SUBTASK 7.1 – STRATEGIC STUDIES

Final Report

(for the period of April 1, 2005 through March 31, 2009)

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Project Manager: Richard Read

Prepared by:

Thomas A. Erickson

Energy & Environmental Research Center
University of North Dakota
15 North 23rd Street, Stop 9018
Grand Forks, ND 58202-9018

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SUBTASK 7.1 – STRATEGIC STUDIES

ABSTRACT

The Energy & Environmental Research Center (EERC) has recently completed 11 years of research through the Cooperative Agreement with the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) focused on fossil energy technology development and demonstration. To support a significant number of the different activities being considered within all of our research contracts with NETL, a subtask (7.1 Strategic Studies) was created to focus on small research efforts that came up throughout the year which would support an existing EERC–NETL project or would help to develop a new concept for inclusion in future efforts. Typical efforts conducted under this task were usually between \$15,000 and \$60,000 in scope and had time lines of less than 6 months. A limited number of larger studies were also conducted, generally at the direct request of NETL.

Over the life of this task, 46 projects were conducted. These efforts ranged from quick experiments to gain fundamental knowledge to support a current effort, to literature reviews, to a few larger engineering efforts.

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SUBTASK 7.1 – STRATEGIC STUDIES

EXECUTIVE SUMMARY

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Over the life of this task, 46 projects were conducted. These efforts ranged from quick experiments to gain fundamental knowledge to support a current effort, to literature reviews, to a few larger engineering efforts. The following is a list of the research projects conducted:

- Systems Engineering
- Climate Change Initiative
- Soil Flushing by Humic Acid Microemulsion
- Geographic Information Systems
- Alternative Sorbents for the Removal of Contaminants from Fluids
- Education Initiatives (Science in North Dakota and Educational Initiatives in Fossil Energy, Air Toxics, and Other Air Quality Issues)
- A Novel CO₂ Photoreduction System via Sol-Gel Processing
- Industrial Relations
- Technology Adoption – Ceramic Materials Market
- Coalbed Methane
- Waste By-Products
- Emission Control Technologies
- Economic Evaluation of the Use of Manure-Based Reburn Fuels for the Reduction of NO_x in Combustion Systems
- Photocatalytic Mercury Capture in Flue Gas
- Filter Blinding Reversal
- Hydrogen Membrane Testing
- Determination of Measureable Outcomes
- Waste Tire Recycling with Subcritical Water
- Feasibility of Using Freeze–Thaw Evaporation[®] (FTE[®]) Technology for Power Plant Cooling Water Treatment
- Effects of Fossil Fuel Power Plant Emissions on Precipitation
- Remediation Seminar
- Short Course – Ash Behavior and Mercury Control in Coal Combustion

- Review of Utility-Scale Energy Storage Technologies
- Evaluation of ChemCAD Software
- Subcritical Water Fractionation of Particulate Matter
- Domestic Energy Parks
- Evaluation of Landfill Gas Applications
- Controlled Spontaneous Reactor
- CO₂ Separation Technologies
- Mercury Measurement in Combustion Flue Gases Short Course
- Installation of an Additional Wet Scrubber on the Energy & Environmental Research Center's 7-kW Combustion System
- Microbial Cycling of CH₄, CO₂, and N₂O in Wetland Environments – A Scoping Study
- Residential Energy Issues
- Hydrogen Storage Material
- Materials Testing
- Oil Field Applications for Low-Btu Associated Gas
- Development of a Novel Petroleum Biotechnology
- Potential for Conversion of Beet Sugar
- Biomass Product Separation and Characterization for the Generation of Fuel Additives
- Analysis of Oil and Gas Environmental Issues Affecting Domestic Production
- Student Involvement Activities
- Filter Cake Properties
- High-Temperature Corrosion of Alloys in Simulated Boiler Tube Conditions
- On-Demand High-Pressure Hydrogen Extraction and Dispensing for Vehicle Fueling
- Indirectly Fired Combined Cycle with Condensing Heat Exchanger
- Engineering Opportunities and Challenges of CO₂ Mitigation Using Microalgae in Fossil Fuel-Fired Power Plants

SUBTASK 7.1 – STRATEGIC STUDIES

SUMMARIES OF RESULTS

Over the life of this task, a variety of different formats were used to identify and track the activities conducted. These varying formats sometimes overlapped and sometimes conflicted with each other. For reporting purposes, the various activity numbers used throughout the years will not be used, but rather, each task will be identified by its title.

For each of the following activities, the period of performance and an identifier to the final report is listed in addition to a brief summary of the activities conducted. Depending upon the size and scope of the project, the final reports range from a short write-up within a quarterly report to a separate final report. Since these projects and reports occurred over a period of eleven years, it is noted that the assumptions and conclusions may be dated significantly, and no effort was made to redo any past studies with the most recent information.

Systems Engineering

Period of Performance: April 15, 1998 – March 31, 2009

Final Report: Appended to April 1 – June 30, 2008, quarterly status report.

Brief Summary: A series of spreadsheet programs have been developed at the Energy & Environmental Research Center (EERC) to recursively calculate energy, mass, and elemental balances for gasification and combustion systems. These programs operate on either Lotus or Excel using an architecture that is adaptable to virtually any fuel or energy process. The user can define input and output streams and characterize their contents based on a property correlations for 52 elements or compounds, along with fuels (coal, oil, or gas) and coal ash. Enthalpies are calculated for elements or compounds as a function of temperature based on regression equations derived from the JANAF tables. The correlation developed to calculate the enthalpy of a fuel on a moisture- and ash-free basis provides estimates of heating values that match experimental data better than the Dulong Formula. Enthalpies for typical coal ash analyses for bituminous, subbituminous, and lignite coals are calculated based on enthalpies for the major constituents SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , and MgO . The relationships between inputs and outputs can be variously determined by fuel and product analyses, chemical equilibrium, or (less often) kinetics. The recursive calculations that are performed to balance elements, mass, and energy use either “Solver” in Excel or a Newton Raphson macro in Lotus. Elemental balances can be performed by changing the amount of any species in any stream containing that element. The energy balance can be performed by changing either amounts or temperatures. The design of a useful spreadsheet for a particular process application depends on making an appropriate choice of the species/streams or temperatures to be changed and the order in which they are changed—which is governed by knowledge and assumptions concerning how the process operates.

Climate Change Initiative

Period of Performance: April 1, 2000 – June 30, 2001

Final Report: In Interim Year 3 Technical Report Including Quarterly Status Report for April 1 – June 30, 2001

Brief Summary: The intensity of the debate over the relative importance of anthropogenic effects on natural¹ climate variability is just beginning. Commonly reported trends in CO₂-related temperature increases in this century appear to point to human influence, although such trends cannot be fully appreciated or resolved until human industrial, agricultural, and domestic impacts are understood in the context of natural changes in climate. The current tone of the debate over cause and effect will undoubtedly become very heated as attempts to implement climate policies that directly influence people's day-to-day lives come to pass.

A key element in any study of climate change (and especially in predictive climate modeling) is an understanding of the pattern of short-term cycles. EERC research in climate change studies has focused on interpreting natural climatic variations in the recent past (i.e., the last 5000 years) and providing a better context in which to examine interpretations of current climate change. The goal of this project was to provide a basis for understanding late Holocene, natural, short-term climate variability through a review of various recently reported studies. Seventy papers covering a wide range of climate interests were examined. Each of the papers was summarized in 11 categories that were present in most of the papers, including 1) basic thesis of the paper, 2) project locality (geographic location), 3) project methods, 4) data source (what kind of materials are being investigated), 5) time frame (years of geological and cultural past covered by analysis), 6) impact (scale of interpretation or consequences; i.e., global, regional, or local), 7) background context (basic information necessary to understand the investigation), 8) summary of research results, 9) interpretation of results, 10) conclusions reached by the investigator; and 11) temporal illustrations (figures that provide climate histories through time). The information in selected categories was carefully coded and input into a database to facilitate the sorting of the data according to area, time coverage, methodology, or other field of interest. By placing these data sets and methods in a position to be evaluated on the same bases, the conclusions can be more appropriately synthesized and compared.

Soil Flushing by Humic Acid Microemulsion

Period of Performance: April 1, 2000 – June 30, 2001

Final Report: In Interim Year 3 Technical Report Including Quarterly Status Report for April 1 – June 30, 2001

¹ In the Climate Change Initiative summary, “natural” refers to ongoing Earth processes that are outside of human influence which result in climate change.

Brief Summary: The EERC performed bench-scale laboratory testing to investigate the potential for humic acid/alcohol solutions to form microemulsions with dense nonaqueous-phase liquids and, thereby, increase their solubility and mobility. The EERC effort focused on evaluating the effects of varying concentrations of surfactants and pentanol alcohol on the solubility of the contaminant trichloroethylene (TCE). The testing was performed using batch water-based experiments to determine partitioning coefficients for each solution concentration. Experimental results in this study have shown significant increases in the solubility of TCE using both commercial surfactant solutions and humic acid solutions.

Geographic Information Systems

Period of Performance: April 1, 2000 – June 30, 2001

Final Report: In Interim Year 3 Technical Report Including Quarterly Status Report for April 1 – June 30, 2001

Brief Summary: The goal of this effort was to better establish geographic information systems (GIS) and decision support tools and expertise to support existing and proposed U.S. Department of Energy (DOE) joint venture projects. This was accomplished through the acquisition of software upgrades, a scanner for the incorporation of hard copy data (e.g., images and maps), and training in the use of the GIS programming language. The programming language allows for customization of the GIS software to suit particular purposes. Additional programming or applications development can simplify and streamline the use of GIS for specific tasks. A field crew was trained in the use of the University of North Dakota's (UND's) global positioning system equipment (coowned by the EERC and the UND Department of Geology and Geological Engineering), which is capable of subcentimeter accuracy.

Alternative Sorbents for the Removal of Contaminants from Fluids

Period of Performance: April 1, 2000 – June 30, 2001

Final Report: In Interim Year 3 Technical Report Including Quarterly Status Report for April 1 – June 30, 2001

Brief Summary: The removal of metal contaminants such as mercury from flue gas streams continues to be a challenge because they are not completely removed in particulate control devices or scrubbers. High-surface-area sorbents may provide a means of removal when contact between the sorbent and the flue gas is maximized. Just as the geometry of chemical reactors can be adjusted to promote or suppress mixing, it should be possible to adjust the configuration of a sorbent to maximize contact with the contaminant through the turbulence of the fluid containing the contaminant. The goal of this project was to compare the effectiveness of a corrugated sorbent configuration with that of a flow-through, packed sorbent bed.

Carbon aerogels were used as the test sorbents because they could be obtained in sheet, powdered, and monolithic forms. The carbon content and surface area of the sheet form of carbon aerogel were compared to those of -400-mesh carbon aerogel that had been tested in the

EERC's bench-scale mercury sorption test system during the performance of an earlier project (U.S. Environmental Protection Agency Grant No. R827649-01). Both forms had quite similar properties, indicating that any differences noted in sorption capability were likely to have been caused by configuration differences rather than physical differences between the sorbent forms.

One mercury sorption test was performed in the EERC's bench-scale mercury system for each corrugation angle. The tests were performed at 250°F using a synthetic flue gas comprising 6 wt% O₂, 12 wt% CO₂, 1600 ppm SO₂, 50 ppm HCl, 14.5 µg/m³ Hg⁰, 8 wt% H₂O, and the balance N₂. The synthetic flue gas flow rate was 0.0435 m³/hr (about 700 cm³/min). The low flow rate was selected to highlight any differences in sorption between the two orientation angles, although it was assumed that such a low gas flow rate would probably not result in complete breakthrough within the amount of time allotted to the tests. At any given time, approximately 70% of the Hg⁰ fed to the system was removed by the corrugated sorbent.

Educational Initiatives

Period of Performance: April 1, 2000 – June 30, 2001

Final Report: In Interim Year 3 Technical Report Including Quarterly Status Report for April 1 – June 30, 2001

Science in North Dakota

Brief Summary: This activity was originally funded to solicit, review, and distribute a series of articles on science research conducted by North Dakota scientists. These articles were to have been publicized through public media (e.g., newspapers, talk shows, etc.) in North Dakota and adjacent states.

This effort was discontinued because the project manager, Joseph Hartman, changed positions within UND, and although still appointed to the EERC, could not allocate adequate time to carry this project to completion.

Contact was made with and initial support for this project was obtained from numerous groups including the North Dakota Academy of Science, Prairie Public Broadcasting, North Dakota high schools, and numerous North Dakota researchers.

Educational Initiatives in Fossil Energy, Air Toxics, and Other Air Quality Issues

Brief Summary: New K-12 science education standards call for activities that engage students in a continuous and integrated process of observing, questioning, investigating, and reflecting, with an emphasis on an interdisciplinary understanding of the relationships between science, technology, societal needs, and community issues. Scattered efforts to produce educational units consistent with the science education standards, including energy and environmentally focused units, have been undertaken in North Dakota, Minnesota, and elsewhere in the region. Teachers burdened with paperwork and regulations desire assistance in implementing the new standards

and in developing curricula to integrate technology and hands-on activities into their classrooms. The EERC is uniquely qualified to provide a central role in the development and implementation of activities consistent with the science education standards with its multidisciplinary staff; comprehensive testing, fabrication, and analytical capabilities; breadth of energy and environmental project experience; proven ability in third-party assessments of critical issues; and practical project focus. Recent EERC proposals for projects providing water-related educational projects for schools and communities received enthusiastic support from a variety of stakeholders, including school districts, educators, and education facilitators; state and federal agencies; and grassroots organizations in both the North Dakota and Minnesota portions of the region. Applying these qualities to the development of hands-on, critical-thinking, and problem-solving teaching units will provide the region's students with a rich education experience. Working with teachers, administrators, and other stakeholders in the education community will ensure that the curricula are accepted and implemented.

The purpose of this 1-year task was to lay the groundwork for establishing a sustainable energy and environmental education program area at the EERC. This project 1) identified areas where the EERC can develop, complement, take part in, or build on existing individual activities, local partnerships, and statewide initiatives; 2) developed the relationships and information base necessary to ensure a relevant, sustainable education initiative; and 3) developed stakeholder-approved project concepts and preproposals.

A Novel CO₂ Photoreduction System via Sol-Gel Processing

Period of Performance: April 1, 2000 – June 30, 2001

Final Report: In Interim Year 3 Technical Report Including Quarterly Status Report for April 1 – June 30, 2001

Brief Summary: Group VIII transition metal oxotitanates containing Co, Ni, and Ru, being explored for CO₂ photoreduction, were synthesized from precursors by sol-gel methods and characterized by infrared spectroscopy. Color and spectra changes are consistent with those expected for the respective metal complexes.

A low reactivity of the Group VIII transition metal oxotitanates for photoreduction of CO₂ was observed for irradiation with visible light. This was also true for most other titania photocatalysts. A method for modifying the light absorbance properties of the oxotitanate catalysts is feasible and should be further explored. This would involve adding complexing reagents to the metal oxotitanate either before or after hydrolysis to the gel state. The resulting complexed metal oxotitanates would be used without calcination for tests to determine absorbance and photoreactivity properties.

Further experimentation with the Group VIII transition metal oxotitanates at shorter wavelengths (ultraviolet [UV]) is warranted. Although titanias have been extensively investigated as photooxidation catalysts for destruction of many pollutants in water treatment under UV irradiation, this kind of treatment has not reached commercialization. Thus the emphasis on design and testing would shift from CO₂ reduction to photocatalytic oxidation of

hydrocarbons, chlorinated hydrocarbons, and many other organic pollutants that produce CO₂ as the final product. The metal oxotitanates may also be useful for related treatment processing such as photofenton and fenton reactions.

Industrial Relations

Period of Performance: April 1, 2000 – June 30, 2001

Final Report: In Interim Year 3 Technical Report Including Quarterly Status Report for April 1 – June 30, 2001

Brief Summary: The EERC implemented a project review approach to attempt to assess the industrial focus of EERC activities. To ensure that all projects within the Cooperative Agreement had significant industrial direction, each project underwent an initial kickoff meeting, a midpoint meeting, and a closeout meeting. Each of these meetings involved review of the activities of the project by senior EERC management and identification of industry needs and direction.

Technology Adoption – Ceramic Materials Market

Period of Performance: April 1, 2001 – June 30, 2002

Final Report: In Appendix A.

Brief Summary: Technology innovation research focuses on the adoption of technological innovations and why some innovations are adopted at a faster or slower rate than others. The rate of adoption is the relative speed at which an innovation is implemented by members of an industry group. Rogers (1) identified five perceptual characteristics of innovations that help explain differences in adoption rates: relative advantage, compatibility, complexity, trialability, and observability.

Relative advantage is the degree to which an innovation is perceived as better than the idea it supersedes. Compatibility is the degree to which an innovation is perceived as being consistent with the existing values, past experiences, and needs of potential adopters. Complexity is the degree to which an innovation is perceived as difficult to understand and use. Trialability is the degree to which an innovation may be experimented with on a limited basis. Finally, observability is the degree to which the results of an innovation are visible to an observer. In general, the rate of adoption is positively related to perceived relative advantage, compatibility, trialability, and observability and is negatively related to perceived complexity of the innovation. Rogers (1) found relative advantage to be one of the best predictors of an innovation's rate of adoption. Relative advantage, along with compatibility and complexity, is the most significant factor in explaining relationships across a broad range of innovation types.

The technological orientation of the United States provides a means for the transfer of technology out of universities. In the corporate sector, years of downsizing have led to the willingness of more companies to consider outsourcing in general and technology licensing in

particular. Licensing in is seen increasingly as complementary to corporate business development strategies (2). Licensing is one strategy that promotes the diffusion of innovation.

Successful commercialization from universities and laboratories occurs when senior administration and management actively support cooperation with industry, with strong positive attitudes and incentives. Other key factors are the degree to which inventors of the technologies exhibit entrepreneurial attributes and have positive attitudes toward commercialization (3). Also, successful universities and laboratories are those in which the cooperating company supports commercialization and where the company's technical people perceive their counterparts in the federal laboratories as willing to take risks and able to deal with ambiguity.

This project was conducted to explore the market factors that influence the adoption of technology innovation. The goal was to better understand methods to help drive technology development to promote commercialization and acceptance of innovation for a specific technology, silicon carbide composites; determine market potential; and assist with the commercialization of the silicon carbide technology.

The market research involved the following objectives:

- Preparation of a material technology overview that is understandable to business and marketing personnel
- Preparation of a market/industry overview that quantifies market size
- Preparation of a competitive analysis
- Identification of market opportunities
- Identification of barriers to entry
- Identification of industry leads
- Recommendations for marketing strategies

Coalbed Methane

Period of Performance: April 1, 2001 – June 30, 2002

Final Report: Appended to April 1 – June 30, 2002, quarterly status report

Brief Summary: The latest and most controversial exploitations of coalbed methane (CBM) are occurring in the Powder River Basin (PRB) of southeastern Montana and northeastern Wyoming. The PRB encompasses approximately 12,145 square miles. There are currently approximately 3100 wells in the PRB, with expectations of up to 39,000 more wells to be drilled over the next 10 to 15 years. A majority of the future exploration and production activities are expected to occur in the Montana portion of the PRB where only approximately 200 wells are currently producing. There have been 270 wells permitted by Montana regulatory agencies; however, a moratorium has been placed on additional permitting until an environmental impact statement (EIS) addressing the accelerated growth is completed.

The methane extraction process involves removing large volumes of water from the aquifer. Lowering the water pressure, which confines the methane within the coal seams, results

in methane release and migration into extraction wells. Because of the potential for thousands of wells, and because CBM extraction consists of continuous pumping and discharge of groundwater, several environmental concerns have been raised.

This activity focused on a review of the current environmental issues related to CBM development in Montana and the identification of research needs.

Waste By-Products

Period of Performance: April 1, 2001 – June 30, 2002

Final Report: Appended to April 1 – June 30, 2002, quarterly status report

Brief Summary: The EERC conducted a limited broad-scope research study to identify industrial by-products/recycling opportunities in the region. The focus was to enhance and expand the coal combustion by-product (CCB) research program by identifying potential waste management opportunities that would combine CCBs with other wastes/by-products to create useful products. In some instances, non-CCB wastes provide opportunities for coal, energy, and CCB management activities. An example of this type of use is in the production of biodiesel from waste cooking oil. The biodiesel has high potential for use in hauling coal and CCBs by truck and reducing emissions related to energy production from coal.

The study indicated that sugar beet tare dirt reuse, biodiesel, food waste, composting, and glass were areas to be considered. Several project ideas were explored, and it was determined that there was a great need for an agriculture consortium in the region.

Emission Control Technologies

Period of Performance: October 1, 2001 – June 30, 2002

Final Report: Appended to April 1 – June 30, 2002, quarterly status report

Brief Summary: Complaints about diesel smoke from trucks and buses, particularly in urban areas, have been a concern for years. Experts have expressed growing concerns about the health risks associated with the emissions from diesel-powered engines. Researchers have reported diesel particulate matter contributes to or aggravates chronic lung diseases such as asthma, bronchitis, and emphysema, and there is growing evidence about the potential cancer risk from exposure to diesel particulates (4). Diesel particulates also impair visibility and contribute to structural damage through corrosion.

Despite these concerns, diesel engines are still an attractive solution in a global marketplace increasingly concerned with its energy supply. Diesel engines are known for their reliability, fuel efficiency, ease of repair, and low operational expense. They typically have a life of 1,000,000 miles in heavy-duty trucks and can power buses for up to 15–20 years (4). Aside from the problems with particulate and NO_x emissions, the diesel engine has very low emissions

of hydrocarbons and carbon monoxide, which also pose risks to public health and the environment.

The environmental issues with diesel engines may be addressed from three angles, namely engine design modifications, diesel fuel and additive technology, and emission control through exhaust gas aftertreatment. Engine and control manufacturers are working to develop, optimize, demonstrate, and commercialize advances in these categories. Emission control issues, especially diesel particulate traps, are the area of interest in this ministudy.

This project was conducted to explore the market environment for diesel emission control devices. The primary goal was to better understand the needs of the marketplace in order to aid in the direction of technology development. In addition, a goal of the project was to identify industry partners with the intent of providing opportunities for demonstration and commercialization of technologies.

The market research involved the following objectives:

- Preparation of a market/industry overview that quantifies market size
- Preparation of a competitive analysis
- Identification of market opportunities
- Identification of barriers to entry
- Identification of industry leads
- Recommendations for marketing strategies

Economic Evaluation of the Use of Manure-Based Reburn Fuels for the Reduction of NO_x in Combustion Systems

Period of Performance: October 1, 2002 – December 31, 2003

Final Report: Appended to October 1 – December 31, 2003, quarterly status report

Brief Summary: Reburning is a mature process used to reduce NO_x levels in flue gas. The typical reburning process provides nominally 50% to 70% NO_x reduction at reburn heat inputs above 20% (5). Advanced reburning is basic reburning with the injection of nitrogen agents and promoter compounds. It has been found to achieve NO_x reductions as high as 85% to 95%. Fuel properties found to have the greatest effect on NO_x control include fuel nitrogen content, volatiles, and ash constituents. The most effective promoters used during advanced reburning have been sodium compounds (5). It is reasonable to assume, therefore, that a fuel produced from a high-nitrogen source such as animal waste by a process that utilizes an alkali-based catalyst or reaction promoter would be effective in a reburn scenario. Such a reburn fuel might more cost-effectively reduce NO_x levels than the current “advanced reburn” combination of fuel, ammonia or urea, and alkali promoter. It is prudent to determine if the costs associated with processing animal waste to produce a reburn fuel are outweighed by the benefits of reduced NO_x levels. This project was a preliminary study of the economics of producing a premium reburn fuel from animal waste for the purpose of reducing NO_x levels in flue gas. Favorable economics would indicate that the process merits additional development.

To estimate the cost-effectiveness of manure-based reburn fuels, a preliminary literature search was performed in which information comparing both various reburn fuels and reburning to other NO_x removal techniques was gathered. The majority of the literature surveyed was available on the Internet; some articles in technical journals were also reviewed. Specific topic areas that were addressed included disposal costs typically associated with animal waste; various processing methods that could be used to produce premium fuels from animal wastes; geographic costs or savings due to processing plant siting; handling, environmental, or safety issues associated with animal waste-related fuels; comparison of animal waste-based reburn fuel to other methods of NO_x control; and comparison of animal waste-based reburn fuel to other reburn fuels.

Photocatalytic Mercury Capture in Flue Gas

Period of Performance: October 1, 2002 – September 30, 2003

Final Report: In July 1 – September 30, 2003, quarterly status report

Brief Summary: This project focused on the development of a photocatalytic NO_x control system. The effort was focused on mercury transformations across the system so as to identify opportunities for multipollutant control. The results showed that NO₂ could be removed from a flowing gas stream by adsorption and reaction on TiO₂. In fact, the NO₂ adsorbed so strongly on the TiO₂ that it could not be removed by a flowing gas stream at ambient conditions. The HNO₃ formed when exposed to UV radiation was removed by rinsing with water.

Filter Blinding Reversal

Period of Performance: April 1, 2003 – September 30, 2003

Final Report: The final results from this activity were previously provided to DOE on a confidential basis and are not included in this report.

Brief Summary: EERC engineers developed a novel process for removing residual filter cakes that remain adhered to a fabric filter even after typical particulate removal methodologies have been employed, such as pulse-jet bag cleaning. The process applies to air or gas filtration media that are normally cleaned in place as part of the existing process. It applies to all cleanable filters used for air pollution control, dust control, or powder product capture.

As this process lowers filter drag, it promises greater system efficiencies by decreasing the power required to operate blowers. It also promises to greatly increase the lifespan of a set of filter bags, reducing labor and materials costs. Finally, it offers a method by which more aggressive baghouse designs may be utilized where pressure drop and filter blinding were once limiting factors.

Hydrogen Membrane Testing

Period of Performance: April 1, 2003 – June 30, 2003

Final Report: Located in April 1 – June 30, 2003, quarterly status report

Brief Summary: Concerns over global climate change, dependence on foreign fuels, and presidential directives, among others, are driving this nation to further explore and greatly enhance the use of hydrogen as a fuel for the transportation sector and electric power generation. Programs such as DOE's VISION 21 initiative also include this as an important goal. One step on this path is to create methods of separating hydrogen from product gas streams such as those generated from coal gasification.

The goal of this work was to start the development of a membrane which can separate hydrogen to purity sufficient for use in devices such as solid oxide fuel cells. Further, it was intended that this membrane be of such integrity as to withstand the environment provided by a coal gasification system.

Determination of Measureable Outcomes

Period of Performance: October 1, 2003 – March 31, 2004

Final Report: Appended to January 1 – March 31, 2004, quarterly status report

Brief Summary: When determining whether research on a particular topic should continue, it is useful to have an idea of the value presented by the work. A cost-benefit analysis is one method of gathering and presenting this type of information, but only when a monetary value can be assigned to the process. Many research projects are not structured in a way that permits a direct calculation of the projects' monetary value. During this project, a methodology was developed by which outcomes of a project (monetary or otherwise) can be measured. The methodology consists of a decision tree containing questions that can be answered by researchers to help them determine the value of their projects. It is hoped that this decision tree can also be used as a guide when research is planned to ensure that the value of a project can be more readily determined.

Cost-benefit analysis techniques were obtained through Internet searches. Documents relating to monetary value were reviewed as well as others dealing with value indicators for projects for which monetary value cannot be assigned.

The projects performed under a multimillion-dollar EERC program over the course of 7 years were reviewed. Similar projects were combined and the groups analyzed for common characteristics. Questions were formulated to help elucidate project value, and interviews with project managers were conducted to streamline the questions. A question flow sheet/decision chart was prepared using information gathered from both the cost-benefit analysis techniques and the project analyses/interviews.

Waste Tire Recycling with Subcritical Water

Period of Performance: April 1, 2003 – March 31, 2004

Final Report: In January 1 – March 31, 2004, quarterly status report

Brief Summary: The purpose of this limited investigation was to determine the ability of subcritical water (water heated up to its critical temperature of 374°C and under enough pressure to maintain the liquid state) and supercritical water (water heated above 374°C at pressures above 218 atm) to degrade and remove the styrene-butadiene copolymer components of waste tires and produce carbon black that can be recycled into new tires. Although some polymer degradation reactions occurred with subcritical water, degradation efficiencies were low. However, supercritical water (at 450°C) was much more effective in degrading the polymer material and yielding a carbon black product that may be useful for recycling (based on a high molar C/H ratio of the product material). The polymer degradation products from the supercritical water treatment were primarily alkyl benzenes, which should be suitable to use as a petroleum refinery feedstock or fuel for waste tire processing.

Feasibility of Using Freeze-Thaw Evaporation[®] (FTE[®]) Technology for Power Plant Cooling Water Treatment

Period of Performance: April 1, 2004 – March 31, 2005

Final Report: Appended to January 1 – March 31, 2005, quarterly status report (Report was mislabeled as Activity 3.7 – Review of Utility-Scale Energy Storage Technologies)

Brief Summary: FTE is an attractive and economical water treatment method for dissolved solids reduction in cooling water ponds at coal-fired power plants. FTE provides the opportunity for cost-effective treatment of brackish or contaminated water. FTE couples conventional evaporation and freeze-thaw for treatment and disposal of wastewater. Natural seasonal cycles are combined with inexpensive control equipment to automatically separate the process streams, offering industrial users reduced process water costs and reduced wastewater disposal costs. This study evaluated FTE system integration into a typical power plant cooling water operation that will ideally provide for brine concentration and disposal as well as high-quality treated water that will reduce the need for freshwater makeup. Additional power generation may be realized as a result of enhanced cooling that would be available because of cold-temperature waters during periods of ice melt.

Effects of Fossil Fuel Power Plant Emissions on Precipitation

Period of Performance: April 1, 2004 – March 31, 2005

Final Report: Appended to January 1 – March 31, 2005, quarterly status report

Brief Summary: Air pollution has been shown to inhibit as well as augment precipitation. For example, smoke from biomass burning is known to suppress warm rain processes (6). On the

other hand, a study has shown that large salt-containing dust particles from the Aral Sea promote precipitation (7). This strategic study investigates the effects of primary particulate emissions from coal-fired power plants on precipitation processes.

Particulate matter (PM) may be solid or liquid, with diameters between 0.002 and 100 μm . Particles may be directly emitted into the atmosphere or formed there by chemical reactions. Particles formed in the atmosphere by chemical reactions are referred to as secondary PM, while those directly emitted from a source are called primary. Both primary and secondary PM may act as nuclei for atmospheric cloud droplets. Based on the hygroscopic properties of these particles, the particles may inhibit or augment precipitation formation.

Little information has been gathered on the interactions of primary PM from coal-fired power plants with clouds and precipitation. However, numerous studies have investigated the effects of secondary PM on precipitation. Secondary PM such as sulfuric and nitric acids leads to acid rain which has been a major air pollution topic since the 1970s. Although science can explain the formation of acid rain, no information has been found on the impact of secondary PM on precipitation amounts.

A comprehensive review of past research on the effects of PM from coal-fired power plants on precipitation is provided by this study. Suggestions for future research activities are made based on the literature review. In addition to PM, heat and moisture emissions from these plants are briefly discussed as also potentially influencing precipitation.

Remediation Seminar

Period of Performance: April 1, 2004 – March 31, 2006

Final Report: Appended to January 1 – March 31, 2006, quarterly status report

Brief Summary: A daylong seminar entitled “Site Remediation Technologies – An Update” was presented by Mr. Jaroslav Solc in Bismarck, North Dakota, on February 16, 2006. The seminar was organized by the North Dakota Department of Health.

The presentation consisted of a compilation of scientific, engineering, and economic principles relevant to environmental remediation technologies, including case studies from EERC sites. The primary goal was to target a broad audience, including federal- and state-level regulatory agencies, insurance companies, and industries responsible for the manufacturing, distribution, and handling of potential petroleum-based contaminants. A total of 42 participants attended the presentation.

Short Course – Ash Behavior and Mercury Control in Coal Combustion

Period of Performance: April 1, 2004 – September 30, 2004

Final Report: In July 1 – September 30, 2004, quarterly status report

Brief Summary: A short course entitled “Ash Behavior and Mercury Control in Coal Combustion” was developed. Presentation materials were gathered and compiled into a PowerPoint presentation for a 2-day short course.

The 2-day short course includes a 1-day presentation on ash transformation and deposition and a 1-day presentation on mercury transformation and emission control. The ash behavior presentation includes an overview of the physical and chemical processes related to ash transformation and deposition in coal-fired boilers; an introduction of the EERC-developed computer models, which predict the characteristics of ash deposits specific to the boiler configuration/operation and the coal fired; and guidelines for identifying and managing slagging and fouling problems.

The Hg emission control presentation covers mercury regulations, the occurrence of Hg in coals, the Hg transformation mechanisms in combustion and postcombustion systems, and the latest measurement and emission control technologies. Emphasis is given to an overview of the technologies promoting oxidation and capture of Hg to achieve the minimum level of Hg emission.

As part of separate DOE projects, the ash behavior short course was presented at the Western Fuels Symposium and at Ameren. We received excellent feedback on the course content.

Review of Utility-Scale Energy Storage Technologies

Period of Performance: April 1, 2004 – December 31, 2004

Final Report: Appended to October 1 – December 31, 2004, quarterly status report

Brief Summary: Bulk energy storage technologies have the potential to offer utilities opportunities to reduce electrical costs and improve energy service to customers. Installation of energy storage technologies can provide improvements in efficiency, reliability, and stability of energy supply by reducing requirements for spinning reserves to meet peak demands, making better use of baseload generation and allowing for better integration of intermittent renewable energy sources. Barriers to utility implementation of energy storage technologies include, but are not limited to, high capital costs, lack of familiarity with more advanced energy storage options and limited field demonstration, and lack of analysis tools for evaluating technical and financial merits of energy storage.

Numerous bulk energy storage technologies are commercially available or nearing commercial applicability today. Such technologies include advanced electrochemical battery storage, pumped hydropower, superconducting magnetic energy storage (SMES), flywheels, compressed air energy storage (CAES), and hydrogen energy storage and regenerative (reversible) fuel cells. Leading technologies (based on proven demonstration and cost-competitiveness) include CAES, SMES, and advanced electrochemical battery storage. Through a review of current literature, this project aimed to identify potential opportunities for energy

storage development and implementation with emphasis on identifying means for improved integration of wind energy into current energy infrastructure in the region.

Evaluation of ChemCAD Software

Period of Performance: July 1, 2004 – September 30, 2004

Final Report: In July 1 – September 30, 2004, quarterly status report

Brief Summary: ChemCAD is a provider of chemical process simulation software. The primary purpose of this task was to determine if this software is appropriate for use within the chemical process research and development activities that the EERC is currently pursuing with DOE.

An academic ChemCAD workstation license was acquired through the UND Chemical Engineering Department for evaluation. The software package was supplied with a tutorial that familiarizes the user with the most basic operations and uses interactive help screens to assist the user with screen options. The tutorial was completed, and much of the help screen information was read to become more fluent in the functionality. A considerable effort was applied toward modeling processes that were previously used at the EERC. The premise was to determine if any information gleaned from the use of ChemCAD could have assisted these projects or, at a minimum, supported the results found through direct measurement. The benefit of this approach was that it helped to quantify the modeling limitations, or at least the modeler's limitations of describing a process adequately through the use of the available operations. However, like most sophisticated software packages, the ability to augment the standard package with user-supplied data, code, and processes blurs the line of ChemCAD's ultimate capability.

Subcritical Water Fractionation of Particulate Matter

Period of Performance: April 1, 2005 – June 30, 2005

Final Report: Manuscript for publication in *Toxicological Sciences* entitled Midpolarity and Nonpolar Wood Smoke PM Fractions Deplete Glutathione in RAW 264.7 Macrophages.

Brief Summary: Wood smoke PM is a complex mixture of components falling in a spectrum of highly polar to nonpolar species. Wood smoke PM is a likely factor in pulmonary disease and induces oxidative damage. Most toxicity studies focus on nonpolar species such as polycyclic aromatic hydrocarbons (PAHs). However, the role of more polar PM constituents as toxicants is not clear. In this work, we evaluated the ability of multiple fractions of varying polarity to deplete glutathione (GSH) in RAW 264.7 macrophages and BEAS-2B bronchial epithelial cells. We utilized hot pressurized (subcritical) water to fractionate wood smoke PM into seven fractions of decreasing polarity. In contrast to polar fractions, midpolarity and nonpolar fractions exhibited greater GSH depletion (ED50 at PM concentrations ~50 µg/mL). GSH depletion caused by nonpolar fractions (extracted at 250°–300°C) was associated with the presence of PAHs. In midpolarity fractions (extracted at 100°–150°C), oxy-PAHs, syringylguaiacyls, disyringyls, and lower-molecular-weight PAHs were found. Direct comparison of GSH depletion by individual oxy-PAHs and PAHs suggests that oxy-PAHs are contributors to oxidative stress

caused by wood smoke PM. However, other unidentified PM constituents contribute to GSH depletion as well. The results indicate the toxicological importance of oxygenated organics found in midpolarity PM fractions.

Domestic Energy Parks

Period of Performance: July 1, 2006 – September 30, 2007

Final Report: Appended to July 1 – September 30, 2007, quarterly status report

Brief Summary: The findings of this study show that coproduction of liquid transportation fuels, heat, and electric power in plants that integrate biomass and coal gasification into existing pulp and paper mills can contribute significantly to moving the nation closer to energy independence. Transportation fuels and electric power can be produced at prices that are competitive with current markets. Fuels produced from biomass are essentially carbon neutral in the environment, and the processes used for gasifying coal and converting syngas to liquid fuels and power offer opportunities for strict control of carbon emissions and priority pollutants. Carbon capture and coprocessing with biomass can appreciably reduce the carbon intensity of the overall process in the interest of using the nation's abundant coal resources to reduce dependency on imported oil.

The driving forces that governed this study were the need to produce alternative transportation fuels from domestic resources at or below market prices and the growing recognition that high levels of carbon management will be required in the future. The objective is to develop energy parks that process biomass and coal to produce transportation fuels, chemicals, and electricity under policies that place strict controls on carbon emissions. This study evaluates the integration of synfuels and power production from biomass and coal in four pulp and paper mills in different regions of the country (South, Northeast, Midwest, and West) to reflect differences in local markets, including coal and electricity prices, environmental regulations, water use restrictions, and demand for various products.

Evaluation of Landfill Gas Applications

Period of Performance: April 1, 2005 – March 31, 2007

Final Report: Appended to January 1 – March 31, 2007, quarterly status report

Brief Summary: Landfill gas (LFG) comprises approximately 50% methane and 50% carbon dioxide and is produced by the decomposition of organic waste under anaerobic conditions. EPA estimates that there are about 6000 landfills in the United States, mostly made up of municipal solid waste, that are producing methane. This is assumed to be the largest source of anthropogenic methane emissions in the United States and is speculated to contribute an estimated 8.8 to 12.7 terragrams (450 to 650 billion cubic feet) of methane to the atmosphere a year (8).

This activity completed a preliminary feasibility study that evaluated potential applications of LFG from a 40-year-old municipal open dump turned into a landfill in the far northern

climatic conditions of Grand Forks, North Dakota. This investigation examined the characteristics and constituents of the potential fuel source, the power generation potential of this site, and the local parameters for using microturbine technology for continuous electricity and heat generation.

Controlled Spontaneous Reactor

Period of Performance: April 1, 2005 – March 31, 2007

Final Report: Appended to January 1 – March 31, 2007, quarterly status report

Brief Summary: The overall goal of this project was to obtain data at a laboratory scale using the pressurized fluidized-bed reactor (PFBR) to establish that the controlled spontaneous reactor (CSR) can be used to remove and concentrate mercury into the CSR exit gas stream prior to the coal or fuel being fed directly into a combustion or gasification system. The CSR is an EERC-patented concept for drying coal at low temperatures or, at higher temperatures, drying and partially devolatilizing the coal with low-oxygen gas for various applications with circulating fluidized-bed boilers, pulverized coal-fired boilers, gasifiers, or other coal- or biomass-fired system. For this testing, the PFBR will be operated in an atmospheric mode over a range of selected operational bed temperatures. A secondary objective was to identify potential economic means of removing the mercury from the gas stream produced by the CSR process.

CO₂ Separation Technologies

Period of Performance: April 1, 2005 – March 31, 2007

Final Report: Appended to January 1 – March 31, 2007, quarterly status report

Brief Summary: The emission of carbon dioxide (CO₂) to the atmosphere has been identified as a leading contributor to global warming. In most countries, burning fossil fuels such as coal and natural gas is far and away the greatest source of CO₂ to the atmosphere, accounting for >95% of the total anthropogenic CO₂ generated in the United States (9). Although emissions from mobile sources such as automobiles and other sources of CO₂ will need to be addressed, it is clear that CO₂ emissions from coal-fired power generation will need to be substantially reduced to have any real effect on global CO₂ levels. Table 1 shows the sources of CO₂ emissions from fossil fuel combustion in the United States in 2002 (9).

Sequestration of CO₂ in geological formations or in the deep ocean is considered to be the leading candidate for disposal. Based on the results from DOE's carbon sequestration program, there is enough CO₂ geological storage capacity for over 3500 billion tons (10). In general, to economically sequester CO₂ requires a relatively pure, high-pressure gas stream. However, in conventional fossil fuel-fired electric generation plants, flue gas CO₂ is only a small portion, 10%–20%, of gases generated during combustion, with most of the remainder being nitrogen (N₂), oxygen (O₂), and water. Therefore, it will be required that CO₂ be separated from the remainder of the flue gas before it can be sequestered or that new fossil fuel-fired systems be developed.

Table 1. Sources of CO₂ Emissions from U.S. Fossil Fuel Combustion in 2002

Sector	CO ₂ Emissions, million tons carbon	Percent of Total
Electrical Generation	2240.1	39.9
Transportation	1764.4	31.4
Industrial	955.8	17.0
Residential	373.1	6.7
Commercial	231.2	4.2
Other	46.5	0.8
Total	5611.0	100.0

Separation of CO₂ from other gas species is not new and has been conducted on the commercial scale for over 50 years (11). Most plants were designed to produce CO₂ to sweeten natural gas (remove H₂S) and purify syngas to produce hydrogen (H₂) in refinery operations and ammonia production. These technologies were designed to treat relatively low volumes of gases compared to what would be needed for large-scale sequestration of CO₂ generated from power plants. In fact, the idea of separating and capturing CO₂ from power plants did not start with concern about climate change but, rather, as a potential economic source of obtaining CO₂ for enhanced oil recovery (EOR). Several commercial plants were built in the United States in the 1970s and early 1980s to produce CO₂ for EOR, but when the price of petroleum dropped in the 1980s, most of these plants were shut down (11).

Mercury Measurement in Combustion Flue Gases Short Course

Period of Performance: April 1, 2005 – September 30, 2005

Final Report: Located in Appendix B

Brief Summary: A comprehensive evaluation of mercury measurement techniques was completed. The study included the following topics:

- Upfront planning that is needed
- Regulations regarding mercury measurement (40 Code of Federal Regulations [CFR], Part 75 and Part 60)
- Wet-chemistry methods for mercury measurements
- Sorbent trap methods (40 CFR, Part 75, Appendix K)
- Continuous mercury monitors

An overriding element of each of these topics was the quality control/quality assurance necessary to ensure that the data generated are of high quality. If the data are collected for regulatory purposes, this will ensure that they are acceptable to the regulating agency, either EPA or the state.

Installation of an Additional Wet Scrubber on the Energy & Environmental Research Center's 7-kW Combustion System

Period of Performance: April 1, 2005 – June 30, 2005

Final Report: In April 1, 2005 – June 30, 2005, quarterly status report

Brief Summary: The capability to conduct dual wet scrubber pollution (SO_x , NO_x , Hg, etc.) removal testing on a small-scale (<10-kW) combustion system is appealing to the pollution control industry. The EERC's 7-kW combustion system, however, is only equipped with one wet scrubber. The existing wet scrubber tower and packing comprise plexiglas and polypropylene, respectively. These materials are not conducive to mercury emission control testing because they readily absorb mercury. An additional pilot-scale wet scrubber at the EERC recently became available. The tower and packing of this additional scrubber comprise glass and stainless steel, respectively. These materials are chemically inert in the presence of mercury and are, therefore, ideally suited for mercury emission control testing. The EERC removed and transported the additional wet scrubber and installed it as a secondary scrubber on the 7-kW combustion system.

Microbial Cycling of CH_4 , CO_2 , and N_2O in Wetland Environments – A Scoping Study

Period of Performance: October 1, 2005 – September 30, 2006

Final Report: Appended to September 30, 2006, quarterly status report

Brief Summary: This activity was undertaken to survey the literature on microbially mediated biogeochemical cycling of CH_4 , CO_2 , and N_2O in terrestrial ecosystems, with the objective of preparing a proposal on microbial cycling of these greenhouse gases in the glaciated North American prairie, which previously supported the largest wetland complex in North America. However, cultivated agriculture has shifted the function of the wetlands from net sinks to net sources of atmospheric CO_2 . Recently, based on changes in soil organic carbon, it has been proposed that restoration of previously farmed wetlands in the Prairie Pothole Region (PPR) may sequester atmospheric CO_2 , but wetland restoration also impacts CH_4 and N_2O cycling in the ecosystem, and the global-warming potential (100 years) of CH_4 and N_2O is 21 and 310 times that of CO_2 , respectively. Therefore, it is necessary to study microbial CH_4 and N_2O cycling in the wetland environment so that an overall budget of CO_2 sequestration by restoring the wetlands in PPR can be obtained. The proposed study is expected to provide experimental data to support development of action plans and long-term postrestoration management strategies so that wetland restoration and management may be economical, sustainable, and environmentally sound.

Residential Energy Issues

Period of Performance: January 1, 2006 – March 31, 2007

Final Report: Appended to January 1 – March 31, 2007, quarterly status report

Brief Summary: Attention is increasingly being placed on the energy and environmental impacts of buildings and homes in the United States. According to DOE, over one-third of the total energy consumed every year is attributed to 87 million homes and commercial buildings in this country—energy derived predominantly from fossil fuels. Further, buildings use two-thirds of all electricity generated nationally, and that usage continues to rise.

The EERC has a focused interest in supporting the development, demonstration, and evaluation of energy-efficient technologies for buildings and in supporting education and outreach opportunities to the varied stakeholders in the building industry, especially those in cold climates. To fully achieve efficient buildings, especially as we move toward a hydrogen economy, a combination of reduced energy demand and increased use of environmentally friendly and/or hydrogen-based distributed power generation will be required, with special attention paid to system interaction and a whole-building approach. The EERC has unique capabilities related to development and integration of energy-efficient technologies to achieve greater energy efficiency in buildings.

Project activities were focused on developing a strategic plan to support commercial activities related to improving building efficiency. Activities included reviewing available literature on state-of-the-art building practices and energy-efficient technologies, communicating with stakeholders to collaborate on more energy-efficient buildings, and quantifying the energy savings associated with several energy-efficient building technologies.

Materials Testing

Period of Performance: January 1, 2006 – September 30, 2006

Final Report: In July 1 – September 30, 2006, quarterly status report

Brief Summary: A new type of reaction-bonded silicon carbide (SiC) has been developed at the EERC that can be cast in complex near-net shapes, maintains its strength to at least 1450°C (above the melting temperature of silicon), and is 35% porous to allow low-temperature secondary materials such as polymers or metals to be infiltrated into its structure to substantially increase its toughness (resistance to fracture). As such, the EERC SiC has both high-temperature and low-temperature uses. Potential high-temperature uses are as heat exchanger tubing, burner nozzles, very high-temperature mechanical fasteners (nuts and bolts), and turbine blades or combustor liners. At lower temperatures, composites of our SiC can be used for tough, abrasion-resistant thin coatings in power and industrial applications, such as solids handling, grinding and cutting of hard materials, and high and hypervelocity impact. It also has potential use as meteoroid protection and thermal protection during aerobraking by spacecraft.

Because of its potential use in spacecraft, we have been given an opportunity to expose coupons of the material to a low-earth environment during the Materials International Space Station Experiment 6 (MISSE-6).

Oil Field Applications for Low-Btu Associated Gas

Period of Performance: January 1, 2007 – June 30, 2007

Final Report: In April 1 – June 30, 2007, quarterly status report

Brief Summary: The EERC explored opportunities to utilize gases associated with oil production. Secondary oil recovery operations produce associated gas that is typically unused. In many cases, the gas has a low heating value <400 Btu/scf. The EERC is exploring opportunities for utilization that will produce energy and reduce emissions. This strategic studies project provided experience for EERC personnel to implement solutions using microturbines and/or burners capable of firing very dilute associated gas.

Training was completed with Capstone Turbine Corporation for service and operation of 30-kW and 60-kW microturbine systems. The training enables the EERC to understand turbine operation and relevant concerns for oil field applications and low-Btu gas implementation. The training was utilized on field installations of microturbines firing gas less than 300 Btu/scf. A certificate was obtained from Capstone, and the project objectives have been completed.

Development of a Novel Petroleum Biotechnology

Period of Performance: January 1, 2007 – March 31, 2009

Final Report: In Appendix C

Brief Summary: This project is an effort to develop a novel biotechnology to mitigate production of hydrogen sulfide (H₂S) in the petroleum industry, to promote methane (CH₄) production in oil and gas fields, and to enhance oil recovery, based on a recently developed EERC sulfide control additive capable of effectively controlling microbial H₂S production.

Potential for Conversion of Beet Sugar

Period of Performance: April 1, 2001 – September 30, 2001

Final Report: In July 1 – September 30, 2001, quarterly status report

Brief Summary: This study was originally focused on producing ethanol and lactic acid from sugar beets; however, because of the poor initial economics, the effort was refocused to look at higher-value products from existing ethanol facilities. The following results are from the conversion of an ethanol facility to a lactic acid facility:

- There is a 3,000,000-ton potential market for ethyl lactate as a biodegradable solvent to replace conventional toxic solvents. The comparative market price of ethyl lactate is \$1.00/lb.
 - Assumed a plant basis of 1% potential market (7,000,000-gallon plant)

- 8,000,000-gallon ethanol plant equivalent; Heartland Grain Fuel in Aberdeen, South Dakota
- 3,000,000 bushels of corn per year
- Produce 3,600,000 gallons of ethanol, 4,600,000 gallons of lactic acid.
- Coproduct: 35,700 tons of distillers grain per year
- Predicted annual revenue \$64,200,000
- Raw materials estimated to be \$8,100,000 annually; predicted product cost of \$43,400,000 per year.
- Cost of equipment approximately \$3,200,000; \$17,100,000 capital investment.
- Estimates give 68% internal rate of return, first-year payback.
- Plant economics most sensitive to product conversion of lactic acid and ethanol.

Biomass Product Separation and Characterization for the Generation of Fuel Additives

Period of Performance: April 1, 2001 – December 31, 2001

Final Report: In October 1 – December 31, 2001, quarterly status report

Brief Summary: Solubilization (low-intensity liquefaction) of biomass and a mixture of coal and biomass was successful in converting >95% of the solids using the initial two steps in a process originally designed for producing refinery stock from coal. High-pressure hydrotreating, originally designed for reducing solubilized coal, was not applied to the biomass-only or biomass-coal liquids. Although the conversion process was highly successful, analysis of the product waited until this project. Liquid products from recent solubilization tests involving low-intensity liquefaction of wood of the genus *Populus* and a 50:50 wt:wt mixture of *Populus* and lignite coal were analyzed using thermogravimetric analysis procedures, gas chromatography-mass spectrometry (GC-MS) and ¹H nuclear magnetic resonance spectrometry (NMR). The liquid from biomass-only was distilled over the range of 50°–370°C, and that of the biomass-coal was distilled over the range of 50°–360°C. NMR showed an aliphatic:aromatic proton ratio for biomass liquids to be 2.96, and hydroxyl proton:aromatic proton was negligible, whereas ratios for the biomass-coal liquids were 3.42 and 0.13, respectively. GC-MS results indicated primarily oxygenated compounds, e.g., guaiacol, alkylated benzofurans, carboxylic acids greater than 10 carbons in length, and small amounts of unidentified homologous series of large compounds. The concentration of guaiacol relative to other compounds in the mixture was much greater in biomass-coal than in biomass-only liquids. Although the reaction is catalyzed and

supplied with hydrogen by H₂S, sulfur compounds were not detected in the liquid product of either biomass-only or biomass-coal by either elemental analysis or GC-MS.

Analysis of Oil and Gas Environmental Issues Affecting Domestic Production

Period of Performance: July 1, 2002 – September 30, 2003

Final Report: In July 1 – September 30, 2003, quarterly status report

Brief Summary: In general, the upstream oil and gas industry appeared to be less inclined to become a financial partner in environmental research activities. There are many reasons for the lack of funding support from industry in the past year: 1) the majors are generally selling their domestic on-shore operations and putting most of their capital into the acquisition and development of offshore and/or foreign on-shore operations and, therefore, have a lessened interest in solving environmental problems that are driven by American regulations; 2) independent producers do not typically have the financial resources to support environmental research activities that address issues other than those that address immediate or very short-term needs; and 3) instability in the prices of oil and gas has made it difficult for companies to commit funding to research projects, especially long-term (greater than 1 year) research projects. The decreased participation by industry in environmental research was reflected by a noticeable decline in attendance at the historically most important petroleum environmental conferences (IPEC and SPE).

Student Involvement Activities

Period of Performance: April 1, 2002 – June 30, 2004

Final Report: NA

Brief Summary: A series of very small studies were conducted by a variety of students in support of other projects at the EERC supported by DOE. Any significant results generated by the students have been reported through other projects.

Filter Cake Properties

Period of Performance: April 1 – June 30, 2004

Final Report: In April 1 – June 30, 2004, quarterly status report

Brief Summary: Efficient removal of particulates from the gas flow prior to reaching the turbine is the key to the success of solid fuel direct-fired turbine power generation. Severe problems of fouling, erosion, and corrosion of the turbine may be caused if the ash is not removed from the gas stream. Currently, removal of the ash particles from the gas stream is accomplished by filtration with ceramic or metallic filters at high temperature to ensure a high system efficiency. However, higher temperatures usually increase the stickiness of the ash particles, causing the

cake to adhere to the filter walls. Such adherence causes an increased pressure drop, thereby increasing the cost of filtration, and can lead to blinding or breaking of filter elements.

The EERC worked with the New Energy and Industrial Technology Development Organization (NEDO) of Japan and DOE to perform research to determine the relationship between two system operating variables that affect the development of dust cakes that are difficult to remove and can bridge between candle filter elements, causing their failure.

High-Temperature Corrosion of Alloys in Simulated Boiler Tube Conditions

Period of Performance: April 1 – June 30, 2004

Final Report: In April 1 – June 30, 2004, quarterly status report

Brief Summary: Current utility boilers operate with steam at 175 bar and 550°C which creates a coal pile-to-busbar efficiency of 35% on a higher-heating-value basis. To improve efficiency, higher pressures and temperatures must be reached. In the next generation of steam-cycle power plants, ultrasupercritical steam will be produced in the near term at 280 bar and 580°C and, in the longer term, at 325 bar and 650°C. One program funded by DOE and several large boilermakers is testing new alloys at these temperatures in bituminous and subbituminous coal-fired power plants. However, no known work has been done under biomass–coal cofire conditions or lignite-fired conditions.

The alloys tested were HR3C, TP347HFG, MA754, MA956, and a modified MA956 alloy. The HR3C is a 25% Cr, 20% Ni super stainless steel, while the TP347HFG contains only 18% Cr and 10% Ni. Each contains minor amounts of alloying elements with a balance of iron. MA754 and MA956 are oxide dispersion-strengthened (ODS) alloys in which yttrium oxide is finely distributed throughout the grain boundaries in a mechanical alloying procedure that gives them excellent high-temperature creep strength. The MA754 is a Ni-based chromia-scale-forming alloy, whereas the MA956 is an iron-based alumina-scale-forming alloy. The modified MA956 is an experimental material being developed by Special Metals Incorporated under a Vision 21 program to have a greater hoop strength than the standard MA956. The temperature to be used in this study is 700°C, and the durations of the exposures are 200, 500, and 1000 hr. At each of the specified times, samples are removed from the furnace and cleaned according to ASTM International Procedure G1-88 for mass wastage calculations. This procedure involves cleaning the samples through a series of chemical baths to remove corrosion products and then weighing the samples to determine mass loss due to metal corrosion.

On-Demand High-Pressure Hydrogen Extraction and Dispensing for Vehicle Fueling

Period of Performance: April 1, 2002 – September 2003

Final Report: Appended to July 1 – September 30, 2003, quarterly status report

Brief Summary: The reforming of natural gas is an industrially established process for the production of hydrogen of sufficient purity to be used for operating a fuel cell. The following

reaction equation for steam reforming can be formulated for methane as the main component of natural gas:

Like the steam reforming of higher hydrocarbons or alcohols, the above reaction for steam methane reforming (SMF) is strongly endothermic, with a standard formation enthalpy of +206 kJ/mol (49 kcal/mol), and is commonly carried out on a suitable catalyst (nickel or noble metals on a substrate material) on an industrial scale at temperatures above 700°C.

A key barrier to commercialization of fuel cell-powered vehicles is the lack of a viable hydrogen fueling infrastructure. Automakers and oil companies are developing technologies for on-board vehicle extraction of hydrogen from gasoline and methanol, but all generally agree that this is a near-term approach to be utilized only until the advent of economical hydrogen fueling via dispensers that are similar in safety and ease of operation to today's gasoline pumps. Project scientists envision a relatively small dispenser-level system where high-pressure natural gas (which is easier, safer, and cheaper to compress than hydrogen) is run through a high-pressure water chamber for hydrogen extraction, and extracted hydrogen is then purified and dispensed into a vehicle.

The objectives of the proposed activity were to assess the technical feasibility and economic viability of high-pressure water extraction of hydrogen from high-pressure natural gas. The overall goal of this activity is to develop sufficient data to pursue (with an industry partner) commercial development of a modular, on-demand, high-pressure hydrogen extraction–purification–dispensing system that will be a key component of a national strategy for distributed hydrogen based on natural gas and the natural gas pipeline system.

Indirectly Fired Combined Cycle with Condensing Heat Exchanger

Period of Performance: July 1, 2004 – June 30, 2005

Final Report: Appended to April 1 – June 30, 2005, quarterly status report

Brief Summary: As the demand for power increases and environmental controls tighten, future power plants will increasingly need to be designed and operated to conserve both fuel and water. Water is becoming scarce and expensive in many parts of the western United States, especially California where there is already a strong economic incentive to reduce the net cooling water requirements of power plant subsystems, cooling steam turbine condensers, and scrubbing stack gases. Future escalation in prices for natural gas and possible restrictions on carbon emissions from fossil fuels will likewise provide a strong incentive for increasing generating efficiencies. Coal utilization would be most severely impacted by climate change policy initiatives since a coal-fired steam plant emits nearly three times more CO₂ than a natural gas-fired combined-cycle plant with similar generating capacity. The three critical factors of water recovery, plant efficiency, and emissions are closely linked, so that technical options for recovering water will open up new opportunities for integration that can improve performance relating to the other two

factors. The potential amount of water that could be recovered from flue gas is sufficient to significantly reduce and, in some cases with air or hybrid air–water cooling, eliminate the need for off-plant sources of water. In addition, condensing water from flue gas may provide opportunities for removing SO₂ and NO_x to lower levels to approach near-zero emissions of acid gases. Further integration with oxygen-blown combustion would both enhance water recovery by increasing the partial pressure of water in flue gas and provide a clean source of CO₂ that could be used for tertiary oil recovery or sequestration.

In this investigation, calculations were performed to determine the amounts of water that could be recovered from flue gases generated from the combustion of different fuels under varying conditions of temperature, combustion mode (air versus oxygen combustion), use of a condensing heat exchanger, and use of a desiccant dehumidification system. The purpose for using a desiccant is to facilitate the recovery of useful amounts of water at flue gas temperatures that can be reasonably achieved in operating a power plant. When a Wyoming subbituminous coal is burned, the temperature required for recovering 50 gal/MWh (0.05 L/MJ) drops from 90°F (33°C) with the desiccant to 50°F (10°C) without. Fifty gal/MWh (0.05 L/MJ) represents 11% of the cooling load on the steam condenser for a supercritical boiler, assuming that the cooling tower operates at ambient conditions of 80°F [27°C]). At a water dew point of 110°F (44°C), the desiccant would recover 43 gal/MWh (0.05 L/MJ). Without the desiccant and at very low ambient temperatures, flue gases could possibly be cooled to 50°F (10°C) using an air–flue gas heat exchanger, but significant engineering and economic problems would have to be resolved (e.g., pressure drop, corrosion and fouling of a condensing heat exchanger, and discharge of nonbuoyant stack gas). Combustion with oxygen instead of air also facilitates condensation of water at moderately elevated flue gas temperatures because of the proportionally higher partial pressure of water vapor in the absence of a high percentage of nitrogen in the flue gas. When a Wyoming subbituminous coal is combusted, oxygen combustion shows slightly more water recovery without a desiccant-based system than air combustion does with the desiccant-based system. Recovery of 50 gal/MWh (0.05 L/MJ) would be possible at 100°F (38°C) in the oxygen-blown mode.

Engineering Opportunities and Challenges of CO₂ Mitigation Using Microalgae in Fossil Fuel-Fired Power Plants

Period of Performance: January 1 – March 30, 2009

Final Report: In Appendix D

Brief Summary: Public concerns over global climate change due to anthropogenic emissions of greenhouse gases such as CO₂ have resulted in significant pressure on all industries to seek effective ways to reduce CO₂ emissions. Because coal-fired electric utilities are one of the largest sources of CO₂ emissions, the pressure has been more intense. All fossil fuels originate from biomass produced by photosynthetic fixation of CO₂, the process in which green plants produce sugar from sunlight, CO₂, and water, with oxygen as a waste product. Photosynthesis is essentially nature's way of recycling CO₂. However, the process of indirect CO₂ capture by planting forests and other agricultural crops has been deemed to be an inadequate solution to the accumulation of greenhouse gases in our atmosphere. The potential CO₂ capture by planting

agricultural crops is expected to result in only a 3%–6% reduction compared to the CO₂ generated burning fossil fuels (12). The one possible exception is to utilize microalgae for the direct treatment of flue gas. Microalgae have the ability to fix CO₂ using solar energy, with an efficiency 10 times greater than that of terrestrial plants (13). In addition, it grows rapidly and can be incorporated into engineered systems such as photobioreactors. It has been found that the high CO₂ content of power plant flue gas, ~14% compared to only 350 ppm in the atmosphere, greatly enhanced algae growth (14). It is estimated that algae produce between 73% and 87% of the net global production of oxygen (15).

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APPENDIX A

FINAL REPORT FOR RESEARCH PROJECT ENTITLED TECHNOLOGY ADOPTION – CERAMIC MATERIALS MARKET

TECHNOLOGY ADOPTION – CERAMIC MATERIALS MARKET

INTRODUCTION

Technology innovation research focuses upon the adoption of technological innovations and why some innovations are adopted at a faster or slower rate than others. The rate of adoption is the relative speed by which an innovation is implemented by members of an industry group. Rogers (1995) identified five perceptual characteristics of innovations that help explain differences in adoption rates: relative advantage, compatibility, complexity, trialability, and observability.

Relative advantage is the degree to which an innovation is perceived as better than the idea it supersedes. Compatibility is the degree to which an innovation is perceived as being consistent with the existing values, past experiences, and needs of potential adopters. Complexity is the degree to which an innovation is perceived as difficult to understand and use. Trialability is the degree to which an innovation may be experimented with on a limited basis. Finally, observability is the degree to which the results of an innovation are visible to an observer. In general, the rate of adoption is positively related to perceived relative advantage, compatibility, trialability, and observability and is negatively related to perceived complexity of the innovation. Rogers (1995) found relative advantage to be one of the best predictors of an innovation's rate of adoption. Relative advantage, along with compatibility and complexity, is the most significant factor in explaining relationships across a broad range of innovation types.

The technological orientation of the United States provides a means for the transfer of technology out of universities. In the corporate sector, years of downsizing have led to the willingness of more companies to consider outsourcing in general and technology licensing in particular. Licensing in is seen increasingly as complementary to corporate business development strategies (Allen, 2001). Licensing is one strategy that promotes the diffusion of innovation.

Successful commercialization from universities and laboratories occurs when senior administration and management actively support cooperation with industry, with strong positive attitudes and incentives. Other key factors are the degree to which inventors of the technologies exhibit entrepreneurial attributes and have positive attitudes toward commercialization (Jaffe and Lerner, 2001). Also, successful universities and laboratories are those in which the cooperating company supports commercialization and where the company's technical people perceive their counterparts in the federal laboratories as willing to take risks and able to deal with ambiguity.

OBJECTIVES

This Energy & Environmental Research Center (EERC) project was conducted to explore the market factors that influence the adoption of technology innovation. The goal was to better understand methods to help drive technology development to promote commercialization and

acceptance of innovation for a specific technology, silicon carbide composites; determine market potential; and assist with the commercialization of the silicon carbide technology.

The market research involved the following objectives:

- Preparation of a material technology overview that is understandable to business and marketing personnel
- Preparation of a market/industry overview that quantifies market size
- Preparation of a competitive analysis
- Identification of market opportunities
- Identification of barriers to entry
- Identification of industry leads
- Recommendations for marketing strategies

SCOPE OF WORK

Material Technology Overview

A technology overview was prepared and presented in a full-color brochure format. The brochure lists relative and competitive advantages of the technology. Presentation of the information was designed to appeal to both technical and marketing managers.

The brochure was completed in April 2002. Copies were distributed at the American Ceramic Society Meeting in St. Louis, Missouri, in April 2002. The brochure provides an excellent marketing tool for the technology.

Preparation of a Market Industry Overview

According to the U.S. Advanced Ceramics Industry Status and Market Projections as of September 1998, the total market value for advanced structural ceramics was \$425 million. According to the latest U.S. reports, the advanced structural ceramics market is expected to grow from \$541 million in 2000 to \$736 million in 2005 and will have the largest average annual growth rate (6.3%) over the next 5 years.

Wear-resistant parts dominate the market at 51.8%. Other applications include heat exchangers (1.9%), aerospace and military (3.9%), bioceramics (24.5%), automotive engines (0.9%), and cutting-tool inserts (17.6%). Applications in catalyst systems and chemical plants were not included in this total market value, nor were applications in semiconductor processing equipment.

Among structural ceramics, 43% are used as wear-resistant parts such as liners, guides, pulleys, dies, nozzles, grinding media, valves, seals, plungers, bearings, and parts for pulp and paper making. Although the cost of many applications of structural ceramics has been a barrier, structural ceramics are being increasingly commercialized. Another important application has been for components used in semiconductor manufacturing equipment.

U.S. Advanced Structural Ceramics Market Shares -1998

According to Richard Tressler of the Pennsylvania State University, the market size for semiconductor equipment is \$200 million worldwide and growing rapidly (Tressler, 2001). This market niche has not appeared in the periodic studies completed on advanced ceramics. The U.S. military has also been contributing to this market by its increased use of ceramic armor.

Competitive Analysis

More than 30 industry interviews were conducted by telephone. The phone contacts were derived from the ceramic industry publications. Any company involved in the manufacture or use of silicon carbide was included in the sampling frame.

In addition, numerous industry contacts were made by participation in two trade shows. EERC staff participated and collected marketing information from competitors at the American Ceramic Society meeting in April 2001 in Indianapolis, Indiana. They also participated in the American Ceramic Society Meeting in April 2002 in St. Louis, Missouri. At the second trade show, they served a dual marketing purpose by presenting marketing materials on the silicon carbide technology in addition to collecting competing marketing information.

The market leader in silicon carbide and advanced ceramics is St. Gobain whose family of companies now includes Carborundum, a former market leader. Although specific market share data were not obtained, respondents indicated that St. Gobain is a clear leader. In fact, one

respondent referred to the company as a monopoly. The advanced ceramics industry is dynamic, with innovative start-up companies and industry consolidation as those companies mature.

Who Is Perceived as Innovative in the Ceramics Industry

One of the questions asked industry experts who they perceive as innovative in the ceramics industry. Smaller start-up and spinoff companies are perceived as innovative. For example, Starfire Systems is a company that was frequently mentioned in the research. Other sources of ceramics innovation are programs like the Small Business Innovation Research (SBIR) program and university research.

The Ceramics Corridor, located in New York along Interstate 86, was also frequently mentioned in the interviews as a source of innovation. The Ceramics Corridor Innovation Center, with both academic and industry links, has launched approximately 20 businesses, and 10 have graduated to off-site locations. Total sales since inception are approximately \$900 million, and 2700 jobs have been created in the region (Peterson, 2001).

Commercialization of Technology – Licensing Technology

Industry contacts were interviewed to learn about their reasons for licensing a technology. On the positive side, many reasons were given for licensing a technology. First, acquiring a technology drives innovation if the capability is not available in-house. Outsourcing from universities, national labs, and smaller firms can reduce the time required to market a technology, reduce the costs of research, and defray the risks associated with developing new technologies. Universities, national labs, and smaller firms are increasingly interested in commercializing the results of their research.

On the negative side, there are some reasons why technology is not licensed from universities. First, some companies rarely license in research from any source. This is also known as the “not invented here” problem. If a company is open to the idea of licensing a technology, a few reasons were stated as potential problems. The research may be at a stage of development too early to license. When asked how to overcome that problem, respondents suggested that there is a learning process as the company becomes familiar with the university and its researchers. This was expressed as “trial and error,” “building relationships,” and getting to know each other. Much awareness can be gained by active participation in trade shows and technical meetings. Relationship building takes more time and energy. In addition, there may be difficulty in reaching agreement and problems with intellectual property issues; however, these are typical problems in any licensing situation.

When asked how to facilitate the commercialization process, interviewees provided several ideas. First, they expressed the need to build awareness and relationships as previously mentioned. For example, Alfred University was mentioned by several respondents as associated with ceramics development. Respondents stated the need to make connections at technical meetings and trade shows. Sometimes they notice publications and patents if actively searching for a technology. They also suggested that providing them one-page technical briefs describing new technologies that present clear benefits and advantages is important to them.

What Factors Interest Industry

From the literature, five perceptual characteristics of innovations that help explain differences in adoption rates were identified: relative advantage, compatibility, complexity, trialability, and observability. From the interviews, two primary market drivers are cost and performance which both fall within the realm of competitive advantage. There is often a tradeoff between these two important factors. In the interviews, the most important factor of the two appeared to be cost. Performance is more relevant in very specific high-end applications such as radiant burner tubes.

Another consideration in technology adoption is product life cycle. Silicon carbide as a product market category could be considered in the mature phase of its life cycle in that it has been available for many years and end-use applications have been identified. To extend the life cycle, new applications for the material (e.g., advanced power systems) or significant cost reductions are needed.

Silicon carbide or, more generally, advanced ceramics are described as in a state of either extension of the product life cycle or, possibly, introduction of new technology innovation. There is expectation. The market has not taken off as anticipated in the 1980s and 1990s. This can be explained by the perceptual characteristics of Rogers (1995). Ceramics are perceived as complex. They are the material of “last resort,” as mentioned in a few of the interviews. It should also be noted that the idea of complexity may be more of a perception than a reality. In addition, the compatibility of advanced ceramics with existing technology was mentioned. Even though performance advancements may be achieved, if the new technology is perceived as a significant change that is not compatible with existing infrastructure, the diffusion process may be delayed. The product life cycle, consisting of four stages— introduction, growth, maturity, and decline— is a well-documented phenomenon. Attempts are made in the maturity stage to extend the cycle.

Five customer types are related to the product life cycle: innovators, early adopters and opinion leaders, early majority, late majority, and laggards. Reaching the innovators and early adopters/opinion leaders is key to diffusion of technology. Thus interviewees were questioned on innovative companies in the ceramics industry.

Market Opportunities

One of the primary objectives of the marketing research was to identify market opportunities. For the joining technique, two market opportunities were discovered. The most market-ready application is joining radiant burner tubes. The potential industry partner is Schunk-Inex. A packet of information was provided to the inventor to describe the company and its existing technologies in order to provide background business information and foster future conversations.

In addition, a “general need” for joining in the ceramic industry was identified. For example, Kanthal has expressed interest in the joining technique. This general market demand establishes market potential for future applications once marketing barriers in the industry are overcome.

In addition to the joining technique, use or the novel process for producing reaction-bonded silicon carbide provides several potential market advantages. The key benefit of interest to industry is if the process is potentially of significantly lower cost. In addition, if other potential advantages of interest are lighter-weight and “tougher.” The cost advantage was of interest to virtually all the interviewees, so there are several potential industry partners.

The greatest near-term market potential for the reaction-bonded silicon carbide material is in armor applications. This is very timely because personnel, vehicle, and building protection have become very important for both the defense and private sector since the events of September 11, 2001 (Brown, 2001). Ceradyne and Simula are leaders in this area. Information on their market environment, including company information such as annual reports, was collected. With this information, technology and market development may be driven to meet or exceed existing industry standards.

Dr. James McCauley, Senior Research Scientist, U.S. Army Research Laboratory, presented advanced materials needs in defense applications at the 2002 American Ceramic Society meeting in St. Louis. He stressed the importance of lightweight material for armor and vehicle and building protection (McCauley, 2002). Follow-up contact was made with Dr. McCauley to obtain more technical details.

Barriers to Entry

From the marketing data collected in the industry interviews via telephone and in person at the American Ceramic Society meetings, several barriers to market entry were identified:

- Time to build industry recognition and relationships
- New technologies expected to be proven and tested
- Engineering issues with ceramics – heating and cooling large structures
- Viewed as expensive material
- Spectacular sales growth of advanced structural ceramics predicted in the 1980s and 1990s, but growth rates did not materialize

Addressing and overcoming these marketing barriers are keys to successful market entry.

Industry Leads

Several industry leads were identified in both the phone and in-person interviews. In addition, each participant was asked (if they did not readily volunteer the information) to offer additional contacts. This was a very effective way to find the right contacts in each company.

Contacting the ceramics companies in most cases was a first contact by the EERC, so it was essentially a “cold call,” setting the stage for further marketing communications. Most of the companies contacted represent potential leads. If not useful for this specific technology, industry contact is a useful marketing strategy for the EERC to provide this industry network with ongoing information about other technologies. This communication will build awareness of EERC capabilities in technology development.

Recommendations for Marketing Strategies

The following recommendations are based on the contacts with industry. First, a technical brief that includes material properties when data are available would be very useful in marketing technologies. Respondents indicated interest in knowing more specifics about the material. Second, follow-up through personal contacts and e-mail with potential industry partners from interviews, trade shows, and technical meetings) is suggested. Having ongoing conversations and an industry feedback process is important to drive the innovation of technology.

Companies that have expressed interest in further conversations are Schunk-Inex, Kanthal, Blasch Ceramics, and Superior Graphite. Both technical and marketing contacts were made at these companies, which provide good insight for both technology and market development. Also, follow-ups should be made with St. Gobain, because of its position as market leader.

In addition, a regional Native American-owned and operated corporation, Sioux Manufacturing, is interested in pursuing the development of the technology with the EERC. Sioux Manufacturing is a subcontractor to both Ceradyne and Simula, ceramics companies that have large defense contracts for armor and other personnel protection products. Ceradyne, Inc., recently announced it has received a \$5.3 million order for lightweight ceramic inserts for use in armor to protect U.S. Army forces. The order was issued by the U.S. Defense Logistics Agency.

Finally, new follow-up funding and business opportunities should be pursued. There is potential for a business spin-off from the EERC to manufacture the ceramic tiles utilized in personnel protection. The Advanced Technology Program has been identified as a funding source to facilitate the development of either a spin-off business or a joint venture between the EERC and Sioux Manufacturing. Sioux Manufacturing has also expressed interest in submitting a joint proposal to the SBIR program.

To evaluate this potential opportunity, silicon carbide tiles are being prepared this summer for ballistic testing by Sioux Manufacturing. This activity is being done as a direct consequence of this study and verifies that marketing research conducted during product development influences innovation.

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APPENDIX B

MERCURY MEASUREMENT IN COMBUSTION FLUE GASES SHORT COURSE

Presentation Outline

- Introduction and background
 - Health
 - Emissions
 - Regulations
- Mercury measurement planning
- Wet-chemistry methods
 - U.S. Environmental Protection Agency (EPA) Method 101A
 - EPA Method 29
 - Ontario Hydro (OH) mercury speciation method
- Sorbent trap methods (Code of Federal Regulations [CFR], Part 75, Appendix K)
 - QuickCEMs™
 - Flue gas adsorbent mercury speciation (FAMS™)
 - E.ON dry sampling method

Presentation Outline

- Continuous mercury monitors (CMMs)
 - Terminology
 - PS 12A and 40CFR, Part 75 (regulatory requirements)
 - Quality assurance/quality control
 - How they work
 - Advantages and limitations
 - Vendors
 - Pretreatment/conversions systems
 - Calibration systems
 - Ash-handling systems
 - Demonstrations
- Wrap-up

Why Regulate Mercury?

Short Answer: Health Concerns

Mercury Toxicity

- All forms of mercury are toxic especially to the fetus, as mercury readily crosses the placenta.
- Organic mercury compounds are the most toxic.
- Mercury is secreted very slowly (half life of 65 days).
- It exhibits high lipid solubility.
- Mercury accumulates in brain, kidneys, liver, hair, and skin.

Mercury Exposure

Chronic mercury exposure by humans is generally NOT through the air.

Almost all methylmercury exposure by humans is through eating fish.

Mercury Exposure

Mercury in Fish

- Freshwater fish – 0.11 ppm
- Ocean fish – 0.21 ppm

EPA reference dose (RfD) – 0.1 µg/kg/day
150-lb person would be able to eat about 2 oz of freshwater fish/day.

US Mercury Advisories

Waterbodies under advisory:
35% of the nation's total lake acres (~101,818 lakes)
24% of the nation's total river miles (~846,310 river miles)
71% of the nation's contiguous coastal waters including 92% of the Atlantic Coast and 100% of the Gulf Coast
100% of the Great Lakes and their connecting waters
31 states with statewide advisories
1.9% of the nation's river miles and 11% of the nation's lake acres had Safe-Eating Guidelines in effect in 2003.

The 2003 NLFWA database lists 3089 advisories in 48 states, the District of Columbia, and the U.S. territory of American Samoa.

Source: 2003 National Listing of Fish and Wildlife Advisories

EPA National Fish and Wildlife Contamination Program

Three Important Forms of Mercury in the Environment

- Elemental Mercury (Hg^0)
 - Dominant species in atmosphere, most pollution sources.
- Ionic or Oxidized Mercury (Hg^{2+})
 - In air, reactive gaseous mercury (RGM). Dominant species in rainfall, water, sediments, soil, some pollution sources (notably incinerators).
- Methylmercury (MeHg)
 - Dominant species in fish and loons; produced by naturally occurring bacteria (especially sulfate-reducing bacteria in anoxic zones of wetlands and lake sediments).

Methylmercury Formation

- Inorganic mercury settles to the sediments of the water body where microbiological activity converts it to MeHg.
- MeHg is easily passed up to animals at the top of the food chain (bioaccumulated).

U.S. Mercury Releases (tons)

Power Plant Mercury Emissions

- Power plants emit inorganic forms of mercury to the air as a result of the combustion of coal, which contains trace amounts of mercury.
- Power plant mercury emissions may be in several forms (none are MeHg):
 - Hg^0
 - Hg^{2+}
 - Particulate-bound mercury (Hg^P)

Mercury Deposition

- Hg^0 and Hg^{2+} emissions create localized or regional-scale deposition as a result of the action of gravity and precipitation.
- Hg^0 emissions create global-scale deposition and have an atmospheric lifetime of approximately 1 year.
- Air deposition of the inorganic mercury contributes to mercury loading of water bodies either by direct air deposition or by indirect deposition on the watershed of the water body.

U.S. Mercury Regulations

Clean Air Mercury Rule (CAMR)
March 15, 2005

Electronic CFR

www.gpoaccess.gov/cfr/index.html

The Regulatory Process for Mercury

- Title III of the Clean Air Act Amendments of 1990 required EPA to conduct special studies of hazardous air pollutant (HAP) emissions from electric utilities to determine if regulation was necessary.
- In December 2000, EPA determined that mercury from coal and nickel from oil-fired electric utilities presented a health hazard and should be regulated under the Maximum Achievable Control Technology (MACT) regulatory program (Section 112).
- In the final rule, the previous EPA determination was rescinded and the decision was made to regulate under a cap-and-trade structure (Section 111).

CAMR

- Under Section 111 of the 1990 Clean Air Act
- Provides for cap-and-trade structure
- Power plants >25 MW net will be regulated
- Two implementation phases: 2010 and 2018
- Works in concert with the Clean Air Interstate Rule (CAIR) for SO_2 and NO_x
- Controversial and being challenged in court by 10 states and a number of environmental groups

40 CFR Amendments

- Part 60 – “Standards of Performance for New and Existing Stationary Sources: Electric Utility Steam-Generating Units”
- Part 63 – “Air Programs”
- Part 72 – “Air Programs Permits Regulation”
- Part 75 – “Continuous Emission Monitoring”

Mercury Allowances, ounce	
2010–2018	2018 and Beyond
1,216,000 (38 tpy)	480,000 (15 tpy)

B-6

A Perspective On Mercury Removal

The Houston Astrodome is big.

If you filled the inside with ping-pong balls, you would need 1 billion balls.

Imagine that 30 of the 1,000,000,000 balls are black.

Finding and removing 27 of the black balls is the same as 90% removal of 30 ppb mercury.

For total realism – all the ping pong balls are moving at 60 mph.

Mercury Control Options

Update on Mercury Control Programs U.S. Department of Energy

www.netl.doe.gov

Tom Feeley

Phone: (412) 386-6134

E-mail: thomas.feeley@netl.doe.gov

Mercury Sampling and Measurement

EERC Mercury Measurement Experience

- Validated OH mercury speciation method, ASTM International Method D6784-02.
- Has over 17 years of experience in characterization and measurement of mercury.
- Has done extensive mercury sampling at 40 different power plants over the past 7 years.
- Has more than 10 years of experience with CMMs.

Mercury Measurement Planning

MERCURY MEASUREMENT IN COMBUSTION FLUE GASES
SHORT COURSE
With an Emphasis on Continuous Mercury Monitors

Sample Collection for Mercury Measurement

- Coal
- ESP or baghouse hopper ash
- Wet scrubber
- Dry scrubber
- **Flue gas**

Project Planning

- Defining overall objectives
 - Define purpose for measuring mercury
 - Determine measuring methods
- Determining the data needed to be taken to meet objectives
- Managing results
- Preparing a quality assurance plan (QAP)

Purpose for Doing Mercury Measurement

- Research
- Control
- Regulations

Research Purposes

- Measurements methods usually need to be very flexible (complex hardware and software are usually the result).
- Measurements are often done at multiple locations under difficult conditions.
- Research tests are usually short(er) term.
- Highly trained engineers and technicians are needed to do the measurements.

Mercury Control Purposes

- Mercury measurement method must be highly automated and with minimal maintenance.
- Method must be reliable and rugged.
- Method must be flexible enough to be used for a variety of control options.

Regulatory Purposes

- Sampling must follow detailed procedures:
 - 40 CFR, Part 75, for continuous emission monitoring
 - PS 12A for CMM specifications
 - ASTM and/or EPA procedures for wet-chemistry methods
 - 40 CFR, Part 75, Appendix K for sorbent trap methods
 - Any additional state procedures
- The simpler the better (cheaper the better!).
- For instrumentation methods, maintenance must be minimal.
- Data must be acceptable to the regulatory body (EPA and/or the states).
 - High level of QA/QC required.
 - Missed data may be costly.
 - Detailed documentation is necessary.
- Sampling is done only at one location, usually the stack.

Flue Gas Mercury Measurements as a Function of Plant Processes

- Other mercury measurements
 - Coal, ash, scrubber liquor, etc.
 - Additional sampling locations
- Plant operational effects
 - Load changes, plant upsets, plant start-up, etc.
 - Balance-of-plant impacts associated with mercury control technologies
 - Additional plant data needed to document mercury emissions (i.e., flue gas flow rates, flue gas moisture, O₂ and CO₂ concentrations)

Management of Results

- May be defined by a regulatory body
- Program management
- Documentation requirements
- Handling missing and/or poor data

Quality Assurance (QA) Plan

- Program definition
- Identification of test methodology
- Project organization
- Description of the project and schedule
- Quality objectives and criteria for data
- Assessment and oversight
- Planned corrective action if QA objectives not obtained
- Safety issues
- Documentation

Wet-Chemistry Methods

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Wet-Chemistry Methods

Wet-Chemistry Methods Outline

- Advantages and disadvantages
- Planning
- Methods
 - EPA Method 101A
 - EPA Method 29
 - OH mercury speciation method

Advantages

- Proven at a number of sites and under a wide variety of conditions.
- Provides good results with a high level of sensitivity, $<0.5 \mu\text{g}/\text{Nm}^3$.
- Currently, the only mercury measurement method considered to be a reference method by EPA.

Limitations

- But ...
 - A high level of QA/QC and well-trained personnel required.
 - A 2-week or more turnaround time for results; in other words, no real-time data.
 - Particulate matter can cause biases in speciation data (total mercury data is still valid).
 - It is expensive.

Up-Front Planning

- Factors to consider when evaluating a sampling contractor:
 - Experience and training
 - Prequalification requirements
 - Frequency of equipment calibration
 - Chain-of-custody procedures
 - Collection and handling of reagent and field blanks
 - Whether or not they routinely do field spikes
 - Procedures for handling glassware

Up-Front Planning

- Factors to consider when doing a site visit:
 - Is there adequate access to sampling locations and ports?
 - Is power available at each location for sampling equipment that will be used?
 - Has there been assigned a plant contact who will be on-site during testing?
 - What data, assistance, or information will be needed from the plant?
- Most importantly, involve representatives of the plant for all processes that will be impacted by the project.

Up-Front Planning

- Factors to consider when evaluating an analytical laboratory:
 - Is there currently a good working relationship with the laboratory that will be doing the analysis?
 - Have they met all prequalification requirements?
 - What are the laboratory's sample-handling, storage, and preservation procedures?
 - Are the analytical techniques used appropriate for the particular sample type and analysis quality desired?
 - Are rigorous procedures for blanks, spikes, calibrations, and replicates implemented?
 - Is an independent auditor needed?

Sample History

Collection ➡ Storage ➡ Preparation ➡ Analysis

Errors can be introduced at any stage.

Accuracy

How well the measured concentration represents the true value.

Precision

To what degree an analysis of the "same" sample can vary based on the error associated with the analysis method.

Accuracy and Precision

On average, the duck was dead.

Sample Blanks

It is clear that obtaining good blank samples is critical to success of a mercury measurement project. In almost every case, bad data is associated with bad blanks.

- Reagent blanks
- Field blanks

Glassware

- Wet-chemistry methods are extremely glassware-intensive.
- Proper cleaning is essential (SW-846-0060)
 - Wash thoroughly with soap and water
 - Rinse with tap water
 - Rinse three times with distilled or deionizer water
 - Soak 4 hours in a 10% nitric acid bath
 - Rinse with distilled or deionized water
 - Air-dry glassware in a clean area
- There are two ways to ensure clean glassware in the field:
 - Set up wash stations to clean the glassware in the field
 - Bring enough glassware to complete the field test

Glassware

Question:
Hey, aren't the methods designed to remove all the mercury? So why go to all this trouble?

Answer:
People make mistakes. If all of the mercury is not removed, not only will the results for that sample be erroneous but so will the next one done with that glassware. If the bottles are cleaned each time, a mistake only affects one sample.

Sample Spikes

A known quantity of mercury is added to a solution.

- Laboratory spikes
- Instrument spikes
- Field spikes
 - Not specifically required as part of ASTM D6784-02 but necessary nonetheless.
 - Spiked train is set up and torn down as if it was a used sample train.

Data Quality Objectives

Accuracy

Sample Type	Objective	Approach
Reagent Blank	0.1 µg/L	Analyze on blank per batch of each reagent
Field Blank	Maximum of 0.5 µg/L and <10% of sampled Hg concentration	Collect and analyze one field blank per unit per day of testing
Field Spike	<15% of true value	Collect and analyze one field spike per unit per day of testing

Data Quality Objectives

Precision

Sample Type	Objective	Approach
Laboratory Spike	<15% of true value	1–10 samples – 1 lab spike per solution 11–20 samples – 2 lab spikes per solution 21–30 samples – 3 lab spikes per solution
Triplicate Analysis	Standard deviation; <0.5 µg/L	1–10 samples – 1 lab spike per solution 11–20 samples – 2 lab spikes per solution 21–30 samples – 3 lab spikes per solution
Duplicate Analysis	Relative standard deviation; <10%	Every sample

EPA Method 101A

- Simplest of the mercury measurement methods (only four bottles).
- Use may be limited by SO₂ concentration in the flue gas.
- Only measures total mercury.
- Not accepted by the EPA as a reference method.

EPA Method 29

- Complex method; requires seven bottles and two different solutions.
- Not only measures mercury but is a multi-metals sampling train.
- Requires a high level of QA/QC.
- Only measures total mercury.

OH Mercury Speciation Method

ASTM D6784-02

Standard Test Method for Elemental, Oxidized, Particle-Bound, and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method)

www.astm.org

OH Impinger Train

OH Impinger Train

OH Method

- Complex method; requires eight bottles and three different solutions.
- Requires a high level of QA/QC.
- Able to speciate mercury (Hg^0 , Hg^{2+} , Hg^{P}).
- Speciation may be biased at high-dust locations because of interaction of mercury and the ash collected on the filter.

OH Method for Regulatory Purposes

- The only method currently recognized by EPA as a reference method for CAMR for the relative accuracy test audit (RATA).
- One of EPA's highest priorities is developing or determining an instrumental reference method.

OH Method as a Reference Method

- Conducted once during initial setup of the CMM.
 - Minimum of nine paired sample trains (averaged) required
 - Relative standard deviation (RSD) must be within 10%
- Annual RATAs are required once CMMs have been set up and verified ($<20\%$ or $\pm 1.0 \mu\text{g}/\text{dscm}$).
- For the sorbent traps method only annual RATAs are required.

Isokinetic Traversing

Based on experience, traversing at the stack is not recommended for the OH method.

- Traversing was designed to ensure an accurate representation of dust loading in a duct (EPA Method 5/17). Mercury is in the gas phase at the stack.
- The OH method is very complex, and moving this train between traverse points is asking for trouble.
- The KCl impingers can offgas mercury if agitated.
- CAMR does not require traversing for CMMs or OH method for RATAs.

Sorbent Trap Methods

40 CFR, Part 75, Appendix K

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Appendix K

- January 2004, published in CFR as Proposed Method 324 – Determination of Vapor-Phase Flue Gas Mercury Emissions from Stationary Sources Using Dry Sorbent Trap Sampling.
- In the final rule, published in March 2005, the concept of a dry sorbent trap method was retitled CFR, Part 75, Appendix K.
- For regulatory purposes, a method that meets the requirements of Appendix K can be an alternative to CMMs.

Example of Appendix K Sample System

Used Courtesy of ADA-ES

Dual-Trap Probe Design

Appendix K

Advantages

- Potential to be low cost
- Minimal operator training required
- Portable
- Low maintenance
- No hazardous chemicals

Appendix K

Disadvantages

- Gives no real-time data.
- Can only be used in low-dust conditions.
- Needs to be validated for different coals and plant configurations.
- Few vendors manufacture traps.
- Currently, analysis costs are high.

Question:

What is 40 CFR, Part 75, Appendix K?

Answer:

Appendix K is a **procedure**, which, if met, allows mercury sorbent traps to be used to measure mercury to meet CAMR.

Question:

How is Appendix K different from proposed EPA Method 324?

Answer:

EPA will not promulgate Method 324; however, the method titled QuickCEMs™ (after some modification) may be used to meet Appendix K requirements.

Question:

Does Appendix K specify what sorbent is to be used or what analytical procedures need to be done?

Answer:

No. If the sorbent and/or analytical methods can pass the requirements as laid out in Appendix K, they can be used.

Appendix K Requirements

- Paired sample trains must have a RSD of <10% to be valid.
- Must sample at a rate proportional to the volumetric gas flow rate.
- Correction for stack gas moisture content is required.
- Annual RATA required.

Appendix K

- Relative accuracy test.
 - Currently, the OH method is the only acceptable reference method.
 - A minimum of nine valid paired sample trains are required.
 - The sorbent trap results must meet a $\leq 20\%$ relative accuracy compared to the reference method.
 - Alternately, if the mercury concentration is $\leq 5 \mu\text{g}/\text{scm}$, the results are acceptable if the mean difference does not exceed $1.0 \mu\text{g}/\text{scm}$.

Key QA/QC Requirements for All Sorbent Trap Methods

- Cleanliness is important when handling the traps.
- Sorbent traps need to be inserted directly in the flue gas duct without any upstream tubing connections.
- Condensation or wetting must not occur in the sample trap.
- Sample volume must be accurately measured.
- Sample trains must be leak-checked.
- Upon sample recovery, cover the end of the traps before wiping off the ash on the outside.

Issues Affecting Paired Trap Agreement

- Each control module has a dry gas meter that is calibrated to within 5%. This means that paired trap agreement could be off by 5%.
- Leak checks need to be within 4% of total flow rate. This can affect paired trap agreement by up to 4%.
- Each trap has its own analytical uncertainty. This depends on the lab but it could easily be 2%–5%.

Issues Affecting Paired Trap Agreement

- The trap mercury concentration is adjusted by the recovery of the last spiked trap section. These recoveries can be off by 20%–30%.
- Some groups have reported only 5% of paired tests failing. Others have reported that 50% of paired tests failed. The groups that reported 50% failures had problems with spike recoveries affecting the results.
- THE BOTTOM LINE IS EVERYTHING HAS TO BE WORKING IN YOUR FAVOR TO PASS THE REQUIREMENT THAT THE PAIRED TRAPS AGREE WITHIN 10%.

Relative Accuracy Test*

Criteria: Relative accuracy (RA) $\leq 20\%$ or $\leq 1 \mu\text{g}/\text{m}^3$ absolute value of mean difference, if mean reference method (RM) is $<5 \mu\text{g}/\text{m}^3$.

Test	Absolute Mean Difference, $\mu\text{g}/\text{m}^3$	Relative Accuracy, %
EPA RATA Site 1	0.79	28.2
EPA RATA Site 2	0.09	9.4

*The reference method was nine paired OH sample trains.

Sorbent Trap Results from an EPRI RATA Test

Criteria:
RA $\leq 20\%$ or $\leq 1 \mu\text{g}/\text{m}^3$ absolute value of the mean difference, if mean RM is $<5 \mu\text{g}/\text{m}^3$

Calculated from 11 valid runs (2–12)
Calculated from best nine runs (1, 5, 9 omitted)

Run	Date	EPRI Sorbent Trap, $\mu\text{g}/\text{dscm}$	Reference Method, $\mu\text{g}/\text{dscm}$	Difference, $\mu\text{g}/\text{dscm}$
1	3/7/05	5.65	7.07	-1.42
2	3/7/05	7.98	7.50	0.48
3	3/8/05	6.20	5.22	0.98
4	3/8/05	4.94	4.44	0.50
5	3/8/05	5.49	4.48	1.01
6	3/9/05	6.99	6.03	0.97
7	3/9/05	5.92	5.55	0.37
8	3/9/05	5.32	4.83	0.49
9	3/10/05	4.27	3.31	0.95
10	3/10/05	3.34	2.71	0.63
11	3/10/05	3.06	2.55	0.51
12	3/11/05	7.54	6.76	0.78
Mean		5.55	4.85	0.70
RA, %				18.14
Mean		5.70	5.07	0.63
RA, %				15.87

Dry Sorbent Trap Methods

- QuickCEMs™
 - Designed to measure total gas-phase mercury for low-dust conditions.
 - Uses impregnated activated carbon.
 - To meet Appendix K criteria, the original specification needed to be modified by adding a third spiked QA/QC trap.
- FAMSTM
 - Designed as a speciation method (includes particulate-bound mercury).
 - Uses two types of traps: KCl/quartz followed by a chemically treated carbon trap.
 - Currently, only Frontier Geosciences provides the traps and does the analysis.

Dry Sorbent Trap Methods

- E.ON dry sampling method
 - Designed as a speciation method for gas-phase mercury.
 - Uses an adsorber resin followed by a chemically treated carbon trap.

Costs Associated with Sorbent Trap Method

- Sampling Equipment
 - Sample box (pump, dry gas meter, etc.)
 - Dual-sample probe
- Sample Traps
 - Chemically impregnated carbon traps (traps 1 and 2)
 - Spiked carbon trap
- Sample Analyses
 - Sending to outside laboratory (may take up to 2 weeks to obtain data)
 - Use instrumental method (i.e., Ohio Lumex)
- Personnel Costs
 - Training
 - Replacing traps on a regular basis
 - Equipment maintenance

Mercury Calculations

- Flue concentrations
- Coal, hopper ash, and wet scrubber mercury concentrations
- Emission factors
- Mercury removal based on coal mercury

Continuous Mercury Monitors

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Continuous Mercury Monitors

EERC Mercury Lab

Definition

- Continuous Emission Monitor (CEM)
 - Refers to just the mercury analyzer
- Continuous Mercury Monitor (CMM)
 - Refers to entire mercury measurement system

Advantages of CMMs

- Give real- or near-real-time results
- Able to assess process variability
- May be used for system optimization
- Provide feedback for Hg control strategies
- Have the potential to be less costly
- Allow direct measure of pollutants
- Critical to a cap-and-trade Hg control scenario
- May provide better public relations

Challenges of CMMs

- Low Hg concentrations
- SO₃ and other acid gases and aerosols
- Moisture condensation (i.e., wet stacks)
- Other trace elements
- Interaction with ash
- Sample transport
- Long-term reliability

Commercially Available CMMs

Vendor	Product	Analysis Method	Pretreatment/ Conversion	Web Site
Durag	HM-1400	CVAA ¹	Thermal catalytic	durag.net
Horiba/NIC	DM-6B	Dual beam CVAA	Thermal catalytic	environ.hii.horiba.com
Cooper Envir.	Xact MM -EM	Filter tape with XRF ²	None needed	Cooperenvironmental.com
Ohio Lumex	RA-915+	CVAA with Zeeman	None	ohiolumex.com

¹ cold-vapor atomic absorption.

² X-ray fluorescence.

Commercially Available CMMs (cont.)

Vendor	Product	Analysis Method	Pretreatment/ Conversion	Web Site
Opsis AB	HG200	CVAA	Dilution system	opsis.se
PS Analytical	Sir Galahad	Au-CVAF ¹	Wet chemistry and Thermal Catalytic	psanalytical.com
Envimetrics	Argus-Hg 1000	Au-plasma emission	Thermal catalytic	envimetrics.com
Semtech Metallurgy AB	Hg 2010	CVAA with Zeeman	Wet chemistry	semtech.se
Tekran, Inc.	3300	Au-CVAF	Dry dilution system	tekran.com

¹ cold-vapor atomic fluorescence.

Commercially Available CMMs (cont.)

Vendor	Product	Analysis Method	Pretreatment/ Conversion	Web Site
Thermo Electron	Mercury Freedom System	CVAF	Thermal catalytic with dilution	thermo.com/com
SICK UPA GmbH	MERCEM	Au-CVAA	Wet chemistry	cems.on.ca
EcoCem Analytics	Hg MKII	CVAA	Thermal catalytic	ecochem.biz
ST ² Technologies	SM-3	CVAA	Thermal catalytic	st2-service.com

Complete CMM Package

- Probe
- Pretreatment/ conversion system
- Calibration system
- Mercury analyzer

Inertial Separation Probes (ISPs)

- Purpose
 - Sample stack gas without water condensation
 - Remove particles from gas stream to minimize contact between the particles and gas stream
- Manufacturers
 - Apogee QGIS probe
 - Baldwin inertial filtration probe
 - Thermo Electron inertial filtration probe
- Materials of construction
 - Silco-coated steel
 - Stainless steel
 - Sintered stainless steel porous tube

Example of an ISP

Pretreatment/Conversion Systems

- Reduce all mercury to the elemental form.
- Remove acid gases that may interfere with the conversion and/or operation of the system.
- To speciate, must strip out nonelemental mercury forms.

Types of Pretreatment/Conversion Systems

- Wet chemistry
- Thermal catalytic
- Thermal catalytic with dilution
- Thermal dilution

Pretreatment/Conversion Wet-Chemistry Systems

- Use a SnCl_2 solution with Hg^0 to reduce all mercury.
- Use a separate solution to strip out oxidized mercury.
- Solutions also remove acid gases.
- Chilled gas-liquid separator removes moisture from sample gas.

Schematic of a Wet-Chemistry Based Pretreatment/Conversion System

Wet Conditioning/ Conversion Units

- They have worked well for research but are not suited to long-term compliance monitoring.
- Extensive engineering or technician support is required.
- The solutions may remove CO_2 from the sample gas.
- Tin plating and crystallization of solutions can cause problems.
- Cold spots.

Pretreatment/Conversion Thermal Catalytic Systems

- May or may not use wet chemicals to remove acid gases and moisture.
- Use a catalyst to reduce all mercury forms to Hg^0 .
- Removal of acid gases prevents conversion back to nonelemental forms during cooling.
- Speciated mercury is obtained using dual detectors or pretreatment systems.
- Life span of the catalyst has been a concern.

Schematic of the PSA Dry-Based Speciation Module

Used Courtesy of PS Analytical

Thermal Dilution Systems

- Use little or no wet chemicals.
- Sample is diluted for transport.
- No catalyst is needed to reduce all forms of mercury to Hg^0 .
- Scrubbing of acid gases prevents conversion back to nonelemental forms during cooling.
- Must have a highly sensitive instrument such as atomic fluorescence (AF).
- Reduces problems with poisoning of gold traps with AF systems.

Example of a Thermal Dilution System

Mercury Analyzers

- CVAA spectroscopy with and without Zeeman modulation
- CVAF spectroscopy
- Differential optical emission spectroscopy (DOAS)
- Plasma emission spectroscopy
- Two-photon adsorption with wavelength modulation

PS Analytical
Sir Galahad

Cold-Vapor Atomic Absorption Spectroscopy

Measures mercury using UV light at a spectra of 253.7 nm

Type	How it works	Example
CVAAS – Gold	Uses gold trap to preconcentrate Hg and remove interferents.	SICK MERCEM
CVAAS – Dual Beam	Measures gas with and without Hg. SO ₂ may be scrubbed.	Horiba/NIC DM-6 B
CVAAS – Zeeman Shift	Uses Zeeman shift to compensate for interferents.	Ohio Lumex

Cold-Vapor Atomic Absorption Spectroscopy

Cold-Vapor Atomic Fluorescence Spectroscopy

- Much more sensitive than atomic adsorption, with a detection limit of <0.1 pg absolute.
- Requires removal of interfering compounds.
- Inherently linear (detector linear over >5 orders of magnitude).

Cold-Vapor Atomic Fluorescence Spectroscopy

Calibration Criteria

- Must be simple and easy to accomplish.
- Must be an acceptable procedure.
- Detector must be separately calibrated.
- Multipoint calibrations required.
- Zero drift and zero gas.
- Instrument calibrated using both elemental and oxidized mercury standards.

Elemental Hg Gas Standards

Schematic of Tekran Calibrator

Oxidized Hg Gas Standards

Costs Associated with CMMs

- Capital costs
- Cost of supplies
- Training costs
- Costs associated with certification (PS 12A)
- Costs associated with on-going QA/QC
 - Calibration
 - Regular maintenance
 - Troubleshooting
 - Cost for RATA

Time Lines

- Time lines associated with federal mandates (monitors required by January 2009)
- Time lines associated with instrument development
- Time line associated with instrument operation
 - Purchase
 - Installation
 - Certification (12 months)

Performance Speciation (PS) 12A (Amended to Appendix B Part 60)

- "Specification and Text Procedures for Total Vapor-Phase Mercury Continuous Emission Monitoring Systems in Stationary Sources"
- PS 12A used for evaluating acceptability of total vapor-phase CMMs at time of or soon after installation

PS 12A

- Amended to CFR, Part 60, as Appendix B.
- Provides details as to the acceptability of a CMM for an affected site.
- Does not include ongoing calibration procedures.

PS 12A

- PS 12A is not:
 - Intended for long-term evaluation of CMMs.
 - Intended to identify specific calibration techniques or auxiliary procedures to assess CMM performance.
- Facilities subject to the requirements of Subpart I of Part 75, Chapter 1 of Title 40 may conduct performance evaluation of the CMMs according to §§75.20(c)(1) of Chapter 1 Title 40 and Section 6 of Appendix A to Part 75 in lieu of PS 12A.

PS 12A

- Provides definitions (CEM, span value, etc.)
- Measurement location
- Measurement error (ME)
- Upscale drift (UD)
- Zero drift (ZD)
- Measuring RA
- Data acquisition
- Data reduction and documentation

Reagents and Standards

- Reference gases
 - Zero-level 0% to 20% of span
 - Mid-level 50%–60% of span
 - High-level 80%–100% of span
- Span value is defined as the upper limit of the intended Hg concentration measurement range.
- Reference gas delivery system
 - Gas flow rate must be the same at all three challenge levels.
 - Gas flow must exceed the flow required by the CMMs.

PS 12A Instrument Location

- Assessable location downstream of all air pollution control devices
- Guidelines for determining location
 - 2 equivalent diameters downstream of the nearest control device
 - ½ equivalent diameters from the effluent exhaust
 - >1 meter from stack or duct wall
- Single-point extraction
 - Free from mercury stratification
 - Conduct a NO_x and/or SO₂ traverse prior to installation to determine stratification.

PS 12A Measurement Error (ME)

- Three-point check – low-, mid-, and high-level.
- National Institute of Standards and Technology (NIST) traceable Hg⁰ and HgCl₂ must be used.
- The reference gas must be injected immediately after the sampling filter.
- ME test must be conducted with both Hg⁰ and HgCl₂ reference gases.
- For each reference gas, the absolute value of the difference cannot exceed 5% of the span value.

PS 12A Upscale Drift (UD) Tests

- Challenge the entire CMM with an upscale reference gas (Hg⁰ or HgCl₂) once each day for 7 consecutive unit operating days.
- Conduct the tests immediately before any automatic zero and span operations.
- Unit operating at more than 50% of normal load.
- NIST traceable Hg⁰ or HgCl₂ standards used.
- The absolute value of the difference cannot exceed 5% of the span value for each day.

$$UD = |R-A| / S \times 100 \leq 5.0\%$$

PS 12A Zero Drift Tests (ZD)

- Challenge the entire CMM once per day for 7 days N₂ or air.
- Conduct the tests immediately before any automatic zero and span operations.
- Unit operating at more than 50% of normal load.
- The absolute difference between the zero level and the instrument reading is expressed as % of span gas.

$$ZD = |R-A| / S \times 100 \leq 5.0\%$$

PS 12A Relative Accuracy Test Procedure

- Unit operating at normal full load.
- Either Method 29 or the OH method can be used as the reference method (RM). *Note: Only OH method is allowed in 40 CFR Part 75.*
- For the RM, use the same traverse point that was used for the CMM.
- Conduct the tests so they will yield results representative of the:
 - Hg concentration
 - Temperature
 - Moisture

Relative Accuracy Test Procedure

- Use paired RM samples.
- Conduct a minimum of nine valid paired RM test runs.
- More than nine RM tests can be conducted but only a maximum of three sets of test results can be rejected.
- Report all data, including rejected data.
- Run RM long enough to ensure a sufficient mass of mercury is collected for analysis (2 hrs is suggested).
- RM data must meet relative deviation (RD) criteria.

Relative Accuracy Test Procedure

$$RD = 100 \times \frac{|(C_a - C_b)|}{(C_a + C_b)}$$

Where,
C_a and C_b are concentration values determined from each of the two samples respectively.

Relative Accuracy Test Procedure

- The minimum performance criteria is:
 - RD ≤ 10% for Hg concentrations >1.0 µg/m³
 - RD ≤ 20% for Hg concentrations ≤ 1.0 µg/m³
- Pairs of data that do not meet these criteria should be eliminated from the data set used to determine RA.

Relative Accuracy Test Procedure

- To correlate the RM and CMM data, confirm that they are reported on consistently:
 - Moisture
 - Pressure
 - Temperature
 - Diluent concentration basis
- Take into consideration response time of CMM
- Tabulate the paired data

Relative Accuracy Test Procedure

Calculate relative accuracy using:

$$RA = \frac{|\bar{d}| + |cc|}{RM} \times 100$$

Where,

- d = The sum of the difference between the RM values and the corresponding CMM values
- cc = The value of the confidence coefficient
- RM = Arithmetic mean of the reference method values

Relative Accuracy Test Procedure

Calculate d using:

$$\bar{d} = \sum_{i=1}^n d_i$$

Where,

- n = Number of data points
- d_i = The difference between a reference method value and the corresponding CMM's value ($RM_i - CMM_i$) at a given point in time i

Relative Accuracy Test Procedure

Calculate the confidence coefficient (one tailed) of a data sets using:

$$cc = t_{0.025} \frac{S_d}{\sqrt{n}}$$

Where,

- $t_{0.025}$ = Student t value (use statistical tables)
- S_d = Standard deviation
- n = Number of data points

Relative Accuracy Test Procedure

Standard deviation is calculated using:

$$S_d = \sqrt{\frac{\sum_{i=1}^n d_i^2 - \frac{\left(\sum_{i=1}^n d_i\right)^2}{n}}{n-1}}$$

Relative Accuracy Test Procedure

The bias test is passed if:

$$\bar{d} \leq |cc|$$

Where,

- d = The mean difference between the RM values and the corresponding CMM values

Relative Accuracy Test Procedure

The RATA data sets are evaluated for bias using:

$$CMM_i^{\text{Adjusted}} = CMM_i^{\text{Monitor}} \times BAF$$

Where,

- CMM_i^{Monitor} = Data provided by the monitor at time i
- CMM_i^{Adjusted} = Data value, adjusted for bias, at time i
- BAF = Bias adjustment factor, calculated to the nearest thousandth

Relative Accuracy Test Procedure

BAF is defined by:

$$BAF = 1 + \frac{|\bar{d}|}{CMM_{avg}}$$

Where,

$\bar{d}$ = Arithmetic mean of the difference obtained during the failed bias test

CMM_{avg} = Mean of the data values provided by the CMM during the failed bias test

Relative Accuracy Test Procedure

If the mercury concentration is < 5.0 µg/dscm during the RATA and the instrument meets the 20% RA or 1.0 µg/scm difference, but fails the bias test, the calculated BAF can be used or a default value of 1.250.

Example of a RATA Calculation

No.	RM 1 µg/dscm	RM 2 µg/dscm	RM avg µg/dscm	RD %	CMM µg/dscm	d µg/dscm
1	10.3	10.5	10.40	1.0	9.9	-0.5
2	9.8	9.9	9.85	0.5	10.6	0.75
3	9.7	10.0	9.85	1.5	10.4	0.55
4	10.2	10.5	10.35	1.4	9.8	-0.55
5	10.7	10.4	10.55	1.4	10.0	-0.55
6	9.9	10.3	10.1	2.0	10.4	0.30
7	9.6	9.8	9.70	1.0	10.1	0.40
8	10.2	10.4	10.30	1.0	10.8	0.50
9	9.5	9.8	9.65	1.6	10.4	0.75
10	10.0	10.3	10.15	1.5	8.2	-1.95
11	9.0	11.02	10.10	10.9	10.7	0.60

$$d = CMM - RM_{avg}$$

$$RD = 100 \times \frac{|C_a - C_b|}{(C_a + C_b)}$$

$\bar{d}$
RD

Example of a RATA Calculation

No.	RM 1 µg/dscm	RM 2 µg/dscm	RM avg µg/dscm	RD %	CMM µg/dscm	D µg/dscm
1	10.3	10.5	10.40	1.0	9.9	-0.5
2	9.8	9.9	9.85	0.5	10.6	0.75
3	9.7	10.0	9.85	1.5	10.4	0.55
4	10.2	10.5	10.35			
5	10.7	10.4	10.55			
6	9.9	10.3	10.1			
7	9.6	9.8	9.70	1.0	10.1	0.40
8	10.2	10.4	10.30	1.0	10.8	0.50
9	9.5	9.8	9.65	1.6	10.4	0.75

$$RD = 100 \times \frac{|(C_a - C_b)|}{(C_a + C_b)}$$

Example Relative Accuracy Calculation

No.	d	d ²
1	-0.5	0.250
2	0.75	0.563
3	0.55	0.303
4	-0.55	0.303
5	-0.55	0.303
6	0.30	0.090
7	0.40	0.160
8	0.50	0.250
9	0.75	0.563
Sum	1.70	2.785
RM avg = 10.1		

$$S_d = \sqrt{\frac{\sum_{i=1}^n d_i^2 - \frac{(\sum_{i=1}^n d_i)^2}{n}}{n-1}}$$

$$S_d = 0.555$$

$$cc = t_{0.025} \frac{S_d}{\sqrt{n}}$$

$$t_{0.025} = 2.306$$

$$cc = 0.427$$

$$\bar{d} = \frac{1}{n} \sum_{i=1}^n d_i$$

$$\bar{d} = 0.189$$

$$RA = \frac{|\bar{d}| + |cc|}{RM} \times 100$$

$$RA = 6.1\%$$

Example Relative Accuracy Calculation

No	RM 1 µg/dscm	RM 2 µg/dscm	RMavg µg/dscm	CMM µg/dscm	d	d ²	RD %
1	10.3	10.5	10.40	9.9	-0.5	0.250	1.0
2	9.8	9.9	9.85	10.6	0.75	0.563	0.5
3	9.7	10.0	9.85	10.4	0.55	0.303	1.5
4	10.2	10.5	10.35	9.8	-0.55	0.303	1.4
5	10.7	10.4	10.55	10.0	-0.55	0.303	1.4
6	9.9	10.3	10.1	10.4	0.30	0.090	2.0
7	9.6	9.8	9.70	10.1	0.40	0.160	1.0
8	10.2	10.4	10.30	10.8	0.50	0.250	1.0
9	9.5	9.8	9.65	10.4	0.75	0.563	1.6
10	10.0	10.3	10.15	8.2	-1.95	3.803	1.5
Average = 10.1					Σ = -0.25	Σ = 6.588	

$$S_d = 0.856$$

$$t_{0.025} = 2.226$$

$$cc = 0.612$$

$$\bar{d} = -0.025$$

$$RA = 6.4\%$$

Example Relative Accuracy Calculation

In both cases, the Bias Adjustment Factor (BAF) test is passed as:

$$\bar{d} \leq |cc|$$

$$\bar{d} = 0.189 < |cc| = 0.427$$

$$\bar{d} = 0.025 < |cc| = 0.612$$

CFR Part 75, Appendix A Ongoing CMM QA/QC Required

- Daily calibration
- Weekly system integrity check
- Quarterly 3-point linearity check
- Annual RATA

CFR 40, Part 75 Continuous Emission Monitoring

- Requirements for SO₂ and NO_x monitoring
- Changed to include requirements for monitoring mercury
- Includes detailed specifications for initial certification of CMMs and ongoing QA/QC requirements
- Includes detailed specifications for monitoring using sorbent traps

40 CFR, Part 75, Changes as a Result of CAMR

- 75.2 Applicability
- 75.10 General operating requirements
- 75.15 Special provisions for measuring mercury mass emissions using the sorbent trap monitoring methodology
- 75.20 Initial certification and recertification
- 75.21 Quality assurance and quality control requirements
- 75.22 Reference methods

40 CFR, Part 75, Changes as a Result of CAMR

- 75.24 Out-of-control periods and adjustment for system bias
- 75.31 Initial missing data procedures
- 75.32 Determination of monitor data availability for standard missing data procedures
- 75.33 Standard missing data procedures for SO₂, NO_x, and flow rate
- 75.38 Standard missing data procedures for CMMs

40 CFR, Part 75, Changes as a Result of CAMR

- 75.53 Monitoring plan
- 75.39 Missing data procedures for sorbent trap monitoring systems
- 75.57 General record-keeping provisions
- 75.58 General record-keeping provisions for specific situations
- 75.59 Certification, quality assurance, and quality control record provisions

40 CFR, Part 75, Appendix Changes

- Appendix A Specifications and test procedures
- Appendix B Quality assurance and quality control procedures
- Appendix F Conversion procedures
- Appendix K Quality assurance and operating procedures for sorbent trap monitoring systems

Equipment Specifications

- The CMM must be setup such that:
 - Known concentrations of elemental Hg and HgCl₂ can be injected.
 - There is an injection point immediately preceding the sample extraction filtration system.
 - The entire measurement system can be checked.
 - A cycle time test must pass with a maximum allowable of 15 minutes.
- Select a measurement range such that the majority of readings are between 20% and 80% of full scale.

Equipment Specifications

- A maximum potential concentration (MPC) must be determined by using:
 - A predetermined fixed-value based on coal type.
 - Site-specific emissions testing.
 - 720 or more hours of CMM data or sorbent trap data.
- A high span for the Hg monitor should be set by rounding the MPC upward to the next highest multiple of 10 µg/scm.

Equipment Specifications

- At a minimum, an annual evaluation of the MPC, span, and range may need adjustment because of:
 - Change in fuel type.
 - Change in unit operations.
 - Installation or removal of emissions control.

Data Acquisition and Handling Systems

- Read and record full range of mercury concentrations.
- Provide a permanent continuous record of all data.
- Capable of converting readings to emission rates or mass emissions in appropriate units.
- Compute and record monitor calibration error, bias adjustments, mercury emission rate and all missing data procedure statistics.

Daily Calibrations

- NIST traceable standards for Hg⁰ or Hg²⁺
- 5% of span value
- Or ≤1.0 µg/scm absolute difference between standard and CMM reading

Weekly System Integrity Checks

- Single point system check
- Use NIST-traceable source of Hg^{2+}
- Use mid- or high-level gas concentration
- Do not have to be performed if a NIST-traceable source of Hg^{2+} is used for daily calibration error tests

Quarterly 3-point Linearity Check

- NIST-traceable Hg^0 reference gas
- Must meet a specification of 10% of standard at three gas levels (low-, mid-, high-level)
- Alternately, specification can be $<1.0 \mu\text{g}/\text{scm}$ absolute difference

Quarterly 3-point Linearity Check

- Linearity check is passed if:

or
$$\text{LC} = \frac{|\overline{R} - \overline{A}|}{\overline{R}} \times 100 \leq 10.0\%$$

$$|\overline{R} - \overline{A}| \leq 1.0 \mu\text{g}/\text{scm}$$

- Must pass for each of the three reference gas levels

Relative Accuracy Test Audit (RATA)

- Same procedures used as discussed for PS 12A
 - CMM must meet 20% RA.
 - Alternately, if mercury concentration is $\leq 5 \mu\text{g}/\text{scm}$, results are acceptable if absolute mean difference between the RM and CMM does not exceed $1.0 \mu\text{g}/\text{scm}$.

Field Experience

MERCURY MEASUREMENT IN COMBUSTION FLUE GASES SHORT COURSE
With an Emphasis on Continuous Mercury Monitors

Mercury CMM Test Programs

- DOE/EPA CMM Testing at Holly Hills, North Carolina
 - Tests done in 1997
 - Unit is cement kiln
 - Substantial variation in flue gas
 - Tests largely unsuccessful
- European TUV certification test results
 - Test primarily conducted on European waste-to-energy systems.
 - A number of CMMs have obtained TUV certification.

Mercury CMM Test Programs

- Batelle ETV program
 - Tests primarily done in 1999 and 2000.
 - Pilot-scale testing at EPA's facility.
 - Only several vendors participated with mixed results.
- RATA Tests at Site 1 (eastern bituminous coal)
 - Tekran
 - Horiba
 - Thermo Electron
 - Foney (Genesis)
 - Sorbent Traps
 - The Tekran, Thermo Electron, and sorbent traps passed

Mercury CMM Test Programs

- RATA Tests at Site 2 (eastern bituminous coal)
 - Tekran
 - Horiba
 - Sorbent traps
 - Tekran and sorbent traps passed
- EERC and other research groups
 - Primary instruments used are Tekran and PS Analytical
 - Used in field for research purpose
 - Substantial short-term data comparing results to OH method

Comparison of CMM Results

Relative Accuracy Test Comparing Two CMMs*

Criteria: $RA \leq 20\%$ or $\leq 1 \mu\text{g}/\text{m}^3$ absolute value of mean difference, if mean RM is $< 5 \mu\text{g}/\text{m}^3$

Test	Site 1		Site 2	
Instrument	Tekran	Horiba	Tekran	Horiba
Mean Difference, $\mu\text{g}/\text{m}^3$	0.51	1.59	0.26	1.57
Relative Accuracy, %	18.9	51.5	10.5	49.3

*The reference method was nine paired OH sample trains.

EERC Field Experiences

- Siting
- Filtration
- Conversion/conditioning units
- Sample transport
- Calibration
- Spiking
- Instruments

Operational Manpower Requirements

- Extensive initial training from vendor
- An instrument technician will be required to perform:
 - Daily calibration error tests
 - Weekly system integrity checks
 - Quarterly linearity checks
 - Annual RATA
 - Maintenance as needed
- Coordination of RATA testing

Siting Issues Practical Considerations

- Power requirements at the sample extraction location
- Available ports (RATA requirements)
- Compressed air requirements
 - Dry, oil-free
 - Hg-free
 - High volume
 - Argon needed for CVAF systems
- Transport of sample
 - Length of sample line
 - Weather conditions
- Instrument shack (temperature must be constant)
- Wet stacks

Wet Stacks Siting Issues

- Plugging of ISP sintered metal filter
- What is a representative sample?
- How do you treat the capture and/or release of Hg from water droplets?

Sample Filtration ISP

- Sintered metal filter may react with mercury in flue gas.
- Plugging of sintered metal filter with some flue gases. Do NOT have cold spots as acid condensation will quickly cause plugging.
- Have a blowback feature as part of your ISP.

Sample Transport

- Materials
- Temperatures
 - 300°F or greater for raw sample gas (Hg² tends to stick)
 - 275°F or greater for conditioned sample gas
- Condensate
 - Selenium
 - SO₃
 - Moisture
- One of the major issues that has not been resolved

Data-Handling Issues

- Software custom-designed for specific facilities
- Instrument vendors need to design for power plants rather than researchers
- Tied to the data acquisition systems that currently exist
- Flags or alarm systems
- Required calculations

Horiba/NIC DM-6B

Pretreatment/Conversion Thermal Catalytic Systems

- Uses a catalyst to reduce all mercury forms to Hg^0 .
- Acid gases must be removed to prevent conversion back to nonelemental Hg forms during cooling; may or may not use wet chemicals to do this.
- Speciated mercury is obtained using dual detectors or pretreatment systems.
- Life span of the catalyst has been a concern.

Summary of EERC Experience Using the Horiba/NIC CMM

Advantages

- Uses CVAA for mercury analysis, which is generally simpler to use than AF-based systems.
- Costs somewhat less.
- Does not use a gold trap or argon.
- Is more portable.
- Has fewer power requirements.

Summary of EERC Experience Using the Horiba/NIC CMM

Disadvantages

- Is less versatile—catalyst life may limit its use to select plants (i.e., those using western coals).
- Catalyst is expensive (approx. \$750).
- May require the addition of HCl to zero gas in order to prevent NO_x -related loss of catalyst life.
- May require more wet chemistry than would be desired from a dry system.
- Has a selenium problem.
- Engineering layout is poor.
- Uses fragile glassware.
- Poor service from Horiba, which is trying to set up its distribution and service network.

Horiba/NIC – Current Research

- Currently testing a higher-temperature catalyst.
- Using a water injection system to flush out selenium buildup in sample line.
- Providing new solenoid valve system so that HCl injection only goes through the total mercury side.
- Testing a new CVA system (NIC AM-4).

Effect of Combustion Modifications on Hg Emissions

Longer-Term CMM Data for a Lignite (hourly averages)

Impact of Selenium on Mercury Measurement Using a Horiba/NIC DM-6B

Tekran Model 3300

Thermal Dilution Systems

- Minimal wet chemicals are used.
- Sample is diluted for transport.
- All forms of mercury are thermally reduced to Hg^0 .
- Scrubbing of acid gases prevents conversion back to nonelemental Hg forms during cooling and eliminates gold trap poisoning problems.
- Must have a highly sensitive instrument such as AF.
- Must accurately calculate dilution ratio.

Summary of EERC Experience Using the Tekran CMM

Advantages

- Has the potential to be usable on a wide range of combustion systems.
- Has no catalyst limitations.
- Has demonstrated longer-term capabilities.
- Is an almost completely dry system.

Summary of EERC Experience Using the Tekran CMM

Disadvantages

- Is a relatively large instrument.
- Is more costly.
- Dilution ratio has the potential to change.
- Requires argon.
- Has a gold trap that has the potential to be poisoned.
- Concentration is reported on a wet basis. Additional measurements will be needed to report on a dry basis.
- SO_3 condensation may be a long-term maintenance issue.
- Is generally more complex than CVAA systems.

Hg Data Collected at a Slipstream Pilot Unit Located at a Lignite Facility

CMM Advice

- Before purchasing an instrument, have the vendor test it at your facility; a dry catalytic system is simpler to operate and troubleshoot but cannot be used at all facilities.
- Be sure to plan all aspects of the purchase, including training of personnel. These instruments have a fairly steep learning curve.
- Understand all aspects of PS 12A. As currently written, the certification of the instrument, locating the instrument, and on going QA/QC will be complex, costly, and time-consuming.

CMM Advice

- Substantial space is required as CMMs are relatively large and heavy; therefore, some type of pulley or trolley system is advisable.
- All CMMs require substantial power and more than one circuit.
- Some type of temperature-controlled area is needed for the analyzer portion of the system. The calibration will drift if the temperature changes.
- There are still unknowns as to the length of heat trace line that can be used between the sample probe and the instrument.

CMM Advice

- In high-acid flue gases or wet stacks, the ISP must be heated to $>260^{\circ}\text{C}$ to prevent plugging.
- A source of dry, clean, compressed air is necessary, particularly for the Tekran.
- Have a Cav Kit or the equivalent on-site for troubleshooting.
- Become GOOD friends with your vendor.

EERC Conclusions and Recommendations

- Currently, CMMs are difficult to use and require a substantial amount of engineering support to operate well. Remember **KISS**.
- More research is needed to provide effective, cheap, and simple pretreatment/conversion systems.
- PS 12A QA/QC procedures must be evaluated over time to determine what is necessary to ensure the high-quality data that is needed for a cap-and-trade structured rule to work properly.

Technologies Not Commercially Available – Many Under Development

Scientists from the R&D Corporation have created this model to illustrate how a "smart computer" could look like in the near future. However, the model technology will not be commercially available for the many years. After the scientific model, which that the computer will require not yet invented technology to actually work, but it may have some scientific progress is required to solve these problems. With adequate hardware and the software language, the computer will be easy to use.

Contact Information

EERC
Energy & Environmental Research Center
University of North Dakota
15 North 23rd Street
PO Box 9018
Grand Forks, North Dakota 58202-9018

World Wide Web: www.undeerc.org
Telephone No. (701) 777-5000
Fax No. (701) 777-5181

Dennis L. Laudal Senior Research Advisor (701) 777-5138 dlaudal@undeerc.org	Grant E. Dunham Research Manager (701) 777-5034 gdunham@undeerc.org
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APPENDIX C

FINAL REPORT FOR RESEARCH PROJECT ENTITLED DEVELOPMENT OF A NOVEL PETROLEUM BIOTECHNOLOGY

DEVELOPMENT OF A NOVEL PETROLEUM BIOTECHNOLOGY

INTRODUCTION

This project is an effort to develop a novel biotechnology to mitigate production of hydrogen sulfide (H_2S) in the petroleum industry, to promote methane (CH_4) production in oil and gas fields, and to enhance oil recovery, based on a recently developed Energy & Environmental Research Center (EERC) sulfide control additive capable of effectively controlling microbial H_2S production.

Sulfate-Reducing Bacteria and Sulfide in the Petroleum Industry

Production of sulfide in oil and gas fields is currently an unresolved issue for the petroleum industry. Sulfide is corrosive and toxic, and the overall economic impact of reservoir souring can be very significant. Sulfate-reducing bacteria (SRB) contribute to the production of sulfide. If SRB are inhibited, production of H_2S will subsequently be controlled.

In addition to causing the souring problem, SRB may also decrease methane production. It is well-documented that SRB are competitors of methanogenic bacteria. SRB compete with methanogens for hydrogen, the electron donor, in forming H_2S and CH_4 . In this competition, SRB always outcompete methanogens, resulting in more H_2S production and less methane formation. Methane is a major component of natural gas, and it is highly desirable to promote biogenic methane formation in oil and gas fields.

Biodegradation of Residual Oil to Methane

In recent years, the ability of anaerobic microorganisms to biodegrade a variety of hydrocarbons has been well-documented. In fact, gases of biological origin are believed to be primary by-products of anaerobic oil decomposition in petroliferous deposits. *n*-Alkanes, a major fraction of most crude oils, have recently been found to be biodegradable under methanogenic conditions, both as pure substrates and in oily mixtures, and could be a substantial source of methane in biodegraded oil resources. In the United States, energy recovery from marginal wells approximates 1 million barrels of oil per day, which equates to about 19% of domestic oil production (www.fossil.energy.gov/programs/oilgas/marginalwells/index.html). It may be possible to increase total energy production in marginal wells by converting a portion of the unrecoverable oil in marginal wells to methane.

Recent Technologies in Oil Recovery

Growing global demand for oil and gas could greatly increase demand for tertiary oil recovery. The National Institute of Petroleum and Energy Research estimate that 27% of oil reservoirs may be good candidates for microbial improved oil recovery. Currently, oil recovery techniques extract only about 45% of in-place oil resources, leaving the remainder stranded in mature fields. Developing new technologies to recover even a fraction of such a large energy pool is of great interest to help nations reduce reliance on foreign imports and increase the value of domestic reserves (www.fossil.energy.gov/programs/oilgas/marginalwells/index.html).

Traditional methods of tertiary oil recovery are costly for widespread use in the oil industry. Recently, some new biotechnologies have been reported. The core of these microbial enhanced oil recovery (MEOR) technologies is to inject inorganic nutrients into an oil and gas well to stimulate some beneficial microorganisms (e.g., denitrifiers) that live in virtually every oil and gas reservoir. These bacteria grow rapidly, outcompeting harmful SRB for basic carbon and nutrients. As SRB are outcompeted, sulfide production is reduced and the by-products produced by the beneficial microorganisms mobilize residual oil trapped within the reservoir. It has been reported that this new technology is capable of significantly enhancing oil production at a reduced cost and prevents the production of poisonous and corrosive hydrogen sulfide in oil and gas reservoirs.

Hypothesis of the Project

Recently, the EERC developed a sulfide control additive that is capable of selectively killing SRB without adversely affecting other microorganisms. This additive (referred to as “EERC additive”) is relatively nontoxic. In the U.S. Environmental Protection Agency’s (EPA’s) “National Recommended Water Quality Criteria,” both “Priority Toxic Pollutants” and “Nonpriority Pollutants” are listed, and none of the EERC additive components is included in either of the lists. It is, therefore, possible to develop a formulation for an additive that may 1) prevent souring of oil, 2) potentially promote methanogens by inhibiting SRB, and 3) enhance total gas (including but not limited to methane) production to improve oil recovery.

Compared to current technologies, it is expected that if an EERC additive formulation is developed, the new formulation would be better than the current commercial ones for the following reasons:

1. Some current technologies only marginally suppress SRB by stimulating denitrification; the EERC additive, however, directly selectively kills SRB.
2. Killing SRB will subsequently promote methanogens because of reduced competition. An increase in methane not only mobilizes residual oil, but also directly increases production of natural gas.

GOALS AND OBJECTIVES

The goals and objectives of this subtask are to:

1. Test the hypothesis that the EERC additive may prevent souring of crude oil and may, potentially, promote methanogens.
2. Conduct preliminary experiments for future development of an EERC additive formulation that may mitigate hydrogen sulfide, enhance oil recovery, and increase methane production.

EXPERIMENTAL

Preliminary Experiment

A preliminary experiment was undertaken to examine the effects of EERC additive on H₂S production. The experiment was conducted with 28-mL anaerobic culture tubes. Since, at that time, a fresh crude oil and formation water sample could not be procured, a wastewater sample collected from a sugar production facility was used for this experiment. Sugar industry wastewater produces a significant amount of H₂S because of the presence of S-containing biochemical compounds (e.g., S-containing proteins) in the wastewater. To ensure a measurable effect, Na₂SO₄ was added to the wastewater sample at a final concentration of 3 g/L. The sample was then dispensed into the tubes, and each tube received 20 mL of the wastewater. EERC additive was then added at a final concentration of 0 (the control group), 0.5, 1, 2.5, and 5 mM, respectively; each concentration group consisted of three tubes (triplicates). The tubes were then sealed with butyl rubber stoppers and aluminum crimpers and incubated at 30°C in the dark for 4 weeks.

After 4 weeks of incubation, headspace gas samples were analyzed for H₂S. Gas samples from the tubes were analyzed using a gas chromatograph (GC) (Agilent GC 6890) equipped with a thermal conductivity detector (TCD). However, GC analytical results showed that TCD was not sensitive to detect H₂S in some samples since the H₂S levels in those samples were too low. The H₂S in the liquid phase was subsequently measured using a sulfide test kit, Model Kit P-7C, manufactured by LaMotte Company, Chestertown, Maryland. The liquid samples were first filtered through a 0.22-μm syringe filter, followed by reacting with the test reagents, and then measuring absorbance at 664 nm using a Beckman DU 650 spectrophotometer.

The results are plotted in Figure 1. The % sulfide reduction is calculated as follows:

$$\% \text{ sulfide reduction} = (\text{control} - \text{experimental}) / \text{control} \times 100\%$$

The control is the mean of the sulfide concentration in the triplicate 0-mM samples. As shown in Figure 1, EERC additive effectively reduced H₂S production in all the experimental groups. Another experiment was then performed to further decrease the EERC additive concentrations to 0.25 and 0.1 mM. The experimental results are plotted in Figure 2. At these two lower concentration levels, EERC additive was still effective, and a 74.8% and 44.5% sulfide reduction was achieved, respectively. These results confirmed that EERC additive is able to effectively mitigate sulfide production, and the inhibitory effect is concentration-dependent.

Crude Oil and Formation Water Experiment

Sour crude oil and formation water samples were collected from the E.L. Gudvangen well, located in the McGregor Field, 4 miles west of the town of McGregor, North Dakota. Sterile (autoclaved) 0.5-gallon mason jars were used as the sample containers. The crude oil and formation water filled to the top of the jars and were sealed with the lids to ensure anaerobic conditions. The samples were then shipped to the EERC and immediately stored in a refrigerator at 4°C.

Figure 1. Effects of EERC additive on sulfide concentration (liquid phase) in a sugar industry wastewater (1). Error bars represent standard deviation of triplicate samples.

Figure 2. Effects of EERC additive on sulfide concentration (liquid phase) in a sugar industry wastewater (2). Error bars represent standard deviation of triplicate samples.

Experiments were conducted to determine the optimal concentration of EERC additive for H₂S control. The experiments were set up in an anaerobic glove box (Coy Laboratory Products Inc. Grass Lake, Michigan). Serum bottles (125 mL) were used as the experimental vessels. Since the concentration of EERC additive that would be effective was unknown, once again, the experiments were started with a concentration profile experiment. There were five experimental groups amended with different concentrations of EERC additive: 0 (control), 0.5, 1, 5, and 10 mM, respectively. Each group consisted of three bottles (triplicates), and each bottle received 70 mL of the oil–water (crude oil and formation water, 1:1) mixture. The bottles were then sealed with butyl stoppers and aluminum crimpers and incubated in the dark at 30°C.

After 14 weeks of incubation, gas-phase samples from the bottles were analyzed using a GC (Agilent GC 7890) with a flame photometric detector (FPD), a selective detector for sulfur compounds with low detection-level capability and high sensitivity. As illustrated in Figure 3, EERC additive completely prevented H₂S production at 5 and 10 mM and significantly reduced H₂S at 0.5 and 1 mM, suggesting that introducing EERC additive into an oil well could potentially prevent souring of the crude oil.

Effects of EERC additive on Methane Production

To determine whether EERC additive is capable of promoting methane formation by suppressing SRB, an experiment was conducted with 160-mL serum bottles (Figure 4). Each bottle received 40 mL of 1:1 oil and formation water mixture, and 40 mL of anaerobic mineral growth medium containing 2 g/L yeast extract (in replacement of vitamins) and methanol, acetate, formate (2 g/L of each). The initial headspace gas was H₂/CO₂ (80/20). EERC additive was added to half of the bottles at a final concentration of 1 mM. The bottles were then sealed with butyl stoppers and aluminum crimpers and incubated at 30°C in dark. Gas-phase samples were taken and analyzed using GC with a flame ionization detector (FID). After 6 weeks of incubation, methane was detected in a culture with EERC additive, carbon, and H₂/CO₂. After another 4 weeks of incubation, methane was detected in several other cultures in the C–H₂–EERC additive group; in contrast, no methane was detected in the cultures without EERC additive. However, after initial methane formation, the methane production stopped, and no further methane production was detected. We postulate that the methane might be converted from the limited-headspace hydrogen; and there may be lack of microorganisms in the culture that were able to degrade the crude oil to hydrogen or prolonged incubation time may be needed to allow the culture(s) to develop this degradation capability. Nevertheless, these results suggest that EERC additive seemed to have the potential to promote methane formation by suppressing SRB.

Total Gas Production

Gas production is an important issue in MEOR since the produced gases (N₂, CO₂, etc.) mobilize residual oil trapped within the reservoir. Currently, MEOR is generally achieved by injecting nutrients and organic carbon into an oil and gas well to stimulate a microbial gas production, and the cost of organic carbon is among the major costs. To develop a potential formulation for MEOR, an experiment was set to determine whether organic carbon is necessary

Figure 3. Effects of EERC additive on hydrogen sulfide (gas phase) produced in the oil and formation water experiment. Error bars represent standard deviation of triplicate samples.

Figure 4. The 160-mL serum bottles as the experimental vessels. The anaerobic tubes in the background were used for MPN enumeration on SRB.

for gas production. The experiment was set up with 160-mL serum bottles, and all bottles received 40 mL of the oil, the formation water, or both (1:1) and 40 mL of mineral medium containing 2 g/L of yeast extract. The initial headspace gas was nitrogen. The bottles were divided into two experimental groups: with and without the addition of the organic carbon (methanol, acetate, formate; 2 g/L of each). The bottles were then sealed with butyl stoppers and aluminum crimpers and incubated at 30°C in the dark. After 6 weeks of incubation, the total gas produced in each bottle was measured with a 50-mL glass syringe (B.D. Yale, Becton, Dickinson & Company, New Jersey, Figure 5). The produced gas volume was certainly underestimated since the weight of the syringe plug (65.8 g) would more or less compress the gases. However, this would not significantly affect the relative comparison of the produced gas volume among these bottles since all bottles were measured in the same way. Regardless of whether the inocula were crude oil, formation water, or a mixture, both “with C” and “without C” groups produced comparable amounts of gases (Figure 6), suggesting that under our experimental conditions the added organic C played a minimal role in gas production; this observation would have practical application potential to significantly cut some material costs in MEOR.

As shown in Figure 6, there was little difference in total gas production between the “crude oil” and “crude oil + formation water” groups. The “formation water” group, in contrast, produced less than ¼ volume of the gas, indicating that the fermentative microorganisms in our sample were mainly present in the crude oil rather than the formation water.

MPN Results

The MPN number of SRB in the original 1:1 oil–water mixture was enumerated and the result was 2.3×10^2 MPN/mL. After 2 months of incubation at 30°C with the mineral medium, yeast extract, organic carbon, and headspace hydrogen, the MPN of the culture without EERC additive amendment was 9.6×10^5 /mL, while the MPN of the culture amended with 1 mM EERC additive was 5.1×10^3 /mL. The results of the SRB MPN determinations are listed in Table 1. These results provide direct evidence that EERC additive effectively reduced the SRB number in the amended culture.

CONCLUSIONS

Experimental results of this project proved that under our experimental conditions, EERC additive was able to mitigate H₂S production in the oil–water mixture, suggesting that introducing EERC additive into an oil well may potentially prevent souring the crude oil. The MPN results further provided direct evidence that EERC additive effectively reduced the

Table 1. Results of SRB MPN Determinations

Experimental Group	MPN/mL	SRB Reduction
Original 1:1 Oil–Water Mixture	2.3×10^2	
After 2 Months at 30°C		
Without EERC Additive	9.6×10^5	
With EERC Additive	5.1×10^3	99.4%

Figure 5. The total gas produced in each bottle was measured with a 50-mL glass syringe.

Figure 6. Results of the total gas measurement. Error bars represent standard deviation of triplicate samples

population of SRB in the amended cultures. Analysis of methane production suggested that EERC additive might have the potential to promote H₂-utilizing methanogens by inhibiting SRB. Measurement of the total gas production revealed that under our experimental conditions, the added organic C played no apparent role in gas production; this observation would have practical application potential to significantly cut some material costs in MEOR. Results of the gas production experiment also indicated that the fermentative microorganisms in our sample were mainly present in the crude oil rather than the formation water.

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APPENDIX D

FINAL REPORT FOR RESEARCH PROJECT ENTITLED ENGINEERING OPPORTUNITIES AND CHALLENGES OF CO₂ MITIGATION USING MICROALGAE IN FOSSIL FUEL-FIRED POWER PLANTS

ENGINEERING OPPORTUNITIES AND CHALLENGES OF CO₂ MITIGATION USING MICROALGAE FROM FOSSIL FUEL POWER PLANTS

Ye Zhuang and Dennis Laudal
Energy & Environmental Research Center

1.0 BACKGROUND

Public concerns over global climate change due to anthropogenic emissions of greenhouse gases such as CO₂ has resulted in significant pressure on all industries to seek effective ways to reduce CO₂ emissions. Because coal-fired electric utilities are one of the largest sources of CO₂ emissions, the pressure has been more intense. All fossil fuels originate from biomass produced by photosynthetic fixation of CO₂, the process which green plants produce sugar from sunlight, CO₂, and water, with oxygen as a waste product. Photosynthesis is essentially nature's way of recycling CO₂. However, the process of indirect CO₂ capture by planting forests and other agricultural crops has been deemed to be an inadequate solution to the accumulation of greenhouse gases in our atmosphere. The potential CO₂ capture by planting agricultural crops is expected to result in only a 3%–6% reduction compared to the CO₂ generated burning fossil fuels (1). The one possible exception is to utilize microalgae for the direct treatment of flue gas. Microalgae have the ability to fix CO₂ using solar energy, with an efficiency 10 times greater than that of terrestrial plants (2). In addition it grows rapidly and can be incorporated into engineered systems, such as photobioreactors. It has been found that the high CO₂ content of power plant flue gas, ~14% compared to only 350 ppm in the atmosphere, greatly enhanced algae growth (3). It is estimated that algae produce between 73% and 87% of the net global production of oxygen (4).

Algae cultivation has been done since the early 1970s for the production of biofuels and is considered an environmentally friendly process. Essentially the only components needed to grow algae are sunlight, CO₂, nitrates, and water. Even the water can be low quality, including most wastewaters and saline water. Although the maximum oil content of microalgae is only about 40% compared to 55% for sunflower seeds, microalgae's very high growth rate and photosynthetic efficiency mean it has the potential to sequester substantially more CO₂ and produce a lot more biofuel than any other crop. Table 1 shows the typical yields of biodiesel for various crops. Algae are the only biofeedstock that can theoretically replace all our current and future petrofuel needs and do not compete with agriculture food products.

The growth in the number of companies directly involved in producing biofuel from algae is quite impressive, as shown in Table 2. The most prominent companies are listed below:

• AquafLOW Bionomic	• PetroAlgae	• Seambiotic
• Cellana	• PetroSun	• Solazyme
• GreenFuel	• Sapphire Energy	• Valcent
• OriginOil		

Table 1. Oil Production Potential for Various Crops (4)

Crop	Biodiesel, gallon/acre
Algae	1600–8550
Corn	13
Soy	47
Safflower	83
Sunflower	80–100
Castor	150
Canola	171
Jojoba	192
Coconut	290
Palm	640
Chinese Tallow	500–1000
Peanut	90

Table 2. Number of Companies Directly Involved in Producing Fuels from Algae (4)

Year	No. of Companies
2001	1
2002	2
2003	4
2004	5
2005	10
2006	15
2007	25
2008	50

A discussion of the status of each of these companies is provided in the *Oilgae Digest* (3).

This report will focus on the status and research needs for using microalgae for sequestering CO₂, in particular from fossil fuel-fired power plants and areas that the Energy & Environmental Research Center (EERC) strengths would be beneficial in solving some of the issues that currently limit the technology.

2.0 CURRENT RESEARCH STATUS

Algae farms have been cultivated for many years to produce high-value products such as biofuels, vitamins, cosmetics, and food. Although there has been some effort to intentionally use microalgae to capture CO₂ from point sources, most of the research and development has been to produce fuel products. However, beginning in the late 1990s, the potential of a carbon-constrained world has resulted in a renewed interest by select companies, universities, research

organizations, and the federal government both in the United States and other countries to optimize the ability of microalgae to sequester CO₂ from point sources. Some of the challenges and research needs are discussed in this section.

2.1 Microalgae Cultivation

The major challenge to industrial microalgae culturing is to devise and develop new procedures for cultivation and the finding of algal strains that have substantially improved solar efficiencies and are better able to utilize CO₂. Much of the early work was primarily to identify strains of microalgae that produced high yields of lipids for biofuel production. The most tested strains of microalgae are from species *Chlorella*, *Chlorophyta*, and *Botryococcus*. Substantial work is still ongoing to identify new strains that may offer greater CO₂ uptake and higher yields of lipids (5). This includes the testing of both natural and genetically modified strains.

2.1.1 Open Pond Systems

Algae are grown either in open pond cultivation systems or closed systems (photobioreactors). Large-scale microalgae cultivation using open pond systems have been in use for some time (6) to produce healthy foodstuffs, food additives, pigments, secondary metabolites, alternative fuel, and in wastewater treatment (7–9). The conventional method for the mass algae cultivation using open ponds is a raceway design, using sun as the light source. Such a system is shown in Figure 1. Open ponds usually consist of either circular ponds with a rotating arm to mix the culture or long channels in a single- or multiple-loop configuration stirred by paddle wheels. The primary advantage of open pond systems is that they are relatively simple to design and only require what nature provides (direct sunlight). However, such an approach suffers from a number of disadvantages, particularly as they relate to treating flue gas from large power plants.

Figure 1. Photograph of Seambiotic small-scale open pond.

2.1.1.1 Low Efficiency in Light Utilization

Light in the wavelength of 400–700 nm is the basic energy source for algae growth; hence, light-harvesting efficiency of algae is of critical importance. The penetration distance of light into algal culture is usually less than 10 cm, depending on algal density. As a result, over 60% of algal culture remains in complete darkness (10), which is the primary reason algal production in open pond systems is far below the theoretical algal productivity (11).

2.1.1.2 Requirement of Large Land Areas and Huge Loss of Culture Medium

As the result of low algae yield and huge volumes of flue gas that need to be treated, enormous land areas are required for open pond systems to capture CO₂ effectively from power plants. For example, it is estimated that a 500-MW power plant will need 8000–16,000 acres of algae ponds. Open algal systems usually perform at their best under high sun irradiation conditions. However, this also results in huge loss of culture medium (water) through evaporation. Using methods recommended by the U.S. Environmental Protection Agency (EPA), it is estimated that approximately 1200 tons of water would evaporate per 1000 acres per day (12, 13), resulting in the need for large volumes of makeup water.

2.1.1.3 Contamination Control

It is almost impossible to keep the culture environment constant and prevent cross-contamination in an open pond system. Many contaminants from the surrounding environment may enter the algae system and affect algae growth. This includes wild algae strains, bacteria, and other inorganic and organic contaminants.

2.1.1.4 High Harvest Cost

Because of low algal cell density requiring large areas, a huge volume of algal cultures need to be harvested. This greatly magnifies the cost of processing, thus substantially increasing the final cost of the product.

2.1.2 Closed Systems (photobioreactors)

As a result of these disadvantages, closed systems (photobioreactors) would most likely be used for larger-scale activities that would be needed to treat flue gas from power plants. Compared to open systems, control of contamination is easier and they provide more accurate control of operational parameters including culture pH, nutrients, temperature, and light irradiation. As a result, closed systems have a much greater potential for improved algae yield. High cell mass productivities attained in a closed system are up to three-fold greater than those obtained in an open system (14). In theory, harvesting of the algae should also be simpler, significantly reducing harvest costs.

Because of their complexity and the intensive capital investment required, closed systems have not been favored by the industry. To become profitable and fully competitive, the challenge is to design a closed system that produces a high concentration of biomass with high metabolite productivity. In this way, the higher capital cost of a closed system can be offset by substantially

lower operating costs compared to open ponds. The use of larger-scale photobioreactors is still in its infancy, and substantial effort is going into designing novel photobioreactors that are less costly and more efficient (15–17). In order to maximize advantages and minimize disadvantages, several key processing parameters need to be optimized.

2.1.2.1 Reactor Design

A reactor with high area-to-volume ratio is needed to improve light penetration to increase photosynthetic efficiency. Some of the reactors that are designed to increase area-to-volume ratio include are tubular, flat plate, pyramid, and fermenter systems. Figure 2 is a photograph of a small pilot tubular photobioreactor. Tubular and flat plate reactors are the most popular choices since they use free sunlight, while the other two use artificial illumination. However, artificial illumination provides more accurate control. Scale-up of these systems is challenging (18). For example, in order to provide enough culture volume and improve the gas transfer rate, the reactor diameter needs to be large which, in turn, decreases the area-to-volume ratio and, consequently, constrains photosynthetic efficiency. Temperature control in a large-scale application is problematic since algae cultivation generates a considerable amount of heat. There is a decrease in photosynthetic efficiency with increases in temperature. Also, depending on the materials of construction and the configuration of the reactor, the cost of the reactor can be high and large area lands would still be needed.

Figure 2. GreenField pilot-scale tubular photobioreactor.

2.1.2.2 CO₂ Transfer

When CO₂ is injected into a culture, a concentration gradient builds up as it is consumed by cells. Mass transfer of CO₂ from the gas phase to the cell phase occurs through sequential stages, with the liquid film providing most of the resistance. Consequently, the liquid film

resistance adjacent to the interface limits the rate of CO₂ transfer to the cells (19). The rate of mass transfer of CO₂ (N_{CO_2}) is given by:

$$N_{CO_2} = k_L \cdot a \cdot (C_{CO_2L^*} - C_{CO_2L})$$

Where:

k_L = liquid-phase mass transfer coefficient.

a = the specific area available for mass transfer.

$C_{CO_2L^*}$ = the concentration of CO₂ in the culture medium that would equilibrate its actual partial pressure on the gas side.

C_{CO_2L} = the concentration of CO₂ in the bulk of culture medium.

The lumped parameter $k_L a$ characterizes the CO₂ mass transfer capability of the reactor and is of primary importance in the design, scale-up, and operation of a biomass culture system (20). One example is that comparative studies (21, 22) have indicated that microporous hollow fibers instead of plain bubbling enhance CO₂ mass transfer. Both passive and active modes have been devised and tested to improve transfer of CO₂ through the interface between the gaseous mixture and the liquid medium culture. Passive gas-to-liquid transfer through a membrane in close algal systems can prevent CO₂ loss to the atmosphere, provide accurate control of the CO₂ transfer rate, and does not require an air/CO₂ mixing chamber. However, passive systems have a high capital investment and suffer from decreasing transfer rate with time as a result of bacterial contamination. Active aeration, on the other hand, is easy to apply in a large-scale system but has to be cleaned periodically because of biofouling and suffers CO₂ loss to the atmosphere as a result of the low residence times of the gas in the culture.

2.1.2.3 Oxygen Removal

Oxygen build-up in the medium results in a decrease in the photosynthetic efficiency of the microalgae (16). Also, once dissolved O₂ in the liquid culture medium gets above 35 mg/L, it is toxic to most algae. Accumulation of O₂ in the liquid culture medium has been one of the most difficult problems to overcome (17) and has been the subject of much research in designing photobioreactors. While different degassing technologies have been tested, the oxygen removal efficiencies from microalgal cultures are still not at a satisfactory level to make the operation profitable. Also a low-cost method to collect oxygen is an essential aspect of many of the scenarios proposed for power plant flue gas treatment. The idea is that the generated oxygen would be pumped back to the combustor, resulting in a more purified CO₂ stream to algae.

2.1.2.4 Mixing

Adequate mixing is required in order to produce a uniform dispersion of microalgae within the culture medium, thus eliminating gradients of light, nutrient concentration (including CO₂), and temperature. However, current mixing techniques are often insufficient since the induced turbulence is random, i.e., not all algae cells are in and out of the illuminated area of the reactor as planned. Low-extent mixing can promote settling and, hence, emergence of dead zones where anaerobic conditions prevail, thus leading to cell deterioration and a consequent decrease in productivity (23, 24). Inadequate mixing also permits clumping of cells into aggregates of varying sizes, which is prone to decreasing mass-transfer rates (25). On the other hand, high mixing rates may lead to shear induced injury of cells (26, 27), which hampers their viability. As distinct microalgae have different sensitivities to shear, there is no single optimum mixing system for all microalgal species.

2.1.2.5 Light Management

The algal biofixation rate of CO₂ is related directly to light utilization efficiency and to cell density of the microalgae; therefore, optimized light management is crucial in maximizing algae yield in a closed system. The use of sunlight is the cheapest source, but the light cycle cannot be controlled, often precluding high biomass productivity. On the other hand, artificially illuminated reactors are typically expensive. To date, reactors that have shown the highest efficiency of light harvest are also the most expensive and most difficult to scale up. One technology that has shown promise is the use of fiber optic-based solar concentrators. These can effectively introduce light inside large-volume reactors, but it has been difficult to achieve a uniform lighting distribution within the photobioreactor.

Table 3 shows a comparison of the open ponds and the closed bioreactors. As can be seen from Table 3, the greatest advantage of open ponds is lower cost. The greatest advantage of the closed system is contamination control and greater productivity. Clearly, additional research and development are needed.

2.2 Power Plant Flue Gas and Microalgal Growth

The direct use of flue gas imposes extreme conditions on algae such as high temperature, high CO₂ concentration, and the presence of acid gases SO_x, NO_x, and HCl. Extensive efforts have been made to evaluate the inhabitation effect of acid gases of SO₂ and NO_x on the growth of algal strains. Some acidophilic algal strains have shown positive growth when aerated with simulated flue gas containing up to 50 ppm SO₂ and 100 ppm NO (28–30). A number of bench-scale investigations have been conducted to characterize the growth rate of microalgae under simulated coal flue gas conditions (31–36). Table 4 lists examples of bench-scale results that show positive growth of microalgae exposed to a variety of conditions.

Table 3. Various Parameters Showing the Relativity of Open Ponds vs. Closed Bioreactors¹

Parameter	Relative	Notes
Capital/Operating Costs	Ponds << PBRs ²	3–10 × lower cost!
Process Control	Ponds < PBRs	Very important in PBRs
O ₂ Inhibition	Ponds < PBRs	O ₂ greater problem in PBRs
CO ₂ Losses	Ponds ~ PBRs	Depends on pH, alkalinity, etc.
Water Losses	Ponds ~ PBRs	Depends upon cooling design
Contamination Risk	Ponds > PBRs	Much reduced for PBRs
Space Required	Ponds > PBRs	A matter of productivity
Productivity	Ponds < PBRs	3–5 times more productive
Biomass Concentration	Ponds < PBRs	3–5 times in PBRs

¹ Source: National Renewable Energy Laboratory.² Photo bio-reactors.**Table 4. Effect of Simulated Flue Gas on Microalgae Growth**

Algae	Temp., °C	CO ₂ , %	SO ₂ , ppm	NO _x , ppm	pH	Light Intensity, μE/m ² /sec	Growth Rate, g/m ³ /day	Ref.
Chlorella sp. T-1	35	10–15	5–20	15–60	6–8	110	~360	31
Chlorella vulgaris P-12	25	8–10	2	143	NA	1150	~2500	33
Chlorella sp.	26	2–15	NA	NA	NA	300	127–605	34
Chlorella KR-1	25	10–15	~50	~100	6.5	450	800	35
Chlorophyta	25	5	~300	~300	7.5	Sunlight	374	36

Limited pilot-scale studies have also been conducted to investigate the feasibility of CO₂ mitigation from power plant flue gas using algae. An example has been the development of a pilot-scale membrane photosynthetic reactor using thermophilic organisms. This type of reactor would be much smaller than those currently being proposed and tested (37). Positive growth of microalgae has been reported when a real flue gas from a pilot slipstream at 48°C was passed through a low-light-intensity (40–80 μE/m²-s) photobioreactor. Pilot-scale testing data (36) also have indicated that CO₂ captured by microalgae was directly dependent on the pH of the culture but was greatly impacted by differences in gas composition. In fact, it was found that maintaining a constant pH value of 7.5 in algae culture, approximately 75% CO₂ capture efficiency was achieved in a flue gas containing up to 300 ppm SO₂ and NO_x, respectively.

Although the tolerances for various components in flue gas will be dependent on the strains of microalgae selected, based on bench- and pilot-scale tests, Table 5 presents an estimate of the most likely limits. Temperature may be the most difficult constraint. A typical flue gas from a wet flue gas desulfurization (FGD) system is about 60°C, which is too high for most known algal strains and, therefore, some form of cooling will be necessary, resulting in higher costs. The SO₂ and NO_x constraints should not be that difficult to overcome. With the implementation of the Clean Air Act, most utility plants are being required to greatly reduce both gases to levels below those listed in Table 5.

Table 5. Estimated Operational Upper Limits of Algal/Power Plant System

Parameter	Value
Temperature, °C	45
CO ₂ , %	50
SO ₂ , ppm	300
NO _x , ppm	300
Dissolved O ₂ , mg/L	35
pH	6–8

Therefore, the emitted flue gas may only need limited or potentially no additional treatment for these components. In fact, NO_x is a required nutrient for microalgae, and it may be possible that a high level of NO_x control such as that provided by an expensive selective catalytic reactor (SCR) may not be necessary or desired. It may be possible that simply installing low-NO_x burners that are already common on most coal-fired utilities in the United States may be adequate.

2.3 Harvesting Algae

Compared to most other energy crops, harvesting algae presents unique problems that are a significant challenge to economical energy production from algae:

- The medium in which algae grows is different – other oilseeds are land crops, while algae grow in water.
- Microalgae's physical characteristics are significantly different from those of the primary oilseeds, the main difference being the size.
- Algae is harvested almost every day, for most, part, or all through the year, whereas harvesting for most oilseeds is quite seasonal in nature.

Owing to these reasons, harvesting algae, especially microalgae, could be a fairly expensive process. Methods that could potentially be used for harvesting include the following:

- Filtration – mechanical harvesting by means of strong membranes, such as microscreens.
- Chemical methods – chemical and/or biological harvesting by means of flocculants.
- Centrifugation

- Froth flotation – water and algae are aerated into froth, with the algae then removed from the water.

The ease in harvesting the algae depends primarily on the organism's size, which determines how easily the species can be settled and filtered. Unfortunately, the most rapidly growing algal species are frequently the smallest and most difficult to harvest. Thus it is necessary to maintain an effective interaction between the development of harvesting technologies and the selection of algal species.

3.0 POTENTIAL RESEARCH AREAS SUITED TO EERC STRENGTHS

It is highly unlikely that the EERC will be directly involved in the biological development of algal strains or in the cultivation process but may well be involved in other aspects of the overall process. For example, the EERC has extensive experience in power plant operation and emission and CO₂ mitigation issues that could be beneficial to the algae industry. Some of these are discussed below.

3.1 Light Management

Enhancing light harvest efficiency is one method that would greatly enhance algae growth. Therefore, providing an optimized light management system would improve the overall photosynthetic efficiency of algae. The efficiencies of solar concentration systems have significantly improved in recent years; 40%–46% overall efficiencies of the solar collector have been reported (38). However, better methods to uniformly and efficiently distribute light into algal cultures need to be investigated. Several approaches have been considered:

- Geometric configuration of algal cultivation system
- Light source arrangement
- Hybrid usage of natural and artificial light

New light management technologies and/or more innovative use of current technologies such as optical fibers may eventually allow closed photobioreactors to be competitive options for CO₂ mitigation for the coal-fired electric utility industry.

3.2 CO₂ Delivery System

A consistent CO₂ supply is a key processing parameter in algae cultivation. Although most of the so-called novel photobioreactors do, in fact, attempt to overcome the constraints related to control of pH, temperature, etc. (19), providing adequate amounts of CO₂ to microalgal cells is still poorly developed.

3.3 Oxygen Removal and/or Utilization

An efficient method of removing oxygen from the culture medium in massive algae-farming applications is important for two primary reasons. First is to maintain a stable algae

yield and, second, the generated oxygen is a valuable product both for oxygen-blown combustion and as a feedstock to produce other chemicals. Investigation of technologies and methods for improving the removal and recovery of oxygen provides the potential to not only facilitate algae growth but would also be beneficial from an economic perspective.

3.4 Water Management

Algae cultivation consumes a lot of water; therefore, an efficient water recovery management system will significantly reduce the cost of large-scale algae applications. One possibility is to recover the water in the flue gas from the power plant and use it as makeup water for the algae system. This would have the added advantage of cooling the flue gas. For example the Siemens technology for water recovery that is being tested at the EERC may hold some potential (39).

3.5 pH Management

Because of the acid gas constituents, continuous flue gas flowing through the algal cultivation system will cause the algae culture to become acidic, which will damage algae growth. However, there is the potential that the solid waste products from wet scrubbers or if a western coal is being fired, the highly basic fly ash can be used to neutralize the acid gases. Study on recycling coal combustion by-products such as fly ash and wet scrubber materials for algae cultivation should be considered.

3.6 Energy Balance Management

Since algae growth is very sensitive to temperature, heat management of the bioreactor is extremely important. The temperature of feed flue gas must be accurately controlled before it enters the algal system. In addition, the algae-drying process needs a low-Btu heat source. By providing an integrated heat-transfer system, the recovered waste heat from the power plant may be used for the algae-drying process. This would include utilizing the heat recovered when cooling the flue gas before it can be provided to the algae photobioreactor.

3.7 Overall Integration of the Algae and Power Plant Systems

The ultimate goal is to maximize the potential cobenefits that can be realized by operating the algae system and power plant in tandem. This includes the following:

- CO₂ to the algae from the flue gas
- NO_x to the algae from the flue gas
- Water recovery from flue gas to algae
- Oxygen from algae to the power plant
- Biomass waste product after removing the oil to be cofired with coal
- Biofuel that can be fired in the power plant used for transportation or as a feedstock for another product

Figure 3 provides a schematic of the potential of such an integrated system.

Figure 3. Schematic of an integrated coal-fired power plant utilizing an algae photobioreactor.

4.0 ECONOMIC COMPARISON

A detailed economic study was made by Kadam in 1997 (40) comparing the economic impact of microalgae fixation of CO₂ to using an monoethanolamine (MEA) CO₂ stripper followed by compression of the gas stream followed by the transport of the CO₂ stream for utilization or sequestration. The economic study was based on a 500-MW power plant located in the southwestern United States. A transportation distance of 100 km was assumed. For the microalgae option, it was assumed that an open pond system requiring 14,000 ha of land with an algal productivity of 45 g/m²/d would be used. Also the economic comparison evaluated a possible revenue stream from biodiesel production. On an annualized basis, the calculated cost for MEA followed by sequestration was \$40.50/ton of CO₂, compared to \$63.80/ton CO₂ for the microalgae facility. However, when the revenue stream from the biodiesel is factor, the microalgae pond may be very competitive depending on the value of the biodiesel. More up-to-date and detailed economic evaluations based on a variety of factors including a closed system are needed.

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