	21
EnviroScrub Pahlman Process	21
Advantages	23
Status and Development Issues	24
Combined Oxidation of NO _x and Mercury	24
LoTOx™	24
ECO™/Powerspan	25
Mercury Control with the <i>Advanced Hybrid</i> ™ Filter	26
Advantages	27
Status and Development Issues	27

Continued . . .

TABLE OF CONTENTS (continued)

SUMMARY 28

UPCOMING EVENTS 29

CONTACT INFORMATION 30

REFERENCES 31

LIST OF FIGURES

1 Conceptual layout for the Pahlman™ Process 22

MERCURY INFORMATION CLEARINGHOUSE

QUARTER 3 – ADVANCED AND DEVELOPMENTAL MERCURY CONTROL TECHNOLOGIES

EXECUTIVE SUMMARY

The topic for this third quarterly report is Advanced and Developmental Mercury Control Technologies. A wide variety of approaches from combustion modification to multipollutant mercury control are under development. A number of unique mercury control technologies have passed the bench- and pilot-scale developmental phases and are now being tested at full scale.

For the near term, from 50% to 80% control may meet regulatory requirements. However, 90% control is a better research and development target for a technology to be considered attractive to meet longer-term needs. Further vendor guarantees of near 95% may be necessary to ensure compliance targets can be consistently achieved. Since the amount of mercury in coal is very small (typically about 0.1 $\mu\text{g/g}$), the total amount of mercury input (and potential emissions) for a 500-MW plant in a year is only about 300 lb and, as liquid mercury, would occupy a volume of only about one-third of a cubic foot. This suggests that there is potential for generating a minimum amount of waste material if the mercury can be effectively captured and concentrated. On the other hand, if the captured mercury is highly dispersed in waste material or by-product, the mercury must be proven to be in a stable form so that there is little possibility of reemission into the atmosphere. Until this question is fully answered, any mercury control technology that produces a large amount of mercury-containing waste material or by-product is not attractive as a long-term mercury control technology.

Many of the developing technologies appear to potentially be capable of achieving >90% control, but in most cases, this level of control has not been demonstrated over the longer term at a large scale. Concentration and sequestering of the collected mercury are also possible for many of the technologies, but this step has not been demonstrated, even at the bench-scale level, for most approaches.

Removal of the mercury from the fuel prior to combustion is a mercury control approach that has been considered for many years, and in current practice, “washed” eastern U.S. bituminous coal has resulted in some mercury removal. Now a commercial process is being developed at a large scale that improves fuel quality and removes a significant fraction of the mercury for lignite and subbituminous coal. Another alternative to back-end mercury control is combustion modification to produce an ash material that has mercury adsorbent properties. Recent developments related to combustion modifications and in situ generation of sorbents for mercury control are discussed in this report.

Several new developments in sorbent composition and use as well as new multipollutant approaches are also discussed. Another attractive approach is the insertion of mercury capture structures into the flue gas downstream from particulate control and scrubbers. Recently issued mercury control patents and published pending patent applications are also discussed.

MERCURY INFORMATION CLEARINGHOUSE

QUARTER 3 – ADVANCED AND DEVELOPMENTAL MERCURY CONTROL TECHNOLOGIES

INTRODUCTION

The Canadian Electricity Association (CEA) identified a need and contracted the Energy & Environmental Research Center (EERC) to create and maintain an information clearinghouse on global research and development activities related to mercury emission from coal-fired electric utilities. With the support of CEA, the Center for Air Toxic Metals[®] (CATM[®]) Affiliates, and the U.S. Department of Energy (DOE), the EERC is developing comprehensive quarterly information updates to provide a detailed assessment of developments in mercury monitoring, control, policy, and related research advances.

Recent developments in the area of mercury regulations from coal-fired power plants in Canada in the form of Canadawide Standards (CWS) and the United States in the U.S. Environmental Protection Agency's (EPA's) Proposed Utility Mercury Reduction Rule illustrate the need for effective mercury control strategies for coal-fired electric utilities. In the first quarterly report, sorbent injection technologies were reviewed in detail. However, many other technologies, at varying stages of development, are being investigated to achieve targeted mercury removal. A review of these technologies is provided in this quarterly report. In the second quarterly report, mercury measurement technologies were reviewed. Since that submittal, no significant advancements have been identified.

In order to adequately address the many topics pertinent to mercury research and development and provide the detail necessary for the various stakeholders to make informed decisions, selected topics will be discussed in detail in each quarterly report. Issues related to mercury from coal-fired utilities include the general areas of measurement, control, policy, and transformations. Specific topics that will be addressed in subsequent quarterly reports include, but are not limited to, the following:

- Mercury policy
 - Upcoming events and news releases
 - Regulation, policy, compliance strategies, and health developments
- Mercury measurement
 - Continuous mercury monitors
 - Advanced mercury-sampling systems
 - Wet-chemistry mercury measurement techniques
- Baseline mercury levels and emissions
- Mercury control
 - Sorbent technologies and control in unscrubbed systems

- Advanced and developmental mercury control technologies
 - Summary of large-scale test activities and associated economics
 - Mercury oxidation and control for scrubbed systems
 - Multipollutant control strategies
 - Impact of mercury control on combustion by-products/fate of captured mercury
 - Summary of mercury-related economics for commercial systems
- Mercury chemistry and transformations
 - Mercury chemistry fundamentals, modeling, prediction, and speciation
 - Mercury fate and transport – impacts on health

One objective of this quarterly report is to provide timely information on developments within the broad field of mercury. In order to address timely issues as well as provide necessary detail on selected topics, additional subject headings will be provided to summarize recent developments not related to the quarterly topic. In this manner, updated information can be provided on topics previously covered or in advance of topics not yet discussed. The primary subject area for this quarterly report is a review of advanced and developmental mercury control technologies.

MERCURY POLICY

The Government of Canada is working closely with provincial and territorial partners to put in place a CWS for mercury emissions from coal-fired power plants that will prevent the release of 60%–90% of the mercury in coal by 2010. Canadian coal-fired generating companies have embarked on a multiyear program to improve the information base around mercury measurement and control that will aid in the development of the CWS. A key component of the CEA Mercury Program is the Coal, Residue, and Flue Gas Sampling and Analysis Program that companies have undertaken. This program has generated a rich database that is being analyzed to provide valuable information around mercury emission inventories and management to this decision-making process. The data can be accessed on the program Web site: [www. ceamercuryprogram.ca](http://www.ceamercuryprogram.ca).

On December 15, 2003, EPA proposed a rule to permanently cap and reduce mercury emissions from coal-fired utilities. EPA is proposing two alternatives for controlling emission of mercury from coal-fired utilities. The first strategy is Maximum Achievable Control Technology (MACT), and the second establishes standards of performance limiting mercury emissions from new and existing utilities. The second proposal would establish a market-based cap-and-trade program. Under the MACT provisions of the Clean Air Act, sources are given 3 years to comply with emission reduction requirements. For the power generation industry, the MACT approach raises concerns about how quickly new control technologies could be put into place. Under the cap-and-trade approach, EPA would allocate allowances for mercury emissions to each state which would then allocate them to utilities. The utilities would then be allowed to trade or bank any allowances above those required to cover their emissions each year. With the cap-and-trade program, emission monitoring and reporting requirements will be stringent. However, this will allow for flexibility in trading which will create financial incentives for utilities to look for new and low-cost ways to reduce mercury emissions. Under both alternatives, a two-step implementation process has been proposed in which more stringent mercury emission limits would be required over time. This stepwise emission control requirement could significantly impact implementation strategies which would need to address short-term requirements while allowing the flexibility to meet more stringent requirements at a later time.

In the United States, EPA extended the comment period for the Utility Mercury Reduction Rule until June 29, 2004, to allow interested parties 90 days to review the document and submit formal comment. In a submission to EPA issued in April 2004, Environment Canada stated its support of U.S. efforts to limit mercury emissions, as mercury reductions in the United States will likely have impacts on air quality for both countries. Environment Canada's comment to EPA goes on to state that its modeling has indicated that as much as 10% of the mercury deposited in Canada and 38% of the mercury in the Great Lakes region each year comes from U.S. sources. This shared impact of air quality illustrates the benefit of collaborative efforts between Canada and the United States, which have, in the past, led to substantial reductions in acid rain pollutants in the 1980s and 1990s and more recently through the 2000 Ozone Annex, which is reducing smog pollutants.

Two specific recommendations to EPA include consideration of a more stringent MACT standard for mercury, resulting in a 60%–90% reduction in mercury from coal combustion.

Alternately, under a cap-and-trade option presented by EPA, Environment Canada recommends implementing a lower Phase I cap, which would result in national capture of mercury from coal combustion in the range of 60%–90%.

In Europe, the European Commission recently issued a consultation document on mercury which evaluated mercury emissions, production, trade, and use and also reviewed health and environmental impacts. The consultation period closed in May, and the Commission will present a proposal to the Council later this year. Specific details of that proposal will be presented in a quarterly report when the document becomes available.

QUARTER 3 FOCUS: ADVANCED AND DEVELOPMENTAL MERCURY CONTROL TECHNOLOGIES

The topic for this third quarterly report is “Advanced and Developmental Mercury Control Technologies” and is intended to serve as a review of technologies not currently commercially available. Control technologies presented in this summary are at various stages of development and, in most cases, have been tested under only limited operational conditions. The objective of this technology review is to present claims and available results of the various advanced and developmental technologies being investigated. Additional research and development work will be needed to adequately address the balance of plant impacts, cost-competitiveness, and technical feasibility of these mercury control approaches. The most commercially available control technology was presented in the first quarterly report entitled “Sorbent Injection Technologies for Mercury Control.” It is anticipated that “Mercury Control for Scrubbed Systems” and “Multipollutant Control” will be addressed separately in future quarterly reports. The intent for this quarterly report is to focus on control technologies not covered in the other quarterly reports.

Removal of mercury from the fuel prior to combustion is a mercury control approach that has been considered for many years. Coal washing of bituminous fuels for the removal of pyrites and other mineral matter also results in the removal of some of the mercury, however, not to the extent that would be needed to meet future control requirements. Coal washing for ash reduction has proven to be effective primarily for bituminous fuels with large mineral grains. With subbituminous and lignite fuels, conventional coal washing is not effective because of the way the inorganic material is distributed within the coal. For subbituminous coals, deep cleaning or pretreatment of the coal, such as with K-fuel process, has the potential to remove a significant fraction of the mercury. A review of the K-fuel developments is presented in this report. Another fuel-upgrading project, conducted by Great River Energy with funding from DOE, is to evaluate the drying of a high-moisture North Dakota lignite at the large-scale level. The process does not claim to remove mercury from the lignite but upgrades the fuel with waste heat, resulting in overall plant efficiency improvement, with some subsequent reduction in mercury emissions. However, even with mild thermal processing of a raw fuel, there is potential for removing some of the mercury along with the moisture by increasing the drying temperature.

Another alternative to back-end mercury control is combustion modification to produce an ash material that has mercury-adsorbent properties. Mercury control may occur as a result of combustion modifications for NO_x control, but deliberate combustion modifications to achieve mercury control are also being considered. A related interesting process is the DOE-developed and -patented Thief process whereby a fraction of the fuel is extracted from the combustion zone to maximize mercury sorption properties and then is reinjected back into the flue gas as a mercury sorbent. Recent developments related to combustion modifications for mercury control are discussed later in this report.

Mercury control with conventional wet and dry scrubbers and sorbent injection upstream of electrostatic precipitators (ESPs) or fabric filters are not included in this quarterly report. However, in many cases, there is significant overlap among the various control approaches.

Technologies that utilize sorbents in new and innovative ways as well as new multipollutant approaches are discussed. In addition, a brief review of recently issued mercury control patents and published pending patent applications is presented.

Evaluation Criteria

For effective mercury control from coal-fired boilers, several important considerations are:

- For the near-term, from 50% to 80% control may meet regulatory requirements. However, for a technology to be considered viable for longer-term control, at least 90% control should be demonstrated in R&D (research and development) demonstrations while vendor guarantees may require 90%–95% removal to ensure long-term compliance.
- Since the amount of mercury in coal is very small (typically about 0.1 µg/g), the total amount of mercury input (and potential emissions) for a 500-MW plant in a year is only about 300 lb and, as liquid mercury, would occupy a volume of only about one-third of a cubic foot. This suggests that there is potential for generating a minimum amount of waste material if the mercury can be effectively captured and concentrated.
- If the captured mercury is highly dispersed such as in fly ash, spent sorbent, or scrubber waste, the mercury must be proven to be in a stable form so that there is little possibility of reemission into the atmosphere. Until this question is fully answered, any mercury control technology that produces a large amount of mercury-containing waste material or by-product may not be attractive as a long-term mercury control technology.

K-Fuel or K-Fuel Plus

Company Profile

KFx Inc. (KFx), founded in 1981, is headquartered in Denver, Colorado. KFx has been developing K-Fuel Plus for over 20 years and has spent nearly \$120 million advancing and refining the K-Fuel Plus technology and process. KFx's K-Fuel Plus technology uses a combination of heat and pressure to transform low-energy coal into high-energy premium fuel containing low levels of sulfur, ash, and mercury.

KFx and Lurgi South Africa (Pty) Ltd. have an exclusive worldwide agreement to combine the K-Fuel Plus technology with Lurgi's technical services and equipment to upgrade low-energy, high-moisture coal into a premium K-Fuel Plus product. The Lurgi equipment that is to be used in the K-Fuel Plus plants is proven equipment technology that has been in use for over 70 years. KFx announced in June 2004 that it will be locating its first commercial plant at the Fort Union site near Gillette, Wyoming. KFx recently purchased the Fort Union Mine site. The location includes approximately 1000 acres of land, a rail loop with load-out facilities, a coal crusher, related buildings, water disposal wells, and remaining coal reserves. The plan is for the initial plant to produce 750,000 tons per year of K-Fuel[®], with raw coal input purchased from adjacent mines.

For further expansion, an agreement was reached with Arch Coal, Inc., wherein Arch has invested \$2 million in the purchase of KFx stock and KFx and Arch will evaluate the potential joint development of an 8-million-ton/year K-Fuel[®] plant at Arch's Coal Creek Mine near Gillette, Wyoming.

K-Fuel Process

K-Fuel[®] precombustion technology applies heat and pressure to boost the heating value of subbituminous coal and lignite by up to 30%, in the process removing more than 70% of the mercury and up to 30% of the sulfur dioxide and nitrogen oxide (1, 2). These reductions are achieved from coal that is already low in mercury and sulfur, and because these constituents are removed prior to combustion, the need for postcombustion controls may be reduced.

The K-Fuel[®] process employs both mechanical and thermal means to increase the quality of subbituminous coal and lignite by removing moisture, sulfur, nitrogen, mercury, and other heavy metals.

To begin the process, raw coal is delivered to the K-Fuel[®] processing plant from the mine. The coal enters the first-stage separator, developed using conventional coal-cleaning technology, where it is crushed and screened to remove the large rock and rock material. The processed coal is then passed on to an intermediate storage facility prior to being sent to the next stage in the process.

From the intermediate storage facility, the coal is sent via a distribution system to the K-Fuel[®] thermal process. This process essentially operates like a giant pressure cooker, utilizing Lurgi Mark IV vessels under high pressure and temperature to place thermal stress on the coal. The coal passes through pressure locks into the processors, and then steam at 460°F and 485 psi is injected into the processors. While the coal is maintained at these conditions, the mineral inclusions are fractured under the thermal stress, removing both the included rock (which contains some mercury) and sulfur-forming pyrites. The inherent moisture of the coal is liberated as well.

After it has been treated for a sufficient time in the main processor, the coal is discharged into a second pressurized lock, which is sealed off from the primary reactor. After sealing, the processor pressure is vented into a water condenser to return the processor to atmospheric pressure and to flash-cool the coal to approximately 200°F. The coal is then discharged onto a belt and further cooled by convection and indirect cooling. After cooling, the coal is sent to a second-stage separator for additional screening to remove sulfur- and mercury-containing mineral matter that has been liberated by the thermal process.

The water liberated from the coal is removed at various points in the process. This water, along with some condensed process steam, is either sent directly to treatment or is reused within the process. The water treatment system removes coal fines and hydrocarbon compounds liberated from the coal in the processor and uses carbon filtering to remove mercury and other heavy metals that were liberated from the coal and rock. The waste products (carbon, mercury,

and heavy metals) from the filtering process are sent to a qualified, permitted disposal site for final disposition.

The claimed environmental benefits for the K-Fuel® include:

- Reduces the mercury content of already-low mercury subbituminous and lignite coals by 70%, as high as 90% in some cases.
- Removes up to 30% of sulfur from parent coals, which are already low in sulfur compared to midwestern bituminous coals.
- Reduces fuel nitrogen by up to 30%.
- Controls mercury while it is in a more concentrated and contained form, permitting significant savings in waste disposal volumes and costs.

Advantages

- K-Fuel® is reported to achieve >70% with up to 90% mercury removal.
- Mercury is removed before the fuel reaches a plant, so there would be no concern over mercury in the fly ash or other combustion by-products. This greatly facilitates fly ash disposal as well as fly ash utilization. It would also be a major advantage to a plant burning the K-Fuel® if the mercury would be low enough so that there was no concern over the level of mercury emissions from the plant. Very likely, the higher Btu fuel would result in hotter combustion conditions which potentially could affect NO_x emissions and the amount of unburned carbon in the ash unless the appropriate low-NO_x burners were implemented.
- The captured mercury can be isolated and concentrated for disposal or permanent sequestering of the captured mercury with minimum volume of material.
- K-Fuel® has potential as a long-term mercury control solution.

Status and Development Issues

- The concept has been under development for many years and has been tested at a large scale. The investment and plans for building a full-scale plant are progressing. The actual level of Hg reduction in the final fuel product as well as the fate of the removed mercury within the process will need to be demonstrated.
- The work to date has focused mainly on the upgrading of the fuel and reductions in moisture and sulfur. Within the process, the potential for optimizing removal of mercury to achieve >90% also makes this a potentially attractive long-term mercury control approach.

- Powder River Basin (PRB) coals already account for about one-third of U.S. production and represent most of the growth in U.S. production in the last 10 years. Whether a significant portion of that production could eventually be upgraded as K-Fuel® or similar products is primarily an economic one and highly dependent on tighter regulations. The current upward trend in world oil prices and focus on CO₂ emission reduction would both appear to make K-Fuel® more attractive in the marketplace. Even a small reduction in CO₂ emissions resulting from improved plant efficiency could make the fuel desirable over conventional coal. However, even with a highly attractive market, the building of new plant capacity to meet increased demand would be a slow process.

Combustion Modification and in Situ Generation of Sorbents

An attractive approach to mercury control is to enhance the capture of mercury by modification of the combustion process to produce fly ash or unburned carbon that results in better mercury retention. One of the challenges is a lack of a good understanding of the fundamental chemistry of mercury capture and retention in fly ash. Subsequently, the exact characteristics of the ash matter that result in optimum mercury capture are unknown. In general, the thought is that either increased carbon in the ash or generation of carbon in the ash with the appropriate characteristics will enhance mercury capture. Since low-NO_x burner (LNB) technology is already known to produce more carbon in the ash, a logical extension of LNB burner approaches is to specifically modify the process for enhanced mercury control, such as is being investigated in a DOE-funded project by General Electric Energy and Environmental Research Corporation (GE EER). Another interesting approach is extracting a portion of the coal from the combustion zone and then quenching it prior to complete combustion to produce a material with good mercury sorption characteristics. This approach is known as the Thief process and is being developed in-house at DOE's National Energy Technology Laboratory (NETL). Another somewhat similar approach is detailed in two EPRI patents that describe a method for in situ activation of carbon-based sorbents by injecting carbonaceous material at the appropriate location in a boiler. A summary of these three approaches follows.

Process and System to Reduce Mercury Emission by Combustion Modification (GE EER)

GE EER is conducting a DOE-funded 2-year field evaluation using a combination of overfire air (OFA) and coal reburn to achieve multipollutant control of both NO_x and mercury. The field testing is at Western Kentucky Energy's R.D. Green Station, which burns a blend of Illinois bituminous coal and petroleum coke. Field measurements of fly ash properties and mercury removal across the ESP will be taken on Unit No. 1 after installation of an OFA and coal reburn system for NO_x control. Data from the Unit No. 1 field testing will be used to optimize the design of the NO_x control system for mercury removal using a 300-kW pilot-scale combustor at GE EER's test facility. Results from the pilot-scale testing will be used for the design of the OFA and coal reburn system to be installed on R.D. Green Unit No. 2. Mercury removal performance will then be tested on Unit No. 2 after installation of the optimized NO_x control system. Results of pilot-scale testing were recently reported (3, 4) to achieve 60% removal with a 5% to 10% loss-on-ignition (LOI) fly ash produced.

In the patented process (5), a method to decrease emission of mercury is described where a factor is selected to control a combustion process to generate a flue gas comprising fly ash with enhanced unburned carbon. The combustion process is controlled according to a factor selected from reburning fuel, flue gas temperature, OFA injection, coal particle size, LNB flow, LNB design, combustion zone air, stoichiometric ratio of fuel, fuel/air mixing in a primary combustion zone, and fuel/air mixing in a secondary combustion zone to produce the flue gas comprising fly ash with enhanced unburned carbon and to vaporize mercury. In pilot-scale testing, the flue gas is allowed to cool, similar to typical particulate control device temperatures, where fly ash is removed containing the enhanced unburned carbon and absorbed mercury.

Thief Process for the Removal of Mercury from Flue Gas (DOE NETL)

The Thief process has been tested in DOE facilities with a 500-lb/hr coal-fired combustor with both bituminous and subbituminous coals. Results reported to date indicate that up to 90% mercury control is possible and that the mercury capacity of the generated sorbents approaches the capacity of commercially available sorbents (6).

A U.S. patent (7) describes the approach where mercury removal is by adsorption onto a thermally activated sorbent produced in situ at the power plant. To obtain the thermally activated sorbent, a lance (thief) is inserted into a location within the combustion zone of the combustion chamber to extract a mixture of semicombusted coal and gas. The semicombusted coal has adsorptive properties suitable for the removal of elemental and oxidized mercury. The mixture of semicombusted coal and gas is separated into a stream of gas and semicombusted coal that has been converted to a stream of thermally activated sorbent. The separated stream of gas is recycled to the combustion chamber. The thermally activated sorbent is injected into the duct work of the power plant at a location downstream from the boiler. Mercury within the flue gas contacts and adsorbs onto the thermally activated sorbent. The sorbent-mercury combination is removed from the plant by a particulate collection system.

The in situ mercury removal system operates by extracting a stream of partially combusted and/or pyrolyzed coal and gases from the combustion zone. The high temperatures of the combustion chamber activate the coal and impart an alteration within the coal. Mercury's affinity to adsorb onto the coal is increased by this alteration so that the coal can be described as a thermally activated sorbent. The size of the extracted coal particles can be similar to the size of coal that was injected into the boiler. A hollow lance, a thief, is inserted into the combustion zone, and suction is applied through the lance to draw the partially combusted coal and gas mixture out of the combustion chamber and through a gas-solid separator such as a cyclone separator. The thief may use a cooling device when located in the combustion chamber in order to reduce further oxidation of the solids. The thief could also be designed to concentrate the solids in the gas stream before removal from the combustion zone in order to further reduce the heat rate penalty and optimize the cost of operation. Additionally, a small flow of inert gas may be injected into the thief to help quench the oxidation of the sampled solids.

As an option, the thermally activated sorbent may also be chemically or physically treated to enhance its reactivity with mercury. Examples of chemical treatment include washing the

sorbent with hydrochloric acid or depositing sulfur on the surface of the sorbent. An example of physical treatment is grinding.

The sorbent, whether chemically treated or untreated, is injected into the duct work of the power plant, preferably where the temperature is 400°F or less. Similar to activated carbon, the sorbent will remove elemental and oxidized mercury from the flue gas which will then be collected in the plant's particulate collection system and removed from the plant along with the fly ash collected by the particulate collection system. In another variation, the sorbent could be injected after the plant's particulate collection system, and a separate particulate collection system just for the sorbent could eliminate sorbent contamination of the fly ash collected in the plant's particulate collection system and increase the sorbent's utilization with respect to mercury capture by recycling of the sorbent. Additionally, in the event that a wet scrubber is installed in the power plant for flue gas desulfurization, the sorbent may be injected into the flue gas either before or after the scrubbing process.

Method for Removal of Vapor-Phase Contaminants from a Gas Stream by in Situ Activation of Carbon-Based Sorbents (EPRI)

Two EPRI patents by Chang et al. describe the process in detail (8, 9). This is a somewhat similar technology to the Thief process in that a sorbent material is generated within the process. However, the process is different than the Thief process because it includes the separate injection of a carbonaceous material at a strategic location in the system, while the Thief process utilizes the feed coal and then extracts from the combustion zone a fraction of the coal before it has undergone complete combustion.

The Chang process has several variations, including the use of a separate combustion system to activate the injected material as well as an option for extraction of a portion of the flue gas to activate a fixed carbon bed. Testing or development of the Chang process has not been reported.

The Chang patents describe the process for removing vapor-phase contaminants from a gas stream, which includes the step of adding a raw carbonaceous starting material into a gas stream having an activation temperature sufficient to convert the raw carbonaceous starting material into an activated material in situ. The raw carbonaceous starting material can be either a solid-, liquid-, or vapor-phase material. The activated material then adsorbs the vapor-phase contaminants, and the activation material containing the vapor-phase contaminants is removed from the gas stream using a particulate collection device. The process is particularly suited for the removal of vapor-phase air toxics, such as mercury, from the flue gas of a combustion process.

In another aspect of the invention, a gas stream source directs a gas stream to an activation region. The gas stream has an activation temperature at the activation region. A raw carbonaceous starting material is positioned at the activation region, such that the gas stream activates the raw carbonaceous starting material into an activated carbonaceous material. The activated carbonaceous material is then positioned in the exhaust stream of a combustion process to adsorb vapor-phase contaminants.

Advantages

- The largest single advantage for all three control technologies is that mercury capture could potentially be achieved with the coal alone (the EPRI/Chang process also includes using coal as one of the options).
- All three techniques could potentially offer a very low-cost approach.
- All three have potential for widespread application, especially for mercury control requirements for less than 90% control.
- The EER process possesses the advantage of very simple implementation.
- With the EER combustion modification process, some NO_x control would also be seen.

Status and Development Issues

- For all three processes, the resulting chemistry of the produced sorbent materials and the preferred process for optimizing mercury capture have not been reported.
- The EER process is the furthest along and is being tested at full scale. A major goal will be to determine the level of control that can be achieved in a full-scale boiler. Another key issue is the extent to which the mercury removal depends on coal type. Of the three processes, this is also the simplest and would appear to be most likely implemented in the near future. One of the main concerns is that the process depends on incomplete combustion and the presence of significant unburned carbon in the ash. This makes fly ash utilization and disposal more challenging.
- The Thief process appears to offer more flexibility in achieving a much higher-capacity carbon than the other two combustion modification and in situ technologies but with significant additional complexity. Since the Thief process can include injection downstream of a primary particulate control device, it also offers an opportunity for separating the fly ash from the spent carbon. However similar techniques can be implemented with many sorbent injection technologies.
- The EPRI process defined in its patent offers flexibility with the raw feed materials which may offer an opportunity to generate a very highly reactive, high-capacity sorbent. Since the generated sorbent material does not have to be collected and reinjected, the process may offer an opportunity to generate a very fine particle-size material. If so, in-flight capture would be enhanced making it an attractive application for ESP controlled units. This process, however, has not been tested yet, so near-term development is unlikely.

New Sorbent Developments

Since sorbent technology was the focus of the first quarterly report, extensive discussion of sorbent developments will not be given in this report. However, two significant sorbent developments that warrant discussion are the development of Amended Silicates™ and activated carbon impregnated with bromine. Both approaches have been previously tested and now will be demonstrated at the full scale as part of the DOE-funded large-scale mercury control demonstration program.

Amended Silicates

ADA Technologies, Inc., has been developing a non-carbon-based sorbent for several years (10–12). The Amended Silicates™ material will be tested under the DOE-funded large-scale mercury demonstration program. Amended Silicates, LLC (a joint venture of ADA Technologies, Inc., and CH2M Hill), Littleton, Colorado, will test the material at Cinergy's 175-MW Miami Fort Unit 6 that burns bituminous coal. The research team also includes the University of North Dakota EERC, Western Kentucky University, and Boral Materials Technologies.

Amended Silicates™ sorbents use silicate materials as substrate particles on which chemicals with a strong affinity for heavy metals (e.g., mercury and mercury compounds) are impregnated. Because of their physical structure, the silicates present extend surface area on each particle with an easily generated particle size of a few micrometers. This configuration promotes maximum exposure of the chemical amendment to the mercury vapor present in the coal-fired flue gas stream.

According to the recently issued patent awarded for the material and process (13), the Amended Silicates™ material is a high-capacity regenerable sorbent for removal of mercury from flue gas. A phyllosilicate substrate, for example, vermiculite or montmorillonite, acts as an inexpensive support to a thin layer for a polyvalent metal sulfide, ensuring that more of the metal sulfide is engaged in the sorption process. The sorbent is prepared by ion exchange between the silicate substrate material and a solution containing one or more of a group of polyvalent metals including tin (both Sn[II] and Sn[IV]), iron (both Fe[II] and Fe[III]), titanium, manganese, zirconium, and molybdenum, dissolved as salts, to produce an exchanged substrate. Controlled addition of sulfide ions to the exchanged silicate substrate produces the sorbent. The sorbent is used to absorb elemental mercury or oxidized mercury species such as mercuric chloride from flue gas-containing acid gases (e.g., SO₂, NO_x, and HCl) and other gases over a wide range of temperature.

ADA Technologies has run pilot tests at the Comanche Station, which burns western subbituminous coal, for three different Amended Silicates™ sorbent formulations (11). One variant produced superior results, and a second showed promise, as it easily matched the performance of carbon. Tests were conducted in several campaigns between November 2002 and March 2003. For these tests, total mercury concentrations in the flue gas stream ranged from about 4 to 8 µg/Nm₃, with the particulate-bound fraction well under 20%. The baseline data showed mercury removal across the pilot baghouse by the native fly ash of about 24%. At an

injection rate of 1.6 lb per million actual cubic feet of flue gas, the mercury removal increased to 60%–70%. The removal was 92% at a rate of 3.8lb/MMacf and 96.7% for the injection of 9.1 lb/MMacf. When fly ash plus spent sorbent samples were subjected to toxicity characteristic leaching procedure (TCLP) tests, no measurable mercury was found in the leachate. More extensive leachability studies are being initiated through a recent DOE solicitation and will be addressed in a quarterly report focusing on by-product utilization.

Amended Silicates™ formulations have also been tested at elevated temperatures and pressures as a possible mercury control technology for next-generation coal gasifiers. Laboratory experiments have shown one variant to effectively capture mercury at a temperature of 770°F and 200 psig, with sorbent mercury capacity in excess of 3% by weight. This is a strong indication that Amended Silicates™ technology could offer significant cost advantages in future coal gasification systems. In this application, the Amended Silicates™ sorbent can be disposable or used in a pressure-swing mode where a significant fraction of the captured mercury is liberated when the pressure is released at operating temperature.

ADA Technologies, Inc., has in place an alliance agreement with CH2M Hill (Denver, Colorado), a major environmental engineering firm, to commercialize the Amended Silicates™ technology through the creation of a new joint venture company to manufacture and sell sorbent. CH2M Hill brings to the joint venture broad expertise in the design and construction of chemical process facilities as well as experience in the delivery of environmental control technologies to a wide range of commercial, industrial, and government clients.

Advantages

- The Amended Silicates™ technology has the potential to achieve >90% mercury removal.
- A sorbent that is non-carbon-based is highly attractive because of the potential for ash utilization without concern over additional carbon in the ash. Based on material properties and test results to date, no impact of the material on the fly ash utilization is expected.
- With regeneration, the mercury can be isolated for disposal, and since the mercury can be concentrated, permanent sequestering of the captured mercury is possible with minimum volume of material.
- Cost appears to be reasonable and with further development may approach the cost of activated carbon.

Status and Development Issues

- The concept has moved beyond the bench-scale level and has been tested at the pilot level at a coal-fired power station. The current DOE-funded project will take the evaluation to the full-scale demonstration level.
- Critical developmental questions concern the level of control that can be demonstrated compared to existing and new activated carbons and the stability of the mercury in the ash.

The ability to manufacture large amounts of the material at a reasonable cost also needs to be demonstrated.

- While regeneration ability is desirable, this does not appear to be a near-term requirement if the mercury is stable and ash utilization is not impaired. Demonstrating that impacts to ash utilization are negligible will be an important factor for further commercialization of the process.

Bromine-Impregnated Activated Carbon

Sorbent Technologies Corporation (STC) has been working to develop better-performing and lower-cost technology to control mercury stack emissions for a number of years. The company's efforts have concentrated on testing inexpensive, novel sorbent materials on both elemental mercury, Hg^0 , and oxidized mercury, Hg^{2+} , on both simulated and real coal-fired boiler flue gases, in both fixed-bed fabric filter simulations, and with actual duct-injection into ESPs. Over this period, STC has developed a number of advanced mercury sorbent materials specifically designed for the conditions found at coal-fired power plants.

Results from the testing with these sorbent materials have previously been reported (14, 15), but the formulation has only been recently disclosed (16–18).

According to a recently published patent application summary (18), the process includes a method for removing mercury and mercury-containing compounds from a combustion gas in an exhaust gas system. The steps involve providing a mercury sorbent, injecting it into a stream of mercury-containing combustion gas for a sufficient time to allow at least an effective amount of the mercury and mercury-containing compounds in the combustion gas to adsorb onto the mercury sorbent, and collecting and removing the mercury sorbent from the combustion gas stream. The mercury sorbent is prepared by treating a carbonaceous substrate with an effective amount of a bromine-containing gas, especially one containing elemental bromine or hydrogen bromide, for a time sufficient to increase the ability of the carbonaceous substrate to adsorb mercury and mercury-containing compounds. The points of injecting, collecting, and removing the mercury sorbent may be varied, depending upon the exact configuration of the exhaust gas system.

According to the application, the mercury sequestration claims have five essential elements. The first three are that 1) a carbon-based adsorbent, such as powdered activated carbon (PAC), is used 2) to capture and concentrate vaporous mercury species from 3) a hot, flowing gas stream of combustion products. The fourth requirement is that the adsorbent material be 4) injected into the flowing gas to intimately mix with it and be separated from the gas in a particulate collector. The fifth and final essential element of the invention is that, at some time before it is mixed with the mercury-containing combustion gas, the carbon material must be exposed to a bromine-containing treatment gas, possibly producing surface complexes that are particularly reactive to gaseous mercury species.

In January 2003, STC field-tested the Type A sorbents at the 18-MW scale (60,000 acfm) at the Lausche Plant of Ohio University (15). This stoker plant burns a high-sulfur bituminous

coal and has a cold-side ESP for emission control. Baseline Ontario Hydro method sampling indicated no intrinsic mercury removal across the ESP at temperatures from 300°–350°F. For comparison, NORIT DARCO flue gas desulfurization (FGD) PAC did not remove much mercury at Lausche. At an injection rate of almost 18 lb/MMacf, it captured less than 20% of the flue gas mercury. This plant's unusually high SO₃ in the flue gas of about 20 ppm, which competes for active adsorption sites on the PAC, may have been responsible for this poor performance. The STC Type A sorbents, on the other hand, performed very well on the difficult Lausche flue gas, achieving about 60% Hg removal at 3 lb/MMacf and almost 70% removal at 4 lb/MMacf. An important feature of the advanced Type A sorbents is that their mercury performance is largely independent of temperature up to over 600°F.

Because of the higher-temperature performance, there is also potential for some level of mercury control with hot-side ESPs. Recently reported results (17) from the Duke Power Cliffside Plant, which burns a low-sulfur bituminous coal, showed that from 40% to 80% mercury control was possible with a hot-side ESP.

The STC sorbents do not appear to leach their captured mercury (15). TCLP testing has not detected any Hg leaching from the Type A sorbents. In one example, a well-saturated fixed-bed sample of Type A sorbent was mixed with ash to 0.9 µg Hg/g fly ash, a representative amount, and sent to EA Group Laboratories for analysis. An additional fly ash blank and a sample with dry FGD were included for comparative purposes. The TCLP results were all below the laboratory's mercury detection limits. Mercury volatilization from saturated Type A sorbents has also been examined and, so far, has not been found to be a concern. Additional leachate and volatilization measurements, however, will need to be performed to be certain, particularly long-term leachate analyses at field pHs.

The STC sorbents will also be tested under the DOE-funded large-scale mercury demonstration program. The project will test a novel sorbent (assumed to be a bromine-impregnated carbon-based sorbent) at Duke Energy's Buck Station or Allen Station, which are both equipped with an ESP and burn bituminous coal, and also at Detroit Edison's St. Clair Station, which burns a mixture of bituminous and subbituminous coal. Joining STC, Duke Power, and Detroit Edison are Fuel Tech, Western Kentucky University's Combustion Laboratory, PS Analytical, Spectra Gases, and Stock Equipment Company.

Direct Bromine Injection

With the reported success of the bromine sorbents, a logical question is whether direct bromine injection into the flue gas might enhance mercury capture by the fly ash or other sorbent materials. Another patent application published within the last year (19) includes this option. The patent application summary discloses a method of treating a coal combustion flue gas, which includes injecting a molecular halogen or thermolabile molecular halogen precursor able to decompose to form molecular halogen at flue gas temperature. The claims specifically list bromine, in addition to chlorine and iodine, as possible molecular halogen and/or thermolabile molecular halogen precursors. The molecular halogen converts elemental mercury to mercuric halide absorbable by alkaline solids such as subbituminous or lignite coal ash; alkali-fused bituminous coal ash capturable in whole or part by ESPs, baghouses, dry flue gas, or

desulfurization solids; and with or without subsequent adsorption by a liquid such as a flue gas desulfurization scrubbing liquor.

Advantages

- Direct bromine injection has the potential to achieve >90% mercury removal
- The use of bromine to enhance mercury control appears to be a unique welcome advancement in the attempts to make better carbon-based sorbents.
- The reasonable level of control with ESPs (hot side as well as cold side) has the potential to make this approach very attractive when compared to reported results to date with commercially available sorbents.
- Cost appears to be reasonable because only a small amount of injected halogen compound may be necessary.
- This technology has potential as a long-term mercury control solution with widespread application.

Status and Development Issues

- The concept has moved beyond the bench-scale level and has been tested at the pilot level at coal-fired power stations. The current DOE-funded project will take the evaluation to the full-scale demonstration level.
- Critical developmental questions are the level of control that can be demonstrated compared to other newly developed activated carbons or non-carbon-based sorbents. The long-term stability of the mercury in the ash also needs to be more fully addressed. The ability to manufacture large amounts of the material at a reasonable cost or pretreat the carbon on-site does not appear to be a significant developmental issue.
- Improved performance and reduced injection rates of these sorbents will need to be sufficient to offset any increase in cost over that of commercially available activated carbon.
- Fate and transport of bromine will need to be evaluated to ensure there are no adverse impacts to by-product utilization, disposal, or human health.

MerCAP™

The general MerCAP™ (Mercury Control via Adsorption Process) concept is to place fixed structures into a flue gas stream to adsorb mercury and then periodically regenerate them and recover the captured mercury (20, 21). While a variety of regenerable sorbent materials could be used, most of the development work has focused on the use of gold-coated substrates in

the form of parallel plates spaced about 0.5 to 1 in. apart. Previous work has shown that the level of control is impaired in an unscrubbed flue gas environment (22). Subsequently, current development efforts seek to achieve high levels of mercury removal in scrubbed flue gases, either downstream from a spray dryer scrubber or a wet scrubber.

DOE NETL is currently funding a demonstration of MerCAP™. In this project, URS Group will test EPRI's MerCAP™ technology for controlling mercury emissions from coal-fired power plants (23–25). The MerCAP™ sorbent structures will be retrofitted into a single compartment in the outlet plenum of the Unit 10 baghouse at Great River Energy's Stanton Station, which burns North Dakota lignite, and will treat 6 MWe equivalence of flue gas. At Southern Company Services' Plant Yates, which burns eastern bituminous coal, gold-coated plates will be configured as a mist eliminator (ME) located downstream of a 1-MWe pilot wet absorber, which receives flue gas from Unit 1. The results of this study will provide data required for assessing the feasibility and estimating the costs of a full-scale MerCAP™ process for flue gas mercury removal. It will provide information about optimal operating conditions for different flue gas conditions, the effectiveness of sorbent regeneration, and the ability of the gold sorbent to hold up to flue gas over an extended period. In addition, if successful, the novel approach of incorporating MerCAP™ structures in existing baghouse compartments will demonstrate a cost-effective means for achieving mercury control using existing baghouse technologies. Testing will occur over a 6-month period at Great River Energy's lignite-fired Stanton Station and at Southern Company Services' bituminous-fired Plant Yates.

Advantages

- The MerCAP™ process by itself has the potential to achieve >90% mercury removal when installed downstream of a scrubber. However, any upstream removal of oxidized mercury by the scrubber makes the total mercury removal of >90% even more likely.
- Captured mercury will not be mixed with the fly ash. This facilitates fly ash disposal as well as fly ash utilization as a by-product.
- With regeneration, the mercury can be isolated for disposal, and since the mercury can be concentrated, permanent sequestering of the captured mercury is possible with a minimum volume of material.
- The fact that good mercury removal up to 2000 hr has been demonstrated indicates that with further advancements an annual replacement and maintenance schedule could be achieved.
- The process has potential as a long-term mercury control solution with widespread application.

Status and Development Issues

- The concept has moved beyond the bench-scale level and has been tested with a small slipstream device at a number of coal-fired power stations. The current DOE-funded project

will take the evaluation to the next level and will attempt to answer a number of critical development questions.

- Since the concept depends on the amalgamation of mercury with gold, a key concern is the absorption ability of the gold as well as the regeneration ability and lifespan of the material. Reported results indicate that the process does not work well in unscrubbed flue gas, but the specific components causing the poor absorption were not disclosed. The scrubbers are expected to remove most of the SO₂, most or all of the HCl, and little of the NO or NO₂. It is well known from continuous mercury monitor (CMM) development work that the gold traps used in many mercury analyzers are poisoned by HCl or a combination of HCl and NO_x. This suggests that HCl may be the main component that impairs absorption. A very critical developmental question is how sensitive the material is to small concentrations of HCl or other gases that affect the absorption of mercury.
- The work to date has focused on the capture of mercury from the flue gas and not the regeneration of the plates or sequestering of the mercury. A viable regeneration process along with a method to concentrate the mercury is a major development step that has not yet been addressed.

W.L. Gore & Associates, Inc.,-Promoted Felt Filter Bag Inserts

W.L. Gore & Associates, Inc., has developed an innovative technology for control of mercury emissions in flue gas streams. Specifically, the configuration involves a mercury control filter placed inside the existing particulate control filter bag, essentially a bag-within-a-bag concept. This concept is similar to the MerCAP™ technology in that both attempt to achieve mercury capture by placing an adsorbent material in a convenient location within the system and then periodically (e.g., every 6 months) removing the components for regeneration and/or mercury concentration. Reported high measured mercury capacities of over 75 mg Hg/g of adsorbent material make this approach feasible (26).

The Gore Mercury Filter System has not been tested as extensively at the MerCAP™ system, but the concept has been tested at the small pilot-scale level both at EPA facilities and at the EERC. Operationally, the mercury filter elements did not appear to impair the pulse cleaning of the bags. Results showed that, initially, nearly 100% mercury removal could be achieved. This is an encouraging result because it indicates that there was good contact with the flue gas and filter elements and there was no mass-transfer limitation. For the materials tested, breakthrough occurred under some process conditions, but one of the purposes of the testing was to gain a better understanding of how the process conditions affected the level of mercury removal.

Details of the process are disclosed in U.S. Patent Application 20040074391, which was published April 22, 2004 (27). The application claims include compositions for the adsorbent material as well as fabrication of a filter system whereby the mercury adsorbent elements are installed as inserts on the inside of conventional pulse-jet filter bags. The inserts have a permeability such that the forward filtration and pulse cleaning of the filter bags are not obstructed.

The adsorbent component of the invention has a unique chemical composition which is capable of capturing mercury under the operating conditions of the filter system employed. A stated goal is to achieve a mercury capture capacity exceeding 20 mg Hg/g of initial dry weight of adsorbent. Stated possible mercury-binding agents may include anions or salts selected from halides, thiocyanates, sulfides, polysulfides, selenium, tellurium, and phosphorus compounds. Particularly, the binding agent could comprise at least one binding compound having a component selected from the group consisting of an anion of a halide, an anion of a thiocyanate, an anion of a sulfide, an anion of a polysulfide, an anion of selenium, an oxyanion of selenium, an anion of tellurium, an oxyanion of tellurium, an anion of phosphorus, and an oxyanion of phosphorus. Preferred binding agents are selected from the group of potassium iodide, copper iodide, zinc iodide, and copper thiocyanate.

A promoter is added to increase adsorption, to reduce volatility of binding agents, and to generate anchoring sites on the high surface area support for bonding to the mercury-binding agent complex. Suitable promoters include compounds having at least one of a multivalent metallic cation and a multivalent metalloid cation that is not spontaneously reduced by iodide. Preferred promoters comprise carboxylate salts of Zn(II) or Mg(II). A particularly preferred combination of binding agent and promoter comprises potassium iodide as the binding agent and zinc acetate hydrate as the promoter. Trivalent or quadrivalent metallic or metalloid cations that meet the reduction potential criterion above are suitable for use. After exposure to heating during preparation or use of the mercury-trapping filter, the nature of the binding agent or the promoter compounds may be altered. The acceptable or optimal ratios of binding agent to promoter vary depending on the specific combinations of ingredients used.

The adsorbent insert of the invention may be flexible or rigid. Examples of flexible inserts include woven or felted materials imbibed with activated carbon particles having the mercury-binding agent/promoter thereon or even activated carbon fibers woven or felted into a flexible sheet having the mercury-binding agent/promoter thereon. The insert may have any desired geometry such as a flat disk or panel, a sleeve or tube, a hub-and-spoke geometry, a canister, or the like, provided the insert fits into the filter element or is somehow attached to the downstream side of the filter element.

Advantages

- The insert has the potential to achieve nearly 100% mercury removal, depending on how often it would need to be changed
- Captured mercury will not be mixed with the fly ash. This facilitates fly ash disposal as well as fly ash utilization as a by-product.
- With regeneration, the mercury can be isolated for disposal since the mercury can be concentrated; permanent sequestering of the captured mercury is possible with a minimum volume of material.
- The insert could be retrofit into existing filter systems.

- The insert has potential as a long-term mercury control solution with widespread application.

Status and Development Issues

- The concept has been tested at the small-scale pilot level. Longer-term endurance testing would be a logical next step toward development.
- A better understanding of how specific flue gas components affect the capacity needs to be determined.
- The work to date has focused on the capture of mercury from the flue gas and not the regeneration or sequestering of the mercury.
- The process appears to have potential, but currently there are no known testing programs outside of Gore to further develop this technology.

EnviroScrub Pahlman Process

A multipollutant control technology that is truly unique is being developed by EnviroScrub (28–30). In 2000, EnviroScrub Technologies Corporation (“EnviroScrub”) acquired the dry Pahlman™ scrubbing technology, which can simultaneously remove SO_x, NO_x, and Hg.

Since June 2003, the company has been granted two U.S. patents, consisting of 104 claims, on its Pahlman™ process technology. Pahlman™ process technology consists of a single-stage, dry system, which can essentially replace three separate emission reduction technology (ERT) systems: wet FGD for SO_x scrubbing, selective catalytic reduction (SCR) for NO_x scrubbing, and activated carbon injection for mercury reduction. High capture percentages coupled with the single-stage capabilities of the system make the technology attractive compared to the standard alternatives of wet FGD, SCR, and activated carbon systems.

A conceptual process diagram is shown in Figure 1.

Manganese is the twelfth most abundant element on earth, constituting about 0.1% of the earth’s crust. As an oxide, it occurs in nature in at least 30 known forms, including over 14 minerals of economic significance, and in numerous synthetic forms. Manganese oxides are used commercially as desulfurizers and alloy metal in steel production, as decolorizers in glass manufacturing, in ceramic glaze, and extensively as depolarizers in dry-cell batteries. Extensive technical literature is available on the subject of manganese oxides. The Pahlman™ process uses a sorbent composed of oxides of manganese. These specialized sorbents have been generically named Pahlmanite™ sorbent in honor of the late Dr. John E. (Jack) Pahlman who led the early research and development work on the process.

The manganese may exist in six different valence (oxidation) states. For purposes of the Pahlman™ process, valence states of interest are 2+, 3+, and 4+. These states correspond to the oxides MnO, Mn₂O₃, and MnO₂. The oxide Mn₃O₄ is likely a solid solution of manganese in the 2+ and 3+ states.

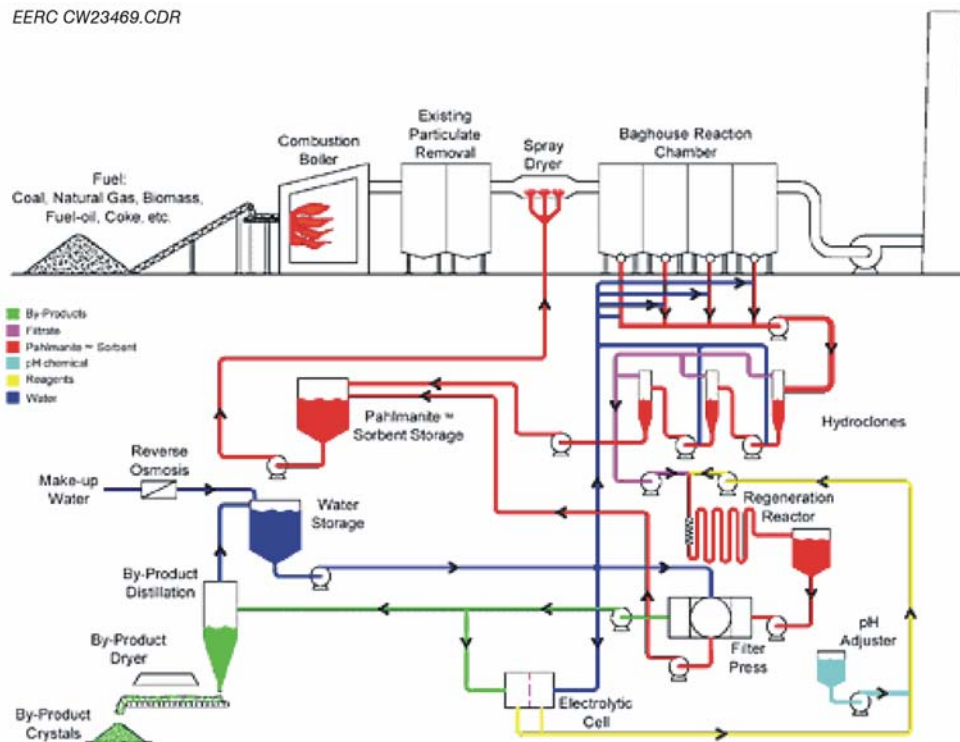


Figure 1. Conceptual layout for the Pahlman™ process (from EnviroScrub Web site).

A characteristic of most oxides of manganese species is nonstoichiometry; that is, most oxides of manganese molecules contain, on average, less than the theoretical number of two oxygen atoms (typically, the average number of oxygen atoms ranges from 1.5 to 2.0). This nonstoichiometry is thought to result from solid–solution mixtures of two or more oxide species and exists in all but the beta (β), or pyrolusite, form of manganese dioxide. The most active types of Pahlmanite™ sorbent usually have the formula $\text{MnO}_{1.7 \text{ to } 1.95}$, which translates into manganese valence states of 3.4+ to 3.9+, as opposed to the theoretical 4.0+ state. It is unusual for average valence states above about 3.9 to exist in most forms of oxides of manganese. The formula MnO_2 symbolically represents all varieties of manganese dioxide.

Some manganese oxides have the ability to absorb oxygen from gas. Manganous oxide (MnO) will oxidize to MnO_2 in the presence of air, for example. Additionally, the dioxides are themselves oxidizers; they readily exchange oxygen in chemical reactions; and they are known to have catalytic properties. This oxygen exchange ability may be related to proton mobility and lattice defects common within most MnO_2 crystal structures. These characteristics are important to the Pahlman™ process's, since removal of NO_x and SO_2 gases and Hg requires oxidation of the species to be removed prior to reaction with Pahlmanite™ sorbent to form manganese sulfates, nitrates, and mercury compounds. It is important to understand and optimize such desirable properties during manufacture of Pahlmanite™ sorbent.

Manganese compounds are soluble in water in the 2+ valence state, but not in the 4+ state. Therefore Mn^{2+} compounds are readily soluble, as opposed to MnO_2 . This property is used in the Pahlman™ process's sorbent capture and regeneration procedure, in that Pahlmanite™ sorbent is reduced from about the 4+ state to the 2+ state during formation of manganese nitrates and sulfates. These species are water-soluble, allowing the sulfate, nitrate, and Mn^{2+} ions to be dissociated and the Mn^{2+} to be oxidized again to about Mn^{4+} .

Chemical reactivity (“activity”) appears to be controlled by a variety of MnO_2 characteristics, including bound water, crystal structure and crystal lattice defects, surface area, particle size, valence state, and presence of other elements within the crystal lattice. Much of the MnO_2 literature deals with electrochemical activity for applications in electric batteries. This type of activity is not always similar to or useful for Pahlman™ process gas removal applications. Part of the chemical activity associated with gas removal appears related to catalytic properties of MnO_2 . These properties are still being investigated at present, but appear to affect oxidation of nitrous oxide (NO) to nitrogen dioxide (NO_2) (and, possibly, sulfur dioxide [SO_2] to sulfur trioxide [SO_3]) as intermediate steps, in the formation of manganese nitrates and sulfates on the surface of Pahlmanite™ sorbent and in the formation of mercury compounds.

EnviroScrub has developed patented and proprietary processes for producing and regenerating hybrid types of manganese-based sorbents, which are very effective for NO_x , SO_2 , and Hg removal applications and have possibilities for other applications. Their sorbents are effective for gas removal because of a combination of properties not found in commercially available oxides of manganese. These properties include high gas permeability, low bulk density, high valence state, extremely high specific surface area, cryptomelanelike crystal structure, and a high degree of hydration.

Advantages

- Very high levels of SO_2 , NO_x , and mercury removal have been reported. A significant advantage is the potential to achieve >90% mercury removal (28).
- This is truly a unique multipollutant control approach that is not based on the combining of several existing approaches.
- As presented, the technology would be placed downstream of a particulate control device so that the captured mercury will not be mixed with the fly ash. This facilitates fly ash disposal as well as fly ash utilization as a by-product.
- Since it includes a regeneration process, there is potential for the mercury to be isolated for disposal and permanent sequestering of the captured mercury with a minimum volume of material.
- The technology has potential as a long-term mercury control solution with widespread application when installed as a multipollutant control technology as an alternative to SCR and FGD technologies.

Status and Development Issues

- The concept has moved beyond the bench-scale level and has been tested with a 1000-acfm trailer-mounted slipstream device at a number of coal-fired power stations. However, only the collection step has been demonstrated. The fairly complex regeneration and recycling steps have not been tested.
- According to the process diagram, the preferred approach would be to spray the material into a reactor; however, specific operational conditions have not been presented. Most of the testing to date has been with dry injection of the adsorbent materials. Whether the same removal levels for SO₂, NO_x, and Hg would be seen with spray injection is unknown.
- How the mercury would be separated and sequestered has not been reported. Adapting the process to separate the mercury is a major development step.
- Much longer-term and larger-scale testing needs to be completed to address all aspects of the process.
- The chemistry of the sorbent materials and the preferred recipe of the materials are proprietary and have not been reported.

Combined Oxidation of NO_x and Mercury

Oxidation technologies to enhance mercury capture in conventional wet scrubbers will be addressed in a later quarterly report. However, two processes that oxidize mercury along with NO_x for capture in an ammonia-based wet scrubber are unique. Both the BOC LoTox™ and ECO™/Powerspan are NO_x control approaches whereby the NO_x is oxidized to a soluble form to allow capture in a wet scrubber. Even though the oxidation approaches for the two processes are different, both of these processes claim that elemental mercury is also oxidized to HgO and subsequently captured in the wet scrubber along with SO₂ and NO_x. Both of the processes are coupled with an ammonia-based wet scrubber.

LoTox™

The BOC LoTox™ system is based on the patented Low-Temperature Oxidation (LTO) Process for Removal of NO_x Emissions, exclusively licensed to BOC Gases by Cannon Technology (31, 32). Marsulex Inc. and the BOC Group have signed a joint marketing agreement that will enable each company to offer electric utilities an integrated multipollutant control solution that provides maximum compliance for emissions of sulfur dioxide, sulfur trioxide, nitrous oxides, mercury, and other heavy metals in conjunction with ammonia-based wet scrubbing. The mercury removal is achieved by oxidizing elemental mercury with ozone to produce soluble HgO, which is captured in a downstream wet scrubber.

The LoTox™ System is a NO_x removal system that injects ozone into the flue gas stream to oxidize insoluble NO_x to soluble oxidized compounds. Ozone is produced on-site and on demand by passing oxygen through an ozone generator. LoTox™ is a low-temperature system;

therefore, it does not require heat input to maintain operational efficiency or to prevent the “slip” of treatment chemicals, such as ammonia, as is common with SCR and selective noncatalytic reduction (SNCR) systems.

Ozone is produced in response to the amount of NO_x present in the flue gas generated by the process. The low operating temperature allows stable and consistent control regardless of variation in flow, load, or NO_x content. There are no adverse effects of acid gases or particles on the LoTOx™ system, and some particles may even enhance the reaction by producing sites for nucleation of moisture and by catalyzing the oxidation reaction.

Ozone rapidly reacts with insoluble NO and NO_2 molecules to form soluble N_2O_5 . The species N_2O_5 is highly soluble and will rapidly react with moisture in the gas stream to form nitric acid. The conversion of NO_x into the aqueous phase in the scrubber is rapid and irreversible, allowing nearly complete removal of NO_x . The nitric acid, along with unreacted N_2O_5 and nitrous acid formed by reaction of NO_2 with water, can be easily scrubbed out of the gas stream in a wet scrubber with water or neutralized with a caustic solution.

The rapid reaction rate of ozone with NO_x makes ozone highly selective for treatment of NO_x in the presence of other compounds such as CO and SO_x , resulting in a high ozone utilization efficiency for NO_x removal with no wasteful consumption of ozone by CO and SO_x .

ECO™/Powerspan

Powerspan Corp. is the primary researcher and proprietary owner for the ECO™ process (33–35). However, Powerspan has entered into an alliance with Wheelabrator Air Pollution Control, Inc., to commercialize the system. Powerspan and First Energy jointly funded the latest pilot plant. In addition, DOE awarded a grant to Powerspan to optimize the mercury removal capability of the technology on a 50-MW demonstration facility at the R.E. Burger Plant. These tests are currently being conducted, but results are not yet available.

In the ECO™ process, flue gas exiting the ESP or fabric filter is routed to the ECO™ reactor where it is exposed to a high-voltage discharge, which generates high-energy electrons. These high-energy electrons initiate chemical reactions that lead to the formation of oxygen and hydroxyl radicals. These radicals then oxidize the pollutants in the flue gas, leading to the formation of particulate matter and aerosol mist. These components are removed downstream in an ammonium salt wet scrubber and wet ESP forming the ammonium sulfate and ammonium nitrate by-products. Approximately 90% of the NO in the flue gas is oxidized to NO_2 and is removed in the scrubber (the other 10% remains unoxidized). Less than 10% of the SO_2 in the gas is oxidized to form SO_3 , which eventually forms sulfuric acid (H_2SO_4). Elemental mercury vapor is oxidized to form mercuric acid (HgO), which is removed by the wet scrubber/wet ESP.

Advantages

- For both processes, combining NO_x , SO_2 , and mercury control within one process makes the approach attractive.

- High mercury removals of >90% should be possible.
- With removal of the mercury from the scrubber liquor, there is potential for mercury concentration and long-term sequestration.

Status and Development Issues

- The concepts are being tested at a large scale so near-term commercialization is viable.
- The level of mercury control that can be achieved has not been demonstrated yet. The fate of the mercury within the scrubber is also unknown, and how the mercury can be removed for disposal is unproven.

Mercury Control with the *Advanced Hybrid*TM Filter

Since 1995, DOE has supported development of a new concept in particulate control, called the advanced hybrid particulate collector (AHPC) (36). The AHPC is licensed to W.L. Gore & Associates, Inc., and is being marketed as the *Advanced Hybrid*TM filter. The *Advanced Hybrid*TM filter combines the best features of ESPs and baghouses in a unique configuration, providing major synergism between the two collection methods, both in the particulate collection step and in the transfer of dust to the hopper. The *Advanced Hybrid*TM filter provides ultrahigh collection efficiency, overcoming the problem of excessive fine-particle emissions with conventional ESPs, and it solves the problem of reentrainment and re-collection of dust in conventional baghouses. The *Advanced Hybrid*TM filter also appears to have unique advantages for mercury control over baghouses or ESPs as an excellent gas–solid contactor. Since most of the sorbent material will collect on the perforated plates, there will be minimal effect on the pressure drop across the filter bags. In addition, better gas–solid contact is achieved than in conventional ESPs because the distance that gas must cross streamlines to reach sorbent particles is much smaller than in ESPs.

The objective of this current DOE-funded project is to demonstrate 90% total mercury control with commercially available sorbents in the *Advanced Hybrid*TM filter. The approach included field demonstration pilot-scale testing with a 2.5-MW *Advanced Hybrid*TM filter at the Big Stone Power Plant, which burns subbituminous coal from several different PRB mines.

Over 90% mercury control was demonstrated at low carbon addition rates upstream of the *Advanced Hybrid*TM filter with commercially available Norit FGD activated carbon. However, the level of control was dependent on other flue gas components. One of the very interesting findings was the discovery that when the plant cofired a small amount of tire-derived fuel, the level of mercury captured in the fly ash, the fraction of oxidized mercury in the inlet flue gas, and the level of total mercury removal with activated carbon all were significantly increased likely due to the increased chlorine content from tire-derived fuel. Another significant result was that the injection of activated carbon for mercury control had no effect on bag-cleaning interval or pressure drop. The perforated plate geometry of the *Advanced Hybrid*TM filter allows sufficient gas–solid contact to achieve over 90% mercury removal at low carbon addition rates, even though most of the carbon is collected on the perforated plates.

Good mercury control was demonstrated at A/C ratios up to 14 ft/min, but the highest mercury removal (94%) was seen with a combination of a lower A/C ratio and somewhat increased carbon injection rate (6 ft/min and 2.5 lb of carbon/million Btu)

Advantages

- The *Advanced Hybrid*TM filter has the potential to achieve >90% mercury removal for both bituminous and subbituminous fuels.
- Even better mercury removal might be achieved with very low addition rates of new, more advanced sorbents.
- At very low addition rates of carbon, fly ash utilization for some applications may still be possible based on the total amount of carbon in the ash. However, the use of fly ash for cement application may be subject to other tests such as the anti-foaming index
- Cost appears to be reasonable because from 70% to 90% control was demonstrated with a low carbon rate (1.5 lb/million Btu) of low-cost Norit FGD carbon
- The *Advanced Hybrid*TM filter has potential as a combined long-term mercury control solution along with ultrahigh collection (99.99% removal) of fine particles.

Status and Development Issues

- The concept for mercury control has moved beyond the bench scale and has been tested at the 2.5-MW pilot level at a coal-fired power station. However, there are currently no plans for a full-scale demonstration to evaluate mercury control effectiveness.
- The availability of the approach depends on the commercial success of the *Advanced Hybrid*TM filter for particulate control. A full-scale evaluation of the *Advanced Hybrid*TM filter technology is being demonstrated at the Big Stone Power Station; however, this demonstration does not include an evaluation of mercury removal capabilities. Subsequent installations will depend on the results from the Big Stone demonstration.

SUMMARY

A variety of approaches for mercury control are under development, ranging from combustion modification to multipollutant technologies. Many of these unique technologies have passed the bench- and pilot-scale developmental phases and are now being tested at full scale.

For the near-term, it appears that 50%–80% control may meet regulatory requirements. However, 90% control is a better target for a technology to be considered attractive to meet longer-term needs. Since the amount of mercury in coal is very small (typically about 0.1 µg/g), the total amount of mercury input (and potential emissions) for a 500-MW plant in a year is only about 300 lb. This suggests that there is potential for generating a minimum amount of waste material if the mercury can be effectively captured and concentrated. On the other hand, if the captured mercury is highly dispersed in waste material or by-product, the mercury must be proven to be in a stable form so that there is little possibility of reemission into the atmosphere. This will be a significant factor in the development of new technologies for long-term mercury control.

Many of the developing technologies appear to be capable of achieving >90% control, but in most cases, this level of control has not been demonstrated over the longer term at a large scale. Concentration and sequestering of the collected mercury is also possible for many of the technologies, but this step has not been demonstrated, even at the bench-scale level for most approaches.

Removal of the mercury from the fuel prior to combustion is a mercury control approach that has been considered and practiced for many years, but now a commercial process, K-Fuel[®], is being developed at a large scale that removes a significant fraction of the mercury for lignite and subbituminous coal. Another alternative to back-end mercury control is combustion modification to produce an ash material that has mercury adsorbent properties. Recent developments related to combustion modifications and in situ generation of sorbents for mercury control show positive results in testing conducted to date; however, large-scale demonstrations and balance of plant issues will need to be addressed.

Attractive alternatives are being developed that focus on multipollutant technology and mercury capture devices downstream of particulate control and/or scrubbers. Development of these technologies and data from full-scale demonstrations will be reviewed as they become available and summarized in subsequent quarterly reports to CEA.

UPCOMING EVENTS

POWER-GEN International

November 30–December 2, 2004, Orlando, Florida

<http://pgi04.events.pennnet.com>

229th ACS National Meeting ACS

March 13–17, 2005, San Diego, California

<http://oasys.acs.org/acs/229nm/topics.html>

30th International Conference on Coal Utilization & Fuel Systems (formerly Clearwater Coal Conference)

April 17–21, 2005

<http://www.coaltechnologies.com>

A&WMA 98th Annual Conference and Exhibition

June 21–24, 2005, Minneapolis, Minnesota

<http://www.awma.org>

230th ACS National Meeting ACS

August 28–September 1, 2005, Washington, DC

<http://oasys.acs.org/acs/230nm/topics.html>

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