

# **BENCH-SCALE TESTS TO EVALUATE MERCURY FLY ASH INTERACTIONS**

EERC Proposal No. 98-0005-R1 Amount Requested: \$40,000

Submitted to:

Ms. Karlene Fine

State of North Dakota State Capitol 600 East Boulevard Bismarck, ND 58505

Submitted by:

Stanley J. Miller

University of North Dakota Energy & Environmental Research Center PO Box 9018 Grand Forks, ND 58202-9018

Starley J. Miller, Project Manager

Dr. Carl A. Fox, Director

Office of Research and Program Development

June 1998

## TABLE OF CONTENTS

LIST OF FIGURES ii							
LIST OF TABLES ii							
ABS	TRACT iii						
1.0	PROJECT SUMMARY 1						
2.0	PROJECT DESCRIPTION32.1 Phase II Statement of Work as Approved by DOE3Task 1 – Program Management4Task 2 – Coal Acquisition and Characterization4Task 3 – Analysis of Coal and Ash for Forms of Occurrence of Inorganic Elements5Task 4 – Forms-of-Occurrence Analysis Using USGS Protocol6Task 5.1 – Bench-Scale Study Focusing on Partitioning: Chlorine and Trace Elements7Task 5.2 – Mercury Sampling and Elemental Analysis8Task 6 – Large-Scale Integrated Combustion Study8Task 7.1 – Evaluation of Field Data on Organic Emissions9Task 8 – Integrated Combustion Study9Task 9.1 – Development of Engineering Model10Task 10 – Bench-Scale Study of Mercury–Fly Ash Interactions12Task 11 – Bench-Scale Study of Mercury–Fly Ash Interactions18						
3.0	STANDARDS OF SUCCESS						
4.0	BACKGROUND						
5.0	QUALIFICATIONS						
6.0	VALUE TO NORTH DAKOTA						
7.0	MANAGEMENT						
8.0	TIMETABLE						
9.0	BUDGET						
10.0	MATCHING FUNDS						

11.0	TAX LIABILITY	39
12.0	CONFIDENTIAL INFORMATION	39
13.0	REFERENCES	39
BUD	GET AND BUDGET NOTES	42
RESU	JMES Appendix	A

1.1

# LIST OF FIGURES

1	Phase II project organizational chart	
---	---------------------------------------	--

# LIST OF TABLES

## BENCH-SCALE TESTS TO EVALUATE MERCURY– FLY ASH INTERACTIONS

## ABSTRACT

The purpose of the project is to determine the mechanisms of trace element species formation and fate in coal-fired boilers and develop a predictive engineering model based on coal and combustion parameters. Participation in this project by the North Dakota Industrial Commission will ensure the testing of North Dakota lignites. This project will provide essential information on the fundamental factors that influence mercury speciation and control in lignite-fired power plants. In Phase I of the program, a team led by Physical Sciences Inc. (PSI) and involving researchers from the University of Kentucky, U.S. Geological Survey, the Massachusetts Institute of Technology, the University of Arizona, the University of Connecticut, and Princeton University has a detailed research program with three major objectives: 1) to elucidate the important mechanisms of toxics formation and partitioning, 2) to develop submodels for the appropriate trace toxic species transformations, and 3) to incorporate these mechanisms into an engineering model to predict trace toxic formation, partitioning, and fate based upon coal and combustion parameters.

The Energy & Environmental Research Center (EERC) was invited by PSI to join the Phase II research team for this project titled, "Toxic Substances from Coal Combustion – A Comprehensive Assessment," which is being funded by the U.S. Department of Energy (DOE) through the DOE "Mega PRDA" (program research and development announcement) solicitation. The EERC participated in Phase I only to the extent of providing samples exposed to mercury for x-ray absorption fine structure (XAFS) analysis. However, the EERC was invited to formally join the Phase II team because of the extensive background and capabilities of the EERC in the areas of mercury measurement and control applied to coal-fired boilers. Under the terms of the PRDA, a Phase II downsizing selection proposal was submitted to DOE in July 1997. Task 11 of the Phase II proposed work, titled "Bench-Scale Study of Mercury-Fly Ash Interactions," would be conducted at the EERC. DOE subsequently awarded PSI a Phase II contract and has approved the Phase II statement of work. One of the requirements of the award is a minimum of 20% industrial cost share. The total Phase II PSI project has a budget of approximately \$2.4 million. Task 11 of the Phase II work has a budget of \$200,000, with a required industrial cost share of \$40K. This proposal requests \$40K from the North Dakota Industrial Commission to meet the Task 11 cost-share requirement. The cost share for the other tasks is being provided by the other team members. Even though the requested cost share is in support of Task 11 only, this participation will provide access to the entire Phase II \$2.4 million project, leveraging the investment by a factor of 60. Phase I test coals included three eastern bituminous and one western subbituminous coal, but no lignite. A key provision of the Phase II work is the inclusion of a North Dakota lignite as one of the study coals. Results from the work will provide an improved understanding of trace metal species formation and fate, with emphasis on mercury. This understanding will help to ensure that North Dakota lignite fuels and byproducts are utilized in an environmentally acceptable manner and that concerns over emissions of toxic species are met with minimal economic impact.

## BENCH-SCALE TESTS TO EVALUATE MERCURY-FLY ASH INTERACTIONS

## 1.0 PROJECT SUMMARY

The goal of the project is to determine the mechanisms of trace element species formation and fate in coal-fired boilers and develop a predictive engineering model based on coal and combustion parameters. In Phase I of the program, a team led by Physical Sciences Inc. (PSI), and involving researchers from the University of Kentucky (UK), U.S. Geological Survey (USGS), the Massachusetts Institute of Technology (MIT), the University of Arizona (UA), the University of Connecticut (UConn), and Princeton University have begun a detailed research program with three major objectives: 1) to elucidate the important mechanisms of toxics formation and partitioning; 2) develop submodels for the appropriate trace toxic species transformations; and 3) to incorporate these mechanisms into an engineering model to predict trace toxic formation, partitioning, and fate based upon coal and combustion parameters.

The Phase II approach, which was proposed to the U.S. Department of Energy (DOE) in July 1997, included eleven tasks:

- Task 1 Program Management
- Task 2 Coal Acquisition and Characterization
- Task 3 Analysis of Coal and Ash for Forms of Occurrence of Inorganic Elements
- Task 4 Forms-of-Occurrence Analysis Using USGS Protocol
- Task 5.1 Bench-Scale Study Focusing on Partitioning: Chlorine and Trace Elements
- Task 5.2 Mercury Sampling and Elemental Analysis
- Task 6 Large-Scale Integrated Combustion Study
- Task 7 Organic Emissions from Coal Combustion

- Task 8 Integrated Combustion Study
- Task 9.1 Development of Engineering Model
- Task 9.2 Assessment of Field Data and Model Validation
- Task 10 Bench-Scale Studies of Postcombustion Interactions
- Task 11 Bench-Scale Study of Mercury–Fly Ash Interactions

Subsequently, funding from DOE was approved for all tasks except Tasks 7 and 8. The Task 11 work is to be performed at the Energy & Environmental Research Center (EERC) and is composed of four series of bench-scale tests to evaluate the interaction of mercury and several fly ashes. A short description of each of the four test series follows:

- <u>Series 1:</u> Baseline data on the effects of temperature and the interactions between elemental mercury (Hg(O) and fly ash samples generated under oxidizing conditions. Two temperatures will be used initially (408K [275°F] and 464K [375°F]).
- Series 2: Designed to evaluate the effect of mercury concentration on the interactions between Hg(O) and fly ash. Operating temperature will be based on results from Series 1.
- <u>Series 3:</u> Designed to evaluate the effect of temperature on the interactions between mercuric chloride (HgCl<sub>2</sub>) and fly ash. Ash samples from three different coals (including a North Dakota lignite) as well as pyrite will be tested. Results will be compared to Series 1 results to assess the effect of mercury speciation on interactions with ash.
- <u>Series 4:</u> Designed to evaluate the effect of coal combustion conditions on the ash and ultimately on the interaction between mercury and ash. Ash will be generated

from combustion of the program coals and pyrite under reducing (SR = 0.6) conditions. The interaction between the Hg(O) or HgCl<sub>2</sub> and the ash will be evaluated at two temperatures. The results will be compared to the results of Series 1 and 3 to allow comparison between ash generated under oxidizing and reducing conditions.

The results from Task 11 should provide stand-alone data that help explain the tendency of fly ash to oxidize and/or capture mercury. However, the data will be most valuable only when interpreted in light of the results from the other tasks in the project and when incorporated into an engineering model.

#### 2.0 PROJECT DESCRIPTION

The project is best described by the overall Phase II statement of work that has already been approved by DOE, presented here in Section 2.1. Further detail for Task 11 is given in the revised proposal from the EERC to PSI, presented in Section 2.2.

#### 2.1 Phase II Statement of Work as Approved by DOE

The Phase II program will utilize the proven integrated approach of coal characterization, coal combustion chemistry, postcombustion reactions, aerosol dynamics, and air pollution control device characterization to provide the tools necessary to go from the empirical characterization of emissions such as is found in the PISCES model to a mechanistic model such as ToPEM which can be applied to coals, combustors, and air pollution control devices (APCDs) outside the range of the measurement. This will be accomplished in Phase II through the following tasks:

### Task 1 - Program Management

Ξ

Program management and reporting activities at PSI will be conducted under Task 1. Specifically, this task will include 1) preparing and submitting all reports and forms required for the performance of this contract, as identified in the Reporting Requirements Checklist; 2) coordinating, managing, and integrating the subcontractor efforts and results; 3) integrating and delivering to DOE the final work output of all tasks; this includes delivery of models, data, and the Phase II Final Report; and 4) planning and conducting program review meetings at a frequency of approximately once per 9 months, including task principal investigators, DOE personnel, members of the Technical Advisory Board, and a representative from VTT/ATG, provider of field samples and data, and Electric Power Research Institute (EPRI), provider of additional financial support to this project. Phase II meetings are tentatively scheduled for 1, 9, 18, 27, and 30 to 33 months after initiation of Phase II work.

## Task 2 - Coal Acquisition and Characterization

Because of the importance of elemental form in partitioning, it is critical that coals representing a broad range of elemental forms are examined in this program. In this task, the Contractor will select, acquire, and study an additional two coals during Phase II. The coals will again be chosen in an attempt to 1) represent a broad range of elemental forms of occurrence and 2) represent the major coal ranks and commercial coal seams used for pulverized coal power generation in the United States. Final selection is also subject to approval by the DOE Contracting Officer's Representative. The tentative list of Phase II coals includes the Wyodak coal from Phase I and two new coals:

 Ohio coal, e.g., Kittanning Seam. This coal has been studied at pilot and full scale and will also provide access to other researchers' data.

- Lignite from North Dakota. While lignites are not major steam-producing coals throughout the United States, they are important regionally. The mineralogy of lignites from this seam is different from that of other coals.
- Powder River Basin (PRB) subbituminous coal, Wyodak seam. This is an important steam coal. As there is variability in the mineralogy of PRB coals, it is important to study more than one PRB coal in the program. Pilot-scale analyses not completed during Phase I will be done during Phase II.

## Task 3 - Analysis of Coal and Ash for Forms of Occurrence of Inorganic Elements

The University of Kentucky will conduct speciation analyses of coal, ash, and sorbent samples produced in the program. Information from various analytical techniques will then be used to determine the mechanisms of transformation, volatilization, and reaction of potentially toxic trace metals (Hg, As, Se) during coal combustion. Complementary analyses of the speciation of Cl, S, and other elements will also be conducted, where needed.

Specific techniques to be applied and the information to be gained from them are summarized below.

- Computer-controlled scanning electron microscopy (CCSEM) will be utilized to determine the mineralogy of the coals and phase distributions of the ashes and sorbents. A new stateof-the-art SEM recently acquired at UK will enable investigations of very small ash particles (down to 100 Å).
- 2. Mössbauer spectroscopy will be used to ascertain the oxidation state of pyrite in coal and iron phases in ash, which are closely related to the oxidation state of some trace metals.
- 3. X-ray fine structure (XAFS) spectroscopy will be applied to speciate the forms of occurrence of the trace metals in coal, ash, and sorbent samples. The XAFS speciation

analysis on coal will complement related work carried out by less direct methods by personnel at the USGS. Work will be initiated at the Advanced Photon Source (APS) at Argonne National Laboratory in order to obtain better sensitivity for mercury.

4. New techniques such as x-ray microprobe and microXAFS will be explored for the investigation of trace metals in individual ash and mineral particles. Both chemical association and forms of occurrence will be examined.

## Task 4 – Forms-of-Occurrence Analysis Using USGS Protocol

Direct and indirect determination of trace element modes of occurrence in Phase II samples will be conducted using an integrated approach that includes selective leaching techniques in conjunction with microbeam analysis, and x-ray diffraction analysis. Forms-of-occurrence analysis will be carried out for the lignite coal, which is new in Phase II. Analysis may be carried out for the Ohio coal if warranted by other experimental evidence showing different behavior or mineralogy from the previously studied bituminous coals. In addition to characterization of the new Phase II coal sample(s), detailed analysis of coal splits (size and density fractions) and/or mineral separates from Phase II coals will be conducted as required. Mineral separates will be analyzed by bulk methods such as instrumental neutron activation analysis (INAA) and inductively coupled plasma-mass spectroscopy (ICP-MS), in order to gain a better understanding of the association of trace elements with specific coal components such as pyrite. Electron microprobe analyses will be used in Phase II to determine the microdistribution of elements such as As in sulfides. Secondary ion mass spectrometry (SIMS) or other advanced microbeam techniques will be used in Phase II to gain information on elements such as Se, Co, and Cd, whose concentrations in pyrite of Phase I coals were below the microprobe detection limit. In the case of specific elements for which the mode of occurrence is determined to be important to the prediction of combustion behavior, statistical

correlations of modes of occurrence with other coal quality parameters will be developed to provide meaningful input data to the model.

# Task 5.1 – Bench-Scale Study Focusing on Partitioning: Chlorine and Trace Elements

## **Chlorine Studies**

Chlorine plays an important role in converting trace metals into more volatile chlorides, particularly when the chlorine is in the form of molecular chlorine. The Phase I studies showed that on the order of 1% of the total chlorine in the flue gases might end up as molecular chlorine based on homogeneous chemistry. Catalytic effects could increase the molecular chlorine significantly. UConn will be providing fundamental studies on the kinetics of chlorine conversion to molecular chlorine. In the University of Utah studies, the molecular chlorine will be measured in the U furnace, which has been designed to provide a cooling rate to ambient conditions more representative of full-scale furnaces. The chlorine concentrations will be compared with the models being developed in the fundamental studies at PSI.

### **Trace Metal Studies**

In this task, the effect of coal type and combustion conditions on the emission of the toxic trace metals will be determined under well-defined temperature and oxygen histories using a laminar flow furnace. The Phase I studies showed that the temperature was a major variable in determining trace element vaporization. Secondary variables such as coal type and particle size will be investigated in Phase II. In addition, data on new coals and a more extensive study of the impact of temperature will be conducted. As before, size- and density-segregated coals will be used in the combustion tests, and the collection probe will be used to capture 100% of the ash on a cascade impactor. The ash samples will be analyzed by Dr. Olmez at MIT using neutron activation analysis combined with ICP-MS. Selected samples will be sent to UK for detailed characterization using CCSEM, Mössbauer spectroscopy, x-ray absorption near edge structure (XANES)/XAFS. The studies in the laminar flow furnace will be used to develop a model for vaporization.

## Task 5.2 – Mercury Sampling and Elemental Analysis

In Phase I, we observed significant capture of mercury with the carbon in fly ash was observed. The capture efficiency, however, did not correlate with carbon amount. In the study, the mercury not captured was vented to the fume hoods. In Phase II, the mercury escaping collection will be captured and analyzed for mercury form. The measurements will be closely coordinated with Dr. Olmez, who will be responsible for determining the amount and form of mercury in the vapor phase. The study will be directed to determining the effect of gas-phase speciation on mercury capture efficiency. One of the probable factors is the amount of chlorine present as mercury chloride. The chlorine in the vapor also will be analyzed for chemical form to determine the effect of reactions of molecular chlorine with elemental mercury on the speciation. Selected runs will be made with the addition of methyl chloride to the inlet gas as a means of determining the effect of chlorine concentration on capture efficiency and metal partitioning.

#### Task 6 – Large-Scale Integrated Combustion Study

During Phase II, ND lignite, Ohio, and the Wyodak coal from Phase I will be burned under "premixed" conditions in the existing pilot-scale downflow combustor utilized under Task 6 during Phase I. Both standard and low-NO<sub>x</sub> conditions will be investigated. Special tests, if warranted, will explore variations in temperature, using oxygen enrichment, preheat, and/or  $CO_2$  dilution. Staged stoichiometries and residence times may also be varied in these tests, the exact delineation of which depends on prior results. The intent of such tests is to improve the accuracy of the model as applied to new low-NO<sub>x</sub> and/or high-efficiency combustion systems in the future.

During furnace testing, samples will be withdrawn from various furnace sampling ports as appropriate to examine the effects of process variables such as time, temperature history, the effect of oxidant levels, etc. Complete impactor samples will be collected, and selected samples will be analyzed for each toxic metal (11 listed in the Clean Air Act Amendments [CAAA] plus U and Th) plus major elements. Samples will be chemically analyzed with graphite furnace atomic absorption (GFAA) or other advanced characterization techniques as required.

Analytical results will yield the particle size-segregated toxic metal composition in the combustion and postcombustion zones, which can be compared to data obtained from other tasks in this program (Tasks 5, 10, 11). Toxic metal composition data will be assembled with other existing data (both obtained from this program and from the literature). All the data will then be examined to determine particle size dependence in order to infer possible mechanisms governing the fate of each metal. Understanding the effect of combustion conditions, flue gas temperature, and cooling rate on mechanisms is a key goal of this task. Correlation with the initial form of the toxic metal will be attempted. Unimportant metals will be removed from consideration from subsequent tests. When possible, trade-offs between  $NO_x$  control and emission of toxic metals will be identified.

## Task 7.1 - Evaluation of Field Data on Organic Emissions

Not funded.

2

### Task 7.2 – Organic Emissions from Coal Combustion

Not funded.

Task 8 – Integrated Combustion Study Not funded.

## Task 9.1 – Development of Engineering Model

3

In this task, all data and submodels obtained from subcontractor and PSI tasks will be combined to create a comprehensive model of the transformations of important inorganic species during combustion. This model, denoted the Toxics Partitioning Engineering Model (ToPEM), will be based on an existing model (the PSI Engineering Model for Ash Formation [EMAF], which predicts ash particle-size and composition distributions). Because the development of this model is strongly dependent on the mechanistic, equilibrium, and kinetic information being developed under the experimental tasks, ToPEM will incorporate information on the mechanisms controlling species behavior, equilibrium modeling where appropriate, and kinetic modeling to mimic kinetic constraints on species behavior.

During the later stages of the Phase II work, sufficient detailed information will be available to support specific modifications to EMAF in order to describe the combustion transformations of important inorganic trace elements. Based on the experimental studies, equilibrium modeling, and kinetic modeling it will be clear which modifications are required. For example, if the experimental evidence suggests that the extent or rate of carbon burnout plays a major role in the release of selected elements, a submodel will be developed to describe the combustion process.

For those elements where the experimental studies and equilibrium modeling have suggested that equilibrium is an appropriate method for predicting species behavior, an equilibrium submodel will be incorporated. Similarly, a kinetic submodel will be developed and incorporated for species so identified during the proposed research effort. The analysis performed during Phase I will be instrumental in meshing the kinetic and equilibrium submodels with the existing model. This is critical to ensure that the overall predictions are not affected by the predictive technique used for each element. In other words, in modifying EMAF to account for trace element behavior, care will be taken to ensure that the predictions of ash particle-size and composition distributions remain accurate.

Once complete, ToPEM, developed under this program, will be validated using a combination of laboratory and field data. As part of the validation effort, coal and size-fractionated ash samples collected from operating utility boilers will be provided by Dr. Esko Kauppinen of VTT, Finland. Once validated, the ToPEM will be used to simulate the behavior of these and other coals under utility boiler conditions. The results from these simulations will then be compared to field data from PISCES obtained through EPRI participation in this program, DOE field-sampling campaigns, and other relevant data in the literature. This validation procedure will ensure that the model developed as the result of the proposed research efforts accurately predicts the behavior of toxic metals species from a wide range of coals during the combustion process in any combustion system.

#### Task 9.2 – Assessment of Field Data and Model Validation

Field data on trace element stack emissions obtained from EPRI (PISCES), DOE, Environment Canada (1997), U.S. Environmental Protection Agency (EPA) (Draft Report to Congress), and VTT were evaluated during Phase I of this program. Efforts to interpret the data from a mechanistic perspective led to the identification of mercury, arsenic, selenium, chlorine, and cadmium as the focus of our Phase II program. In Phase II of this program, we will use these data to validate trace element emission levels predicted by the ToPEM model. Specifically, we will use information on rank-specific forms of occurrence from Tasks 2, 3, and 4; vaporization (partitioning) data from Tasks 5 and 6; and ESP penetration data from the literature (including VTT-provided data) with an existing model for ash particle-size and composition distributions to determine the mass emissions rate of trace metals from the facilities in the EPRI PISCES and DOE databases. Adjustments to any of the submodels will be identified as part of this effort, and will lead to either additional experiments to fill data gaps or model refinements, or both. This validation procedure will ensure that the model developed as a result of the proposed research effort accurately predicts the behavior of toxic metal species from a wide range of coals and combustion systems.

## Task 10 – Bench-Scale Studies of Postcombustion Interactions

## Arsenic

The mechanism proposed in the Phase I Final Report suggests that arsenic will be present exclusively as As(V) in systems with an excess of available calcium oxide. Lignite and subbituminous coals, which possess a high percentage of organic calcium, would therefore be expected to produce primarily calcium arsenate in the ash. In contrast, the formation of As(V) in bituminous coals should depend upon the concentration of organic calcium in the coal, the presence of excluded calcite (included calcite may react with aluminosilicate minerals, rendering the calcium unavailable for arsenic), competition of the reaction (4) with sulfation reactions, and the oxidation rate of As(III) to As(V). These will be examined in a fundamental bench-scale study using both flatflamed and tube furnace reactors. The flat-flamed burner system will consist of a water-cooled stainless steel burner surrounded by an insulated 1.5-m-tall quartz tube. This will provide residence times of greater than 2 s and postflame cooling rates of approximately 500 Ks<sup>-1</sup>, an order of magnitude comparable to postflame cooling rates in the back end of coal-fired boilers. The tube furnace system comprises a Lindberg tube furnace surrounding a 2.54-cm-diameter quartz tube. A thin bed of reactant solid (to minimize mass-transfer resistance) located normal to the direction of gas flow will be supported between quartz wool plugs. Whereas the flame reactor provides a temperature profile in which reactions can be studied, the tube furnace can be used to extract global rate data under isothermal conditions.

To conclusively identify the rate-controlling phenomena in the oxidation of arsenic under combustion conditions, these facilities will both be used to study the heterogeneous oxidation of arsenic trioxide. Using the flat-flamed burner, aqueous arsenic-containing cacodylic acid solutions will be injected into the center of a fuel-lean gas flame. Methane will be used initially; other fuels including acetylene and hydrogen can be used if higher temperatures are needed. The particulate products of combustion will be collected using an existing stainless steel water-cooled sampling probe that quenches the products of combustion at cooling rates exceeding 10<sup>4</sup> Ks<sup>-1</sup>. By sampling at conditions under which the different arsenic species are thermodynamically favored, we can determine conditions under which equilibrium is an appropriate description of arsenic speciation.

To simulate the interaction of arsenic species with other inorganic compounds present in coal combustion-derived fly ash, experiments will be conducted using arsenic in combination with a) 1- $\mu$ m spherical silica particles, produced in the laboratory through solgel techniques; b) 1- $\mu$ m silica particles that have been doped with a range of calcium concentrations, continuing the early effort to determine whether calcium associated with silicates can chemically react with arsenic; c) calcium acetate and lime, to determine the rate of reaction of calcium oxide with arsenic oxide vapors; d) reactions b) and c) in the presence of SO<sub>2</sub> to assess competition for reactive calcium sites. Because the final reaction in the sequence (1)–(5) above is hypothesized to be kinetically limited, a thin coating of arsenic trioxide on an inert core should react to form arsenic pentoxide faster than a solid arsenic trioxide particle. Selected experiments using a cascade impactor to size segregate particles will also be conducted to assess this. Finally, experiments with arsenic trioxide, both in bulk form and as a thin coating on silica particles, will be conducted in the tube furnace to derive rate information. In all cases, ion chromatography at UConn supplemented by XAFS (Task 3, UK, this program) will be used to determine arsenic speciation.

Completion of this task should quantitatively determine the conditions required to produce As(V) in combustion environments. It will also provide global oxidation rate data that can be used in conjunction with arsenic vaporization and ash formation models (under development in separate tasks in this program) to provide an overall model that predicts arsenic transformations for all coals.

#### Mercury

The oxidation state of mercury is an important factor in determining the extent of mercury capture by residual carbon and carbon sorbents. Oxidized mercury, Hg(II), is more readily adsorbed than is Hg(0). Thermodynamic equilibrium calculations indicate that all mercury should be present in the oxidized form, either as HgCl<sub>2</sub> or as HgSO<sub>4</sub>, at stack conditions. Field data obtained in testing programs sponsored by DOE and by EPRI, however, indicate that between 50% and 90% of the mercury is present in oxidized form in the stack. Mercury capture ranged between 0% and 90% in the same test series.

This behavior can be explained by a frozen equilibrium model, similar to that used to explain the dominance of SO<sub>2</sub> at stack temperatures under which SO<sub>3</sub> is thermodynamically favored. At temperatures above approximately 800K, Hg(0) is thermodynamically favored. At lower temperatures where HgCl<sub>2</sub> is favored, it is hypothesized that reaction rates are too slow for complete conversion to the chloride. This model will be verified in Phase II in experiments conducted in the flat-flamed burner system described above. Mercury vapor of known concentration will be generated in a permeation tube and fed to the flat-flamed reactor. Mercury concentrations will be adjusted to be representative of those encountered in pulverized coal flames. Chlorine will be introduced with the burner gases first as HCl, and later as mixtures of HCl and Cl<sub>2</sub> to determine the relative rates of reaction. Gases will be sampled after cooling to 400–500K through a glass-lined sampling probe similar to that described in EPA Method 29. The Ontario Hydro modification of the EPA Method 29 impinger train will be used for separation of Hg(O) and Hg(II). Analysis will be by cold-vapor atomic absorption (CVAA). Particles will be excluded from these experiments to avoid complications introduced by the potential interaction of mercury vapor with ash and char. The results of these experiments will be used in conjunction with data generated by the EERC under Phase II, Task 11, to develop a model for mercury speciation that can be incorporated into ToPEM.

Homogeneous kinetic calculations conducted in Phase I of this program by Dr. Sarofim indicate that less than 1% of chlorine should be present as Cl<sub>2</sub> under all conditions. If measurements made in Phase II indicate that molecular chlorine concentrations greater than 1% are needed to convert significant fractions of mercury to HgCl<sub>2</sub>, additional study of the HCl–Cl<sub>2</sub> system will be conducted as described below.

## Chlorine

During the Phase II program, Sarofim and coworkers (MIT, U of Utah) will be measuring the speciation of chlorine during combustion of several program coals. Gas-phase kinetic calculations conducted during Phase I indicated that molecular chlorine levels should not exceed 1% of total chlorine. Detection of significantly higher concentrations would thus indicate that heterogeneous (surface-catalyzed) reactions are converting a portion of HCl to molecular Cl<sub>2</sub>. Note that the recent DOE-sponsored field study (Miller et al., 1996) reported molecular chlorine levels of 4%, 5%, and 45% of total chlorine for the three plants reporting such data. Although such heterogeneous reactions are well known, they typically require a catalyst such as CuCl<sub>2</sub> or other copper-based compound. Copper compounds are present in very low (ppm level) concentrations in coal combustion fly ash. If heterogeneous conversion of HCl does occur, conversion measurements will be conducted using the tube furnace reactor described above. Iron oxide, iron sulfate, and several fly ash samples generated from the program coals (extracted to remove any residual chloride) will be considered as

catalysts. Once suitable catalysts have been identified, experiments will be repeated in the flatflamed burner system described above to assess the extent of HCl conversion likely to occur in the (cooling) postflame gases. In all cases, chlorine-containing gases will be separated in an acid/alkali impinger train.

## Task 11 - Bench-Scale Study of Mercury-Fly Ash Interactions

A bench-scale sorbent evaluation system will be used to increase our understanding of the interactions between gas-phase mercury and coal ash. The system is composed of three subsystems: the mercury vapor delivery system, the fixed-bed reactor, and the mercury measurement system. Mercury (elemental or chloride) will be generated using permeation tubes and added to a simulated flue gas mixture passing through a fixed bed of ash or other material. The fixed bed consists of a Teflon-coated filter holder located in an oven to allow precise control of the temperature. After the flue gas passes through the fixed bed, a slipstream is pulled through the mercury-sampling equipment. A continuous analyzer will be used to measure total mercury and mercury speciation during the experiments. The tests will run for an average of 4 hours each, and the runs will be duplicated. After testing is complete, the material in the fixed bed will be analyzed for total mercury and for speciation of mercury and other elements by XAFS (Task 3).

Ash samples will be generated from combustion of the program coals at either PSI or UA. A variety of combustion conditions will be used to generate ash samples. Limited experiments will also be performed using ash collected from a utility power plant burning one of the program coals.

Experiments will be organized into four test series as follows:

<u>Series 1:</u> Baseline data on the effects of temperature and the interactions between elemental mercury and fly ash samples generated under oxidizing conditions. Two temperatures will be used initially (408K [275°F] and 464K [375°F]).

- <u>Series 2:</u> Designed to evaluate the effect of mercury concentration on the interactions between Hg(O) and fly ash. Operating temperature will be based on results from Series 1.
- <u>Series 3:</u> Designed to evaluate the effect of temperature on the interactions between  $HgCl_2$ and fly ash. Ash samples from the test coals as well as pyrite will be tested. Results will be compared to Series 1 results to assess the effect of mercury speciation on interactions with ash.
- Series 4: Designed to evaluate the effect of coal combustion conditions on the ash and ultimately on the interaction between mercury and ash. Ash will be generated from combustion of the program coals and pyrite under reducing (stoichiometric ratio = 0.6) conditions. The interaction between the Hg(O) or HgCl<sub>2</sub> and the ash will be evaluated at two temperatures. The results will be compared to the results of Series 1 and 3 to allow comparison between ash generated under oxidizing and reducing conditions.

## 2.2 EERC Revised Proposal to PSI

February 26, 1998

Mr. William J. McManus Manager, Contracts Department Physical Sciences Inc. 20 New England Business Center Andover, MA 01810-1077

Dear Mr. McManus:

Subject: EERC Proposal No. 98-0005-R1

This letter proposal is in response to the request from Physical Science Inc. (PSI) that the Energy & Environmental Research Center (EERC) put together a revised test plan and budget for a series of bench-scale tests to help explain mercury's behavior in coal combustion flue gas. The bench-scale tests are in support of the project "Toxic Substance from Coal Combustion – A Comprehensive Assessment" that was recently selected by the U.S. Department of Energy (DOE) for Phase II funding.

The scope of work and budget have been reduced by approximately 25% from the original Phase II proposal the EERC submitted to PSI July 16, 1997. The reduced scope of work is based on a total subcontract budget of \$200,000, including \$40,000 in cost share. As stated in the original EERC proposal, the proposed source of the 20% cost share is the North Dakota Industrial Commission (NDIC), subject to funding of Phase II by DOE and subsequent submittal and acceptance of a formal proposal to NDIC. A letter of interest and potential funding from Dr. Clifford Porter, technical advisor to the Lignite Research Council and North Dakota Industrial Commission, was included with the original proposal. A copy of this letter is also enclosed with this revised proposal. Upon implementation of a subcontract to PSI, the EERC will submit the formal proposal to NDIC for at least 20% cost share of the EERC subcontract.

The bench-scale test plan is divided into four test series shown in Table 1. The independent variables that will be evaluated are as follows:

- Ash type (Wyodak subbituminous, North Dakota lignite, and Ohio bituminous)
- Mercury species (Hg<sup>0</sup> and HgCl<sub>2</sub>)
- Gas temperature (temperature at the filter holding the fly ash)

- Mercury concentration
- · Stoichiometric ratio (SR) for the combustion condition when the ash sample is generated

In addition, a number of contingency tests are planned which will be determined based on previous results or on new information that may become available. These tests will allow some flexibility in the test program.

Each series is based on a full-factorial design, with some of the variables blocked. In addition, some of the test data from a previous series may be used as part of the factorial design. A simulated flue gas will be used for all tests. The flue gas for the respective fly ash samples will replicate flue gas concentrations from the combustion of the respective coals. It is assumed the tests will run an average of 4 hours each, and runs will be duplicated. Mercury emissions will be continually monitored with a continuous emission monitor (CEM) at the outlet of the system for elemental and total mercury concentrations (the difference will represent the oxidized mercury concentration). Select sampling will also be conducted with the Ontario Hydro mercury speciation method to verify the speciation information obtained with the continuous mercury analyzer.

In addition to the fly ashes, a number of tests (see Table 1) will be conducted with pyrite samples for direct comparison with the fly ash results.

A short description of each test series is provided below.

Series 1 – This series will provide baseline data on the effects of temperature on the interactions between elemental mercury and the fly ash samples (SR = 1.2). Information gained from these tests will be used to refine the temperature ranges for future tests. There are two contingency tests which may be run at midpoint temperatures. If interactions occur at only one temperature (i.e., no interaction at 275°F, but conversion of elemental mercury to oxidized mercury at 375°F), a contingent test may be run at a different temperature (i.e., 225° or 400°F).

Series 2 – This series is designed to evaluate the effect of mercury concentration on the interactions between the Hg<sup>0</sup> and fly ash samples. The operating temperature will be based on results from the first test series. Information gained during this test series will be used to refine mercury concentrations for the remainder of the tests. There are no contingent runs in this series.

Series 3 – This test series is designed to evaluate the effect of temperature on the interactions between HgCl<sub>2</sub> and the fly ash samples. The results will also be compared with the results from Series 1 to determine the effect of mercury species. The operating temperature range and mercury concentrations may be modified based on the results from the first two test series. There are two contingency tests to evaluate midpoint temperatures.

Series 4 – This test series is designed to evaluate the effects of mercury species (Hg<sup>0</sup> and HgCl<sub>2</sub>) and operating temperature on the interactions between mercury and the fly ash samples (SR = 0.6). The results from these tests will be compared with the results from the ash samples prepared at a stoichiometric ratio of 1.2. There are four contingency runs in this series.

The anticipated time for completion of the work is 2 years from the date of project implementation. Since the exact schedule for completing the work is highly dependent on the generation and availability of ash samples from another subcontractor of PSI, a more detailed schedule for the work will be decided at a later date by mutual agreement among DOE, PSI, and the EERC. Results from the tests will be submitted to PSI and NDIC on a quarterly basis during the quarterly periods for which project work is done. However, reports will not be completed for the quarterly periods in which no experimental work is conducted at the EERC. It is assumed that all quarterly reports submitted by PSI to DOE for the project will also be made available to NDIC and the EERC.

Stanley Miller, Senior Research Manager, will serve as the project manager and principal investigator and will be the primary contact between the EERC and the rest of the project team. Dennis Laudal, Research Manager, will serve as co-project manager and co-principal investigator.

Attachments to this proposal include the following:

- · Letter of interest and funding from Clifford Porter
- Detailed budget
- Budget notes
- DOE-required Representations and Certifications
- Revised Environmental Questionnaire

Sincerely yours,

Stanley J. Miller Senior Research Manager

Approved by:

Dr. Carl A. Fox, Director Office of Research and Program Development

SJM/mro

Enclosures

c/enc: Dennis Laudal, EERC Grant Dunham, EERC

## TABLE 1

Test No	Ash	Stoichiometric Ratio	Hg	Temperature,
Test file.	1	Tutto	Species	
Test Series	• 1			
1	ND Lignite	1.2	Hg <sup>0</sup>	275
2	ND Lignite	1.2	Hg <sup>0</sup>	375
3	Ohio	1.2	Hg <sup>0</sup>	275
4	Ohio	1.2	Hg <sup>0</sup>	375
5	Wyodak	1.2	Hg <sup>0</sup>	275
6	Wyodak	1.2	Hg <sup>0</sup>	375
7	Pyrite	1.2	Hg <sup>0</sup>	275
8	Pyrite	1.2	Hg <sup>0</sup>	375
9-10	Contingency	1.2	Hg⁰	TBD <sup>1</sup>
Test Series	s 2			
11	ND Lignite	1.2	$Hg^0 \times 5$	TBD
12	ND Lignite	1.2	$Hg^0 \times 25$	TBD
13	Ohio	1.2	$Hg^0 \times 5$	TBD
14	Ohio	1.2	$Hg^0 \times 25$	TBD
15	Wyodak	1.2	$Hg^0 \times 5$	TBD
16	Wyodak	1.2	Hg <sup>0</sup> × 25	TBD
<b>Test Serie</b>	s 3			
17	ND Lignite	1.2	HgCl <sub>2</sub>	275
18	ND Lignite	1.2	HgCl <sub>2</sub>	375
19	Ohio	1.2	HgCl <sub>2</sub>	275
20	Ohio	1.2	HgCl <sub>2</sub>	375
21	Wyodak	1.2	HgCl <sub>2</sub>	275
22	Wyodak	1.2	HgCl <sub>2</sub>	375
23	Pyrite	1.2	HgCl <sub>2</sub>	275
24	Pyrite	1.2	HgCl <sub>2</sub>	375
25-26	Contingency	1.2	HgCl <sub>2</sub>	TBD

EERC Bench-Scale Test Matrix for Determining Interactions Between Fly Ash and Mercury Species

	Ash	Stoichiometric	Hg	Temperature,
Test No.	Parent	Ratio	Species	۴
<b>Test Series</b>	4			
27	ND Lignite	0.6	Hg <sup>0</sup>	275
28	ND Lignite	0.6	Hg <sup>0</sup>	375
29	ND Lignite	0.6	HgCl <sub>2</sub>	275
30	ND Lignite	0.6	HgCl <sub>2</sub>	375
31	Ohio	0.6	Hg <sup>0</sup>	275
32	Ohio	0.6	Hg <sup>0</sup>	375
33	Ohio	0.6	HgCl <sub>2</sub>	275
34	Ohio	0.6	HgCl <sub>2</sub>	375
35	Wyodak	0.6	Hg <sup>0</sup>	275
36	Wyodak	0.6	Hg <sup>0</sup>	375
37	Wyodak	0.6	HgCl <sub>2</sub>	275
38	Wyodak	0.6	HgCl <sub>2</sub>	375
39	Pyrite	0.6	Hg <sup>0</sup>	275
40	Pyrite	0.6	Hg <sup>0</sup>	375
41	Pyrite	0.6	HgCl <sub>2</sub>	275
42	Pyrite	0.6	HgCl <sub>2</sub>	375
43-46	Contingency	0.6	TBD	TBD

TABLE 1 (continued)

<sup>1</sup> To be determined. <sup>2</sup> Not applicable.

ð



## INDUSTRIAL COMMISSION OF NORTH DAKOTA

Governor, Edward T. Schafer Attorney General, Heidi Heitkamp Commissioner of Agriculture, Roger Johnson

LIGNITE RESEARCH, DEVELOPMENT AND MARKETING PROGRAM

July 8, 1997

Steven E. Benson, Ph.D. University of North Dakota Energy & Environmental Research Center P.O. Box 9018 Grand Forks, ND 58202-9018

HECENVEL. JUL 1 0 1997 EERC-SAB

SUBJECT: "Toxic Substances from Coal Combustion - A Comprehensive Assessment" - Phase II Program

Dear Steve:

The North Dakota Lignite Research, Development, and Marketing Program (Program) is committed to the development and commercialization of advanced environmental control technologies for the power generation industry. The development of innovative technical approaches in the area of toxic substance formation and partitioning in coal combustion systems is a critical need. As outlined, the Phase II PSI program addresses this critical need and meets funding requirements for the Program. We look forward to your favorable review of the PSI proposal.

This letter of interest and potential funding from the North Dakota Program is subject to submission of a proposal by PSI and the Energy & Environmental Research Center at the University of North Dakota. North Dakota Program funding is subject to submission of a proposal which meets Program guidelines, a funding recommendation by the Lignite Research Council and approval by the North Dakota Industrial Commission.

Environmental issues including toxic substances from coal combustion are priorities for the North Dakota Program. Funding guidelines require matching industrial funds, and activities, which preserve and enhance the use of North Dakota lignite.

Sincerely,

clifford RPorter

Clifford R. Porter, Director Lignite Research, Development, and Marketing Program Technical Advisor Lignite Research Council, and North Dakota Industrial Commission

LIGNITE RESEARCH COUNCIL John Dwyer Clifford Porter Chairman Director & Technical Advisor P.O. Box 2277 Bismarck, N.D. 58502 (701) 258-7117 (701) 258-2755 Fax INDUSTRIAL COMMISSION OF NORTH DAKOTA Karlene Fine Contracts Officer 600 E. Blvd., State Capitol Bismarck, N.D. 58505 (701) 328-3722 (701) 328-2820 Fax

## 3.0 STANDARDS OF SUCCESS

Task 11 of the project will be conducted in the mercury research laboratory at the EERC. This laboratory has been developed specifically to perform bench-scale experiments to evaluate mercury measurement techniques, mercury control options, and the interaction between mercury and fly ash. The experiments are conducted in a flue gas environment that closely matches the actual flue gas concentrations produced when a specific coal is burned. Complete control over all of the gas constituents allows parametric evaluation of the effects of any combination of gases on the oxidation and capture of mercury. Because of the difficulty of performing experiments with trace amounts of mercury, the EERC has implemented rigorous quality assurance/quality control (QA/QC) procedures to ensure that the highest-quality data are generated. Based on thousands of mercury experiments and measurements at the EERC over the past 5 years, we believe that all bench-scale tests must be run in duplicate to determine the precision of the results. By pooling the paired differences from a number of duplicate experiments, a very accurate measure of the experimental precision is obtained. Only when a good measure of precision is available can a valid determination be made of whether a parametric effect reflects a real change or is simply the result of random noise. Duplication of all of the tests might appear excessive, but this requirement is the single most important factor that will lead to valid interpretation of the data.

A second important QC step in the experimental design is independent analysis of mercury retained in the ash. This value is then compared with the amount of mercury capture indicated by integrating the area under a mercury breakthrough curve measured with a continuous mercury monitor. These independent measurements provide additional confidence in the results.

A third backup QC step is the inclusion of the Ontario Hydro mercury speciation method for select samples to verify the mercury speciation information obtained with the continuous mercury analyzer.

A fourth important QC step is the completion of blank runs with the apparatus to ensure no mercury oxidation or capture within the system other than the effects that occur as a result of the interaction of mercury with the fly ash.

Fly ash and Ontario Hydro impinger samples are analyzed in the EERC Analytical Research Laboratory (ARL), which has additional QA/QC. A Leeman Labs PS200 CVAA mercury analyzer is used for mercury determination. The instrument is set up for absorption at 253.7 nm with nitrogen as the carrier gas and 10% stannous chloride in 10% HCl as the reductant. The drying tube and acetate trap, containing magnesium perchlorate and soda lime, respectively, are replaced daily. Also, the tubing is checked and replaced, if necessary, and the rinse container is cleaned and filled with a fresh solution of 10% HCl. After a 45-min warmup period, the aperture is set to the manufacturer's specifications. A four-point calibration curve with matrix-matched standards is used to calibrate the instrument. The detector response for each standard is logged and compared with the specifications to ensure proper instrument setup and response. A QC standard of a known analyte concentration is analyzed immediately after the instrument is standardized to verify the calibration. This QC standard is prepared from a different stock than the calibration standards, and the values obtained must read within 5% of the true value. The values obtained from the initial QC analysis are plotted on a OC chart to monitor the precision of the instrument. After the initial QC standard, periodic check standards are run every five samples to check the slope of the calibration curve. The check standards must read within 5% of the expected value.

Solid samples analyzed for mercury are acid-digested first using a CEM MDS-2100 microwave sample digestion system. The system is equipped with temperature and pressure controllers, as well as heavy-duty Teflon<sup>®</sup>-lined digestion vessels designed for high-pressure applications, such as coal dissolution. The vessels are sealed to prevent loss of volatile analytes.

The solutions used for the analytical methods pertaining to trace metal analysis including mercury are all trace metal grade. Other chemicals used in the preparation of analytical reagents are analytical reagent grade. The calibration standards used for instrument calibration and the QC standards used for calibration verification are purchased commercially, certified accurate to within  $\pm$ 5%, and traceable to NIST (National Institute of Standards and Technology) Standard Reference Materials. All solutions are made in the ARL, with the exception of the blind standards, which are submitted to the ARL on a periodic basis.

All glass volumetric flasks and transfer pipets used in the preparation of analytical reagents and calibration standards are designated as Class A to meet federal specifications. Special cleaning procedures are required for all laboratory glassware and plasticware used in mercury analysis. In the ARL, the procedure includes washing with hot, soapy water and then several rinses with tap water followed by several rinses with distilled, deionized water. All vessels were then soaked in a 5% BrCl solution for a minimum of 30 min, followed by several rinses with distilled, deionized water. The glassware is stored in closed containers until use.

Precision is maintained in the ARL by performing duplicate samples at random on one of every ten samples, with a minimum of one duplicate analysis per run. The results from the duplicate analysis must be within 10%, and any variation must be justified in the procedure. The precision of the duplicate sample analyses is recorded and charted in a precision control chart.

The ARL is certified by EPA through the state of North Dakota by annual participation in the states's water pollution study. An on-site evaluation is conducted every 3 years by the state in order to maintain full certification. The ARL has also participated in a number of round-robin tests, including one on mercury in coal. The results have always been excellent.

An external audit of the QA/QC procedures at the EERC was conducted by Advanced Technology Systems and International Technology Corporation as part of a mercury speciation methods evaluation project in March 1995. The auditors reported that the work being done by ARL showed a high level of quality control.

The primary dependent experimental results will be a determination of the amount of mercury captured and/or oxidized. The project will be considered successful if these results are generated with a known precision for all of the planned tests.

### 4.0 BACKGROUND

The use of coal in the United States has been increasing every year and in 1997 passed the 1 billion ton mark (20% of the total world coal production of 5.1 billion short tons per year) (*Monthly Energy Review*, 1998). Coal is now the primary source of anthropogenic mercury emissions in the United States, accounting for 46% (U.S. EPA, 1997). On a worldwide basis, assuming healthy economic growth, the projected increase in coal usage over the next two decades in China and India will bring the total world coal consumption to about 10 billion tons per year (*International Energy Outlook*, 1998). Coal may be the cause of significantly increased worldwide mercury emissions unless effective control strategies are implemented. Within the state of North Dakota, lignite production the last several has been steady at about 30 million tons per year. On a mass basis, the mercury concentration in ND lignite is in the typical range for U.S. coals. However, on a Btu basis,

the mercury concentration in ND lignite is on the high side of U.S. coals. Of the eight coals for the field sites evaluated by DOE for toxic emissions, only one (an Ohio blend) had higher mercury than the ND lignite (Miller et al.). The amount of mercury in the coal is only part of the issue. The form of mercury exiting the stack and amount of mercury retained by the fly ash both will determine the impact (if any) that the mercury will have on the environment. Since Hg(O) emissions are thought to be globally dispersed, this form of mercury emissions is not likely to have a regional impact on the mercury in lakes and streams. Soluble ionic mercury, on the other hand, is thought to be rapidly washed out of the atmosphere and has the potential to impact the mercury in regional waters. From the perspective of mercury emissions, any mercury retained by the fly ash is considered beneficial. However, from an ash utilization perspective, mercury in the fly ash may be considered undesirable, even if it is simply a perception issue. Fly ash is also known to affect the mercury speciation. Data show that some fly ashes play a significant role in oxidizing the mercury, but prediction of the amount oxidized has proven difficult (Laudal and Heidt, 1997; Senior et al., 1997). Because of these issues, understanding of the interaction between mercury and fly ash is critically important.

As indicated earlier, in Phase I of this program, a team led by PSI, involving researchers from the University of Kentucky, USGS, MIT, the University of Arizona, the University of Connecticut, and Princeton University began a detailed research program with three major objectives: 1) to elucidate the important mechanisms of toxics formation and partitioning, 2) to develop submodels for the appropriate trace toxic species transformations, and 3) to incorporate these mechanisms into an engineering model to predict trace toxic formation, partitioning, and fate based upon coal and combustion parameters. Results of the Phase I effort are detailed in the 500-page final report, to DOE (Senior et al., 1997). Mercury is present in coal in low concentrations on the order of 0.1 ppm. In the combustion zone, all the mercury in coal is vaporized, yielding vapor concentrations of mercury in the range of 10 to 20  $\mu$ g/m<sup>3</sup> (1 to 2 ppbv). At furnace exit temperatures (1700K), all the mercury is expected to be Hg(O) in the gas phase. In the postfurnace region, 1700 to 500K (2600° to 400°F), equilibrium predicts the oxidation of Hg(O) to HgCl<sub>2</sub> in the gas phase. Measurements in pilot- and full-scale systems show on the order of 75% of the vapor-phase mercury as the oxidized form, which is likely to be HgCl<sub>2</sub>, although measurement methods cannot identify specific oxidized species of mercury (Prestbo and Bloom, 1990; Fahlke and Bursik, 1995; Meij, 1994). However, the fraction of Hg(O) in flue gas from the combustion of many western coals is higher.

The fraction of the mercury in flue gase is bound with the particulate matter in some cases can be more than 50%. The mechanism for mercury capture on particulate matter in coal combustion flue gas seems to be chemical or physical adsorption on the fly ash and depends on the gas-phase speciation of the mercury. Although the major reaction pathways for mercury in coal combustion flue gas can be identified, we cannot yet make quantitative predictions of mercury emissions from coalfired power plants. The goal is to advance the state of knowledge such that a predictive model can be formulated. The questions that need to be addressed are:

- 1. What is the rate of oxidation of Hg(O) in the convective air heater? leading to prediction of gas-phase mercury speciation at the inlet to the APCD.
- 2. What are the properties of coal fly ash that affect the oxidation of gas-phase mercury and the conversion of gas-phase to particulate-bound mercury? *leading to prediction of speciation and gas-solid partitioning in the APCD*.

Understanding gas-phase speciation of mercury in coal-fired power plant flue gas is not sufficient to describe the transformations of mercury in the combustion system. In order to understand the capture of mercury in APCDs and the effectiveness of sorbents for mercury capture, better understanding of the gas-to-particle conversion is also needed, particularly the relationship between fly ash properties and oxidation and/or adsorption of mercury.

Two further questions can be posed: first, what is the process by which fly ash (and certain other solids) seem to catalyze the transformation of gaseous Hg(O) to oxidized forms; second, what are the mercury species adsorbed on fly ash? Answering both these questions will require a detailed look at the constituents of the fly ash and how they interact with mercury at temperatures characteristic of the flue gas (400 to 600K) as it enters the APCD.

Gas-phase Hg(II) is readily captured by activated carbon, while Hg(O) has a much lower affinity for carbon. The surface of the carbon is crucial to mercury sorption; adding sulfur or iodine can dramatically increase the capacity of activated carbon for Hg(O) (Dunham and Miller, 1996; Krishnan et al., 1994; Vidic and McLaughlin, 1996). Residual carbon from coal combustion is not the same as activated carbon. The pore structure, surface properties, and inorganic content may be strikingly different. Nevertheless, there is evidence for the adsorption of mercury on coal fly ash (Carey et al., 1996) although which specific compounds are adsorbed is not known.

Based on the experimental work in Phase I, it can be concluded that all three coal chars studied (Illinois No. 6, Pittsburgh, and Wyodak) have some degree of Hg(O) and HgCl<sub>2</sub> adsorption capacity. Higher temperature reduces the initial reaction rate and has an inverse relationship to the overall mercury adsorption. The three chars studied in Phase I show consistently higher mercury capture when HgCl<sub>2</sub> (versus Hg(O)) is the mercury source. A physical adsorption process seems to be indicated for the sorption of HgCl<sub>2</sub> based on the correlation with char surface area. Hg(O), on the

other hand, appears to react chemically with sulfur in the char. Thus,  $HgCl_2$  does not appear to be reacting with sulfur in the char. The organic sulfur content of the char appears to be the best predictor of the affinity of the char for Hg(O), while the char surface area appears to be the best indicator of the affinity of the char for  $HgCl_2$ .

In addition to adsorption, laboratory- and pilot-scale evidence suggests that solids such as activated carbon and fly ash can act as catalysts for the oxidation of Hg(O). Kinetic experiments in a continuous-flow reactor showed that the oxidation of Hg(O) by oxygen occurred only in the presence of activated carbon (Hall et al., 1991). A series of bench-scale experiments explored the catalytic effect of solids, including traditional metal catalysts, activated carbon, and coal fly ash, on the oxidation of Hg(O) in simulated flue gas in a fixed-bed reactor (Carey et al., 1996). The results showed that coal fly ash converted gaseous Hg(O) to a mixture of gaseous Hg(II) and adsorbed mercury at temperatures from 420 to 640K (300° to 700°F). Fly ash from five different coals was tested. At 420K, 20%–50% of the Hg(O) was converted to a gaseous oxidized form, probably HgCl<sub>2</sub> based on equilibrium considerations, while 0%–80% was converted to an adsorbed form on the solids. The adsorbed species might be HgCl<sub>2</sub>, HgO, or HgSO<sub>4</sub>. There was a wide variation in the amount of adsorbed mercury depending on coal type. At 640K, less Hg(O) was typically converted.

Information on the reactions of mercury species with fly ash can be obtained by identifying specific mercury species on the surface of char or carbon and then inferring the reaction pathway. In Phase I, a preliminary analysis of the forms of mercury on four carbon-based sorbents was completed. These sorbents were obtained from the EERC and were generated as part of a study of mercury sorbents (Dunham and Miller, 1996). The samples were treated with a simulated flue gas containing  $N_2$ ,  $0_2$ ,  $C0_2$ ,  $S0_2$ ,  $H_20$ , HCl, and Hg(O). In order to better understand the forms of adsorbed mercury, XAFS spectra were collected at the mercury  $L_{til}$  edge at approximately 12,284 eV at the

Stanford Synchrotron Radiation Laboratory. Combining both the XANES and EXAFS evidence, one could speculate that the mercury bonding in the three different mercury sorbents is different. In the iodine-impregnated activated carbon, the mercury bonding appears consistent with Hg-I. In the sulfur-impregnated carbon and the lignite-based activated carbon, the bonding is more consistent with Hg-Cl or Hg-S. Further study, particularly of the Cl-edge XAFS spectra in the sulfur-impregnated carbon and lignite-based activated carbon samples is required.

Thus, particulate matter can promote oxidation of Hg(O) and can collect a significant amount of mercury in flue gas. The amount retained in the particulate matter seems to depend on carbon content, properties of the carbon surface, inorganic constituents in carbon particles, and mercury speciation in the flue gas.

A major goal of the Phase II work is to achieve a much better understanding of how these factors together determine the amount of relevant and Hg(II).

## 5.0 QUALIFICATIONS

The EERC of the University of North Dakota is one of the world's major energy and environmental research organizations. Since its founding in 1951, the EERC has conducted research, testing, and evaluation of fuels, combustion and gasification technologies, emission control technologies, ash use and disposal, analytical methods, groundwater, waste-to-energy systems, and advanced environmental control systems. The main EERC facilities—with 169,000 square feet of laboratory, pilot plant, and office space—are located on the southeast corner of the University of North Dakota campus. Laboratory- and pilot-scale combustors and gasifiers with capacities of up to 4.0 million Btu/hr, as well as diesel and gas turbine simulators, are available for evaluating new fuels and assessing new emission control technologies. Testing equipment is also available for fullscale sampling and measuring of system flow and temperature. Analytical techniques and instrumentation are available for the characterization of solid, liquid, and gaseous materials.

Over the past 6 years, the EERC has conducted literally thousands of mercury measurements and has evaluated and developed appropriate mercury speciation methods for coal-fired boilers. Protocols for performing bench-scale, pilot-scale, and field measurements have all been developed through previous work. Because of this, there is a high likelihood of generating meaningful results that can be supported statistically. Most of the project budget will be in support of well-planned parametric tests rather than in developing test methods.

The overall Phase I project, managed by PSI, was initially selected by DOE under a highly competitive procurement. The PSI team (including the EERC) was again selected by DOE for the Phase II continuation. These facts speak highly of the team qualifications and their ability to plan and complete cutting edge work focusing on trace element behavior in coal-fired systems.

Mr. Stanley Miller, Senior Research Manager, will serve as the project manager and principal investigator, and will be the primary contact between the EERC and the rest of the project team. Dennis Laudal, Research Manager, will serve as co-project manager and co-principal investigator. Mr. Miller has over 20 years of research experience at the EERC, and Mr. Laudal has over 18 years of research experience at the EERC in coal-related pollution control issues. Mr. Miller and Mr. Laudal have been responsible for conducting extensive mercury research at the EERC in mercury measurement, mercury speciation, mercury control, and fly ash-mercury interactions and together have authored more than 30 publications on mercury. Resumes for Mr. Miller and Mr. Laudal are attached as Appendix A.

## 6.0 VALUE TO NORTH DAKOTA

This project will specifically benefit the North Dakota lignite industry by providing information that will lead to the most cost-effective strategy to alleviate concern over mercury emissions from power plants. The work will lead to a much better understanding of the factors that influence Hg speciation and the interaction between lignite fly ash and mercury, which will help to define logical approaches for mercury control, should control be necessary. For example, if results show that lignite ash has the capacity to capture significant mercury under some conditions, then it may be possible to use this information as the primary control strategy. It might even be possible that the lignite ash has unique properties and could be used as a base to develop value-added mercury sorbents for the market outside of North Dakota. If results show that lignite ash has a low tendency to oxidize mercury, then the predicted mercury species emitted from lignite-fired plants would be primarily Hg(O). This information, along with field measurements from power plants, could be used as a basis for the position that mercury emissions from lignite power plants have no direct impact on mercury levels in regional waters. If results should indicate that the lignite fuel will form primarily Hg(II), then a different approach might be taken to mitigate regional concern. In any case, reliable information as to the formation of mercury species and ultimate fate in the environment will be critical to ensure that the most cost-effective strategy is implemented. This information will also help to ensure that lignite fuel used in North Dakota is sustained either by showing that lignite fuels have advantages for trace element control or by providing a better scientific basis for the most effective and economical control approach.

## 7.0 MANAGEMENT

### **Team and Key Personnel**

The complexity of the proposed effort requires a broad range of talents beyond the capabilities of a single organization. Fundamental expertise in a variety of areas including coal chemistry, coal geology (mineralogy), coal combustion, and aerosol dynamics are all essential. Perhaps more importantly, *transition* of this work from fundamental science to a *form useful to utilities and coal companies* requires the applied talents of engineers and scientists working in the private sector, with the goal of *commercial application of the technology*. Clearly, a teaming approach is the only way to assemble the required skills.

Our team has already demonstrated the flexibility and creativity needed to advance the state of the art. The Phase II team brings together the top researchers on the characterization of mineral matter in coal, on its transformation during combustion, and on field measurement. The team has been selected to cover all aspects of the problem from the microscopic characterization to fieldtesting. As in Phase I, the team and the project will be managed by Dr. Connie Senior of PSI, an engineer with over 10 years of experience managing and contributing to large, integrated development programs in the energy and environmental fields.

In Phase II, we have modified the team and the scope of work in order to provide a strong foundation for the remaining tasks needed for ToPEM model development. The core team, led by PSI and consisting of the University of Kentucky (Drs. Huffman and Huggins), MIT (Dr. Sarofim, now at the University of Utah, and Dr. Otmez), the University of Arizona (Dr. Wendt), University of Connecticut (Dr. Helble), Princeton (Dr. Wornat), and the USGS (Dr. Finkelman), will remain intact during Phase II. In Phase II, Mr. S. Miller of the EERC will join the team, adding expertise on mercury-ash interactions. Leaving the project at the end of Phase I are Profs. Peterson and Shadman of the University of Arizona. During Phase I, it was recognized that postcombustion transformations of Hg, Se, and As may determine emissions of these elements. Simultaneously, it was recognized that the time-temperature profiling needed to obtain data for ToPEM could not be generated in the UA facilities available to these two investigators. The elimination of their tasks from Phase II and the addition of EERC and work at UConn and Utah will provide the postcombustion data needed for ToPEM development. Changes are highlighted below and in Figure 1.

- Prof. J. Helble of UConn will continue activities in the area of field data evaluation and will initiate a new task to study the homogeneous and heterogeneous chemistry of mercury, chlorine, and arsenic in the postcombustion zone.
- Prof. M.J. Wornat of Princeton will continue activities in the area of organic field data evaluation and will initiate a new task to study the formation of soot and soot precursors in coal combustion, which has particular bearing on the interactions of gaseous mercury and soot postcombustion.
- Prof. Adel Sarofim, formerly at MIT, will continue his Phase II program at the University
  of Utah. Prof. Sarofim will be moving his MIT drop tube to Utah later this year to continue
  his work on this project; in addition, he will have access to the Utah U-shaped furnace,
  allowing him to study chlorine transformations in flue gas at the pilot scale as well as bench
  scale while continuing his flame zone vaporization studies.
- Mr. S. Miller at EERC will lead an effort to study the interactions between gas-phase mercury and ash at low temperatures. The bench-scale study will build on the Phase I UA work, taking advantage of facilities and expertise in the area of mercury measurement that are unique to the EERC.



Figure 1. Phase II project organizational chart.

## 8.0 TIMETABLE

The overall project is scheduled to be completed in 3 years based on a starting date of March 1, 1998. Task 11 is scheduled to be completed in 2 years from the date of project implementation, assumed to be July 1, 1998. Since the exact schedule for completing the work is highly dependent on the generation and availability of ash samples from another subcontractor of PSI, a more detailed schedule for the work will be decided at a later date by mutual agreement among DOE, PSI, and the EERC. Results from Task 11 will be submitted to PSI and NDIC on a quarterly basis during the quarterly periods for which project work is done. However, reports will not be completed for the quarterly periods in which no experimental work is conducted at the EERC. All quarterly reports submitted by PSI to DOE for the project will also be made available to NDIC and the EERC.

## 9.0 BUDGET

Please see attached budget.

## **10.0 MATCHING FUNDS**

Details of other matching funds are given in Table 1. All other funding for the project has been committed. Note that the \$40,000 requested from NDIC is only \$1.7% of the overall budget and represents a leveraging factor of 60.

TABLE 1	
---------	--

Total Fliase in Duuget						
Sponsor	Share, \$					
DOE	1,800,000					
EPRI	240,000					
Other Industrial Partners (1)	75,000					
Universities (2)	270,641					
NDIC (proposed)	40.000					
Total Non-DOE Cost Share	625,641					
Total Phase II	2,425,641					

## Total Phase II Budget

## **11.0 TAX LIABILITY**

None.

## **12.0 CONFIDENTIAL INFORMATION**

None.

## **13.0 REFERENCES**

- Carey, T.R.; Hargrove, O.W.; Brown, T.D.; Rhudy, R.G. "Enhanced Control of Mercury in Wet FGD Systems," Presented at the 89<sup>th</sup> Annual AWMA Meeting, June, 1996, Nashville, TN; Paper 96-P64B.02.
- Dunham, G.E.; Miller, S.J. "Evaluation of Activated Carbon for Control of Mercury from Coal-Fired Boilers," Presented at the First Joint Power and Fuel Systems Contractors Conference, July 9–11, 1996, Pittsburgh, PA.

- Fahlke, J.; Bursik, A. "Impact of the State-of-the-Art Flue Gas Cleaning on Mercury Species Emissions from Coal-Fired Steam Generators," *Water, Air, Soil Poll.* **1995**, *80*, 209–215.
- Hall, B.; Schager, P.; Lindqvist, O. "Chemical Reactions of Mercury on Combustion Flue Gases," Water, Air, Soil Poll. 1991, 56, 3–14.

International Energy Outlook. DOE/EIA-0484 (98), April 1998.

- Krishnan, S.V.; Gullet, B.K.; Jozewicz, W. "Sorption of Elemental Mercury by Activated Carbon" Env. Sci. Tech. 1994, 28, 1506–1512.
- Laudal, D.L.; Heidt, M.K. "Evaluation of Flue Gas Mercury Speciation Methods," final report for Electric Power Research Institute and U.S. Department of Energy; EPRI TR-108988, Dec. 1997.
- Meij, R. "Trace Element Behavior in Coal-Fired Power Plants," Fuel Process. Tech. 1994, 39, 199–217.
- Miller, S.J.; Ness, S.R.; Weber, G.F.; Erickson, T.A.; Hassett, D.J.; Hawthorne, S.B.; Katrinak,
  K.A.; Louis, P.K.K. "A Comprehensive Assessment of Toxic Emissions from Coal-Fired
  Power Plants," Phase 1 results from the U.S. Department of Energy study; Sept. 1996.

Monthly Energy Review, DOE/EIA-0035 (98-04), April 1998, p. 86-92.

- Prestbo, E.M.; Bloom, N.S. "Mercury Speciation Adsorption (MESA) Method for Combustion Flue Gas: Methodology, Artifacts, Intercomparison, and Atmospheric Implication," *Water, Air, Soil Poll.* 1991, 80, 145–158.
- Senior, C.L. et al. "Toxic Substances from Coal Combustion A Comprehensive Assessment," final report; PSI-1245/Tr-1505, Sept. 1997.
- U.S. Environmental Protection Agency. "Mercury Study Report to Congress," EPA-452/R-97-010; Dec. 1997.

Vidic, R.D.; McLaughlin, J.B. "Uptake of Elemental Mercury Vapors by Activated Carbons," J. Air Waste Manage. Assoc. 1996, 46, 241-250.

## SUMMARY BUDGET

## BENCH-SCALE TESTS TO EVALUATE MERCURY FLY ASH INTERACTIONS

PSI PROPOSED START DATE: 01-Jul-98 EERC PROPOSAL #98-0005-R1

		ΤΟ	TOTAL		<b>PSI SHARE</b>		NDIC SHARE	
		HOURS	\$ COST	HOURS	\$ COST	HOURS	\$ COST	
TOTAL DIRECT LABOR		2414	\$55,299	1984	\$45,449	430	\$9,850	
FRINGE BENEFITS - % OF DIRECT LABOR	52%		\$28,755		\$23,633		\$5,122	
TOTAL LABOR	,		\$84,054		\$69,082		\$14,972	
OTHER DIRECT COSTS					***********			
TRAVEL			\$10,262		\$8,444		\$1,818	
SUPPLIES			\$4,000		\$3,291		\$709	
EQUIPMENT > \$750			\$2,800		\$0		\$2,800	
COMMUNICATIONS - PHONES & POSTAGE			\$906		\$753		\$153	
PROJECT OFFICE SUPPLIES			\$919		\$756		\$163	
<b>REPAIR &amp; REPLACEMENT PARTS</b>			\$1,696		\$1,395		\$301	
FEES			\$33,231		\$25,868		\$7,363	
TOTAL OTHER DIRECT COST			\$53,814		\$40,507		\$13,307	
TOTAL DIRECT COST			\$137,868		\$109,589		\$28,279	
INDIRECT COST - % OF MTDC	46%		\$62,132		\$50,411		\$11,721	
TOTAL ESTIMATED COST			\$200,000		\$160,000		\$40,000	
					which there are been been and and and			

NOTE: Due to limitations within the university's accounting system, the system does not provide for accumulating and reporting expenses at the Detailed Budget level. The Summary Budget is presented for the purpose of how we propose, account, and report the expenses. The Detailed Budget is presented to assist in the evaluation of the proposal.

# BENCH-SCALE TESTS TO EVALUATE MERCURY FLY ASH INTERACTIONS PSI

#### PROPOSED START DATE: 01-Jul-98 EERC PROPOSAL #98-0005-R1

28-May-98

		HOURLY	TOTA	L	PSI SI	HARE	NDIC S	SHARE
LABOR	LABOR CATEGORY	RATE	HOURS	\$ COST	HOURS	\$ COST	HOURS	\$ COST
C. MILLED	DROJECT MANAGED / DRINCIDAL INVESTIGATOR	\$36.11	286	\$10 328	235	\$8 486	51	\$1 842
S. MILLER	CO DEDICIDAL INVESTIGATOR	\$29.47	286	\$8 478	235	\$6 925	51	\$1,503
D. LAUDAL	DESEADOU SCIENTIST/ENGNIEED	\$21.05	477	\$10.041	302	\$8 252	85	\$1 789
G. DUNHAM	RESEARCH SCIENTIST/ENGINEER	\$22.14	130	\$7 878	107	\$2 369	23	\$509
R. SCHULZ	RESEARCH SCIENTIST/ENGINEER	\$17.56	130	\$2,070	352	\$6 181	76	\$1 335
	RESEARCH SCIENTIST/ENGINEER	\$17.30	420	\$4 203	99	\$3 531	10	\$762
	SENIOR MANAGEMENT	\$40.12	107	\$4,293	21	\$3,331	5	\$106
	QUALITY CONTROL MANAGER	\$21.21	20	\$331	247	\$2 601	53	\$773
*********	RESEARCH TECHNICIAN	\$14.58	300	\$4,574	247	\$3,001	11	\$173
************	PILOT PLANT OPERATOR	\$15.76	60	\$940	49	\$774	11	\$174
	RES. EQUIP MECHANIC	\$15.80	60	3748	49	\$174	17	\$1/4
	STUDENT ASSISTANTS	\$0.15	94	3078	122	34/4	17	\$104
	TECHNICAL SUPPORT SERVICES	\$10.40	160	\$1,004	132	\$1,373	28	3291
			2414	\$52,545	1984	\$43,183	430	\$9,362
ESCALATION ABOVE	CURRENT BASE		VAR	\$2,754		\$2,266		\$488
TOTAL DIRECT LABO	R			\$55,299		\$45,449		\$9,850
FRINGE BENEFITS . %	OF DIRECT LABOR	52%		\$28,755		\$23,633		\$5,122
TRANGE BENEFILD V				\$84.054		\$60.082		\$14 972
TOTAL LABOR				\$04,034		\$07,002		\$14,772
OTHER DIRECT COS	TS							
TRAVEL				\$10,262		\$8,444		\$1,818
SUDDI IES				\$4,000		\$3,291		\$709
FOURDMENT > \$750				\$2,800		\$0		\$2,800
COMMUNICATIONS -	PHONES & POSTAGE			\$906		\$753		\$153
PROJECT OFFICE SUP	PLIES			\$919		\$756		\$163
DEDAID & DEDI ACEM	IENT PARTS			\$1,696		\$1,395		\$301
CUODE ODE SUDDORT	LIVITARIS			\$210		\$173		\$37
CD A DUICS				\$1,467		\$1,207		\$260
COALLAR				\$1,684		\$1,386		\$298
ANAL VTICAL DESEAL	PCHIAR			\$6,251		\$5,143		\$1,108
PARTICULATE LAB	Ken LAD.			\$23,619		\$17,959		\$5,660
TOTAL OTHER DIRE	CCT COST			\$53,814		\$40,507		\$13,307
TOTAL DIRECT COS	T			\$137,868		\$109,589		\$28,279
NUMBER OF COST	OF MTDC	46%		\$62,132		\$50.411		\$11.721
INDIRECT COST - %	OF MIDC .	4070						¢40.000
TOTAL ESTIMATED	COST			\$200,000		\$100,000		\$40,000

#### **DETAILED BUDGET -- TRAVEL**

BENCH-SCALE TESTS TO EVALUATE MERCURY FLY ASH INTERACTIONS EERC PROPOSAL **#98-0005-R1** 

#### RATES USED TO CALCULATE ESTIMATED TRAVEL EXPENSES

				CAR	
PURPOSE / DESTINATION	AIRFARE	LODGING	PER DIEM	RENTAL	REGIST.
Conference / Unspecified Location (USA)	\$1,225	\$125	\$42	\$50	\$375
Contractor or Project Review Mtg. / Pittsburgh, PA	\$1,080	\$83	\$38	\$50	\$0

PURPOSE	TRIPS	NUMBER OF PEOPLE	DAYS	AIRFARE	LODGING	PER DIEM	CAR RNTL	MISC.	REGIST.	TOTAL
Conference Contractor or Project Reveiw Mtg	2 2	1 2	3 3	\$2,450 \$4,320	\$500 \$664	\$252 \$456	\$300 \$300	\$90 \$180	\$750 \$0	\$4,342 \$5,920
TOTAL TRAVEL										\$10,262

# BENCH-SCALE TESTS TO EVALUATE MERCURY FLY ASH INTERACTIONS EERC PROPOSAL #98-0005-R1

	ITEM		TOTAL
DESCRIPTION	COST	QTY	COST
computer & peripherals	\$2,800	1	\$2,800 (1)
TOTAL EQUIPMENT		=	\$2,800

(1) prior invoices

#### **BUDGET NOTES**

#### **ENERGY & ENVIRONMENTAL RESEARCH CENTER (EERC)**

#### Background

The EERC is an independently organized multidisciplinary research center within the University of North Dakota. The EERC receives no appropriated funding from the state of North Dakota and is funded through federal and nonfederal grants, contracts, or other agreements. Although the EERC is not affiliated with any one academic department, university academic faculty may participate in a project based on the scope of work and expertise required to perform the project.

The proposed work will be done on a cost-reimbursable basis. The distribution of costs between budget categories (labor, travel, supplies, equipment, subcontracts) is for planning purposes only. The principal investigator may, as dictated by the needs of the work, reallocate the budget among approved items or use the funds for other items directly related to the project, subject only to staying within the total dollars authorized for the overall program. The budget for this proposal has been prepared based on a specific start date; this start date is indicated at the top of the EERC detail budget or identified in the body of the proposal. Please be aware that any delay in the start of this project may result in an increase in the budget. Financial reporting will be at the total project level.

#### **Salaries and Fringe Benefits**

As an interdisciplinary, multiprogram, and multiproject research center, the EERC employs an administrative staff to provide required services for various direct and indirect support functions. Direct project salaries are estimated based on the scope of work and prior experience on projects of similar scope. Technical and administrative salaries are charged based on direct hourly effort on the project. Costs for general support services, such as grants and contracts administration, accounting, personnel, purchasing and receiving, as well as clerical support of these functions, are included in the indirect cost of the EERC.

Fringe benefits are estimated based on historical data. The fringe benefits actually charged consist of two components. The first component covers average vacation, holiday, and sick leave (VSL) for the EERC. This component is approved by the UND cognizant audit agency and charged as a percentage of direct labor on permanent staff employees eligible for VSL benefits. The second component covers actual expenses for items such as health, life, and unemployment insurance; social security matching; worker's compensation; and UND retirement contributions.

#### Travel

Travel is estimated based on UND travel policies, which include estimated GSA daily meal rates. Travel includes scheduled meetings and conference participation as indicated in the scope of work.

#### **Communications (Phones and Postage)**

Monthly telephone services and fax telephone lines are included in indirect cost. Direct project cost includes long-distance telephone including fax-related long-distance calls; postage for regular, air, and express mail; and other data or document transportation costs.

#### **Office (Project Specific Supplies)**

General purpose office supplies (pencils, pens, paper clips, staples, Post-it notes, etc.) are provided through a central storeroom at no cost to individual projects. Budgeted project office supplies include items specifically related to the project: special research notebooks, binders, and other project organizational materials; duplicating, printing, special covers or paper, and binding of reports; project data forms, transparencies or other presentation materials; literature searches and technical information procurement, including subscriptions; manuals, computer diskettes, memory chips, laser printer paper, and toner cartridges; and other miscellaneous supplies required to complete the project.

## **Data Processing**

Data processing includes items such as site licenses and computer software.

#### **Supplies**

Supplies in this category include scientific supply items such as chemicals, gases, and glassware and/or other project items such as: nuts, bolts, and piping necessary for pilot plant operations.

#### Fees

Laboratory and analytical fees are established and approved at the beginning of each fiscal year and are charged based on a per sample or hourly charge depending on the analytical services performed. Additionally, laboratory analyses may be performed outside the University when necessary.

Engineering support fees are based on an established per hour rate for drafting services related to the production of drawings as part of EERC's quality assurance/quality control program for complying with piping and pressure vessel codes.

Graphic services fees are based on an established per hour rate for overall graphics production such as report figures, poster sessions, standard word or table slides, simple maps, schematic slides, desktop publishing, photographs, and printing or copying.

Shop and operation fees are for expenses directly associated with the operation of the pilot plant facility. These fees cover such items as training, safety (protective eye glasses, boots, gloves), and physicals for pilot plant and shop personnel.

#### General

Membership fees (if included) are for memberships in technical areas directly related to work on this project. Technical journals and newsletters received as a result of a membership are used throughout development and execution of the project as well as by the research team directly involved in project activity.

General expenditures for workshops and conferences may include such items as food (some of which may exceed the institutional established limits), room amenities (e.g., place cards, music, banners, floral arrangements), speaker gifts, security, interpreters, technical tour transportation, and room and equipment rental necessary to conduct workshops and conferences.

#### Indirect Cost

The indirect cost rate included in this proposal is the rate which became effective July 1, 1995. Indirect cost is calculated on modified total direct costs (MTDC). MTDC is defined as total direct costs less individual items of equipment in excess of \$750 and subcontracts/subgrants in excess of the first \$25,000 of each award.