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POC-TESTING OF OIL AGGLOMERATION TECHNIQUES AND EQUIPMENT FOR RECOVERY AND CLEANING OF FINE COAL FROM FINE COAL PROCESSING STREAMS

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POC-SCALE TESTING OF A DRY TRIBOELECTROSTATIC SEPARATOR FOR FINE COAL CLEANING

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INTRODUCTION

Numerous advanced coal cleaning processes have been developed in recent years that are capable of substantially reducing both the ash and sulfur contents of run-of-mine coals. The extent of cleaning depends on the liberation characteristics of the coal, which generally improve with reducing particle size. However, since most of the advanced technologies are wet processes, the clean coal product must be dewatered before it can be transported and burned in conventional boilers. This additional treatment step significantly increases the processing cost and makes the industrial applicability of these advanced technologies much less attractive.

In order to avoid problems associated with fine coal dewatering, researchers at the Pittsburgh Energy Technology Center (PETC) developed a novel triboelectrostatic separation (TES) process that can remove mineral matter from dry coal. In this technique, finely pulverized coal is brought into contact with a material (such as copper) having a work function intermediate to that of the carbonaceous material and associated mineral matter. Carbonaceous particles having a relatively low work function become positively charged, while particles of mineral matter having significantly higher work functions become negatively charged. Once the particles become selectively charged, a separation can be achieved by passing the particle stream through an electrically charged field. Details related to the triboelectrostatic charging phenomenon have been discussed elsewhere (Inculet, 1984).

The TES process has been proven in bench-scale tests to be capable of better than 90% removal of pyritic sulfur and greater than 70% reduction of ash for several eastern U.S. coals (Link, 1987). The potential of this technique for achieving high separation efficiencies was demonstrated by its first place ranking in an interlaboratory round-robin test program conducted by DOE (see Figure 1). Since this technology is a dry process, it offers the advantages of lower ancillary costs and improved environmental acceptability as compared to wet processes. Furthermore, the TES process can be installed in-line at a power station, which allows existing pulverization equipment to be used for size reduction.

OBJECTIVE

The primary objective of this research and development project is to demonstrate the technical merits of a proof-of-concept (POC) triboelectrostatic separator at a continuous capacity of 200-250 kg/hr. The POC module will be constructed, installed and operated at the Coal Preparation Facility (CPF) at Virginia Tech. The test unit will combine the triboelectrostatic charging system developed at PETC with a novel triboelectrostatic separator developed by Carpco, Inc. The Carpo design has been used successfully for the upgrading of triboelectrostatically charged particles of both minerals and plastics. The POC test unit will be totally self-contained and will include the necessary dry pulverization equipment for feed preparation and the gas-solid separation equipment for clean coal and refuse recovery. The continuous test unit is designed to be scaleable to larger pilot-plant and industrial sizes. Detailed test programs will be carried out to establish the performance capabilities of this process in terms of energy recovery, ash and sulfur rejection, and throughput capacity. Scale-up parameters will be identified and evaluated through testing at the POC and bench-scale. Independent technical and economic evaluations of the test system have been incorporated in the scope of work to provide critical information necessary to promote the future commercialization of TES technology.

PROPOSED WORK

The successful completion of the proposed work will require the active participation of several different research, engineering, manufacturing and industrial organizations. These will include the Center for Coal and Minerals Processing (CCMP), Carpco, Inc., Roberts & Schaefer Company (R&S) and Babcock & Wilcox (B&W). CCMP will serve as the prime contractor and will provide the contractual management, technical guidance, and overall supervision necessary to complete the proposed work in a timely and orderly fashion. Technical personnel from CCMP will also be primarily responsible for the design, installation, shakedown and testing of the proposed circuitry with assistance from the various participants. In addition, a variety of raw coal characterization studies and product sample analyses will be conducted in the coal analysis laboratories at CCMP. Carpco will design and fabricate the triboelectrostatic separator and will provide expertise related to the installation, shakedown and operation of the test unit. They will also assist in the analysis and interpretation of the experimental test data. R&S will provide basic engineering services, which will include such tasks as the layout of unit operations, specification of equipment and materials, detailing of miscellaneous contractual services, etc. Finally, B&W will provide services related to the technical and economic evaluation of the proposed technology.

The project is expected to begin in the third quarter of 1995 and continue for a period of 36 months. The proposed work has been broken down into ten individual tasks:

Task 1 - Project Planning
Task 2 - Sample Acquisition
Task 3 - Engineering Design
Task 4 - Procurement and Fabrication
Task 5 - Installation and Shakedown
Task 6 - Operation/Detailed Testing
Task 7 - Sample Analysis/Characterization
Task 8 - Process Evaluation
Task 9 - Decommissioning
Task 10 - Reporting

Tribocharger Design and Testing

In previous test work conducted by PETC, tribocharging was accomplished by passing finely pulverized coal through a helix formed from a long strand of copper tubing. More recently, tribocharger designs consisting of static in-line mixers constructed of various types of materials have been employed. For triboelectric charging, static mixers have the advantage that superb particle contact can be achieved in a very short distance. The enhanced rate of contact is a result of the tortuous path traveled by the particle suspension. Studies have shown that static mixers provide a large degree of mixing in the radial direction. For the case of triboelectric charging, this characteristic provides a large number of particle-particle and particle-wall collisions over a very short period of time. The flow regime along the axial length of a static mixer is very close to plug-flow despite the fact that the flow through the static mixer is turbulent (Bor, 1971). As a result, particle charging along the length of a static mixer is relatively uniform, with the maximum degree of charging taking place at the exit of the static mixer. Both of these features are desirable characteristics of a triboelectric charger.

Numerous schemes have been presented in the literature for selecting static mixers for a given application. Unfortunately, nearly all of these guidelines apply to fluid blending or dispersion applications. The explicit use of static mixers for contacting particles in a gas stream is a relatively new area which has not been widely investigated. As a result, engineering criteria for establishing the number, type and size of static mixers required for triboelectrostatic charging must be developed and validated prior to the final commercialization of this technology.

In the present work, bench-scale test work will be carried out to establish scale-up criteria for the PETC tribocharger. Various static mixer geometries and element configurations will be examined over a wide range of operating conditions in order to establish the most effective system for triboelectric charging. The effectiveness of the charging process will be determined by passing finely pulverized coal dust and air through a given static mixer and monitoring the charging efficiency. Charging efficiency will be determined by passing the charged particle stream between two charged plates and measuring the capture efficiency.

Since it is likely that a wide range of static mixer configurations can be used for particle charging, the test data will need to be normalized before it can be used for scale-up. The normalization will be accomplished by converting each static mixer to an equivalent open-pipe length and diameter. Previous test work (Hartung and Hiby, 1972) indicates that complete gas homogenization occurs in an unrestricted pipe when the length-to-diameter (L/D) ratio of the pipe reaches 90. A static mixer having the same equivalent L/D ratio is capable of achieving the same degree of mixing at an actual L/D ratio of only 5. Although particle suspensions have not been studied, these results suggest that equivalent open-pipe L/D ratios may be used as the basis for triboelectrostatic charger scale-up. This procedure assumes that the efficiency of particle contact is maintained so long as the equivalent L/D ratio and superficial gas velocity is maintained through laboratory and full-scale test units. This assumption will be validated from the test data and modified accordingly. The test data will also be used to develop expressions for pressure drop across the various tribocharger designs. This information will be useful for determining the air flow rate and power requirements necessary for triboelectric charging.

Electrostatic Separator Design and Testing

Design deficiencies associated with the original PETC electrostatic separator will be corrected through the use of the Carpo's commercially successful triboelectrostatic separator. However, for the POC unit, it is planned to orient the rolls horizontally and feed the pulverized coal perpendicular to the rolls (see Figure 2). This design has been chosen because the separation of fine coal occurs very rapidly. This is due to the fact that the charge to mass ratio for individual particles is quite large, resulting in rapid movement of the charged particle in a turbulence-free atmosphere. In previous mineral and plastic systems tested by Carpco, the particles are much larger and the charge/mass ratio is smaller. As a result, the separation occurs by deflecting the particle from a vertical "free-fall" path as opposed to having the particle become attached to the electrode.

The conceptual flowsheet for the proposed Carpco design is shown in Figure 3. As shown, pulverized coal from a gas-swept impact mill will be forced under pressure through the static mixer tribocharger system. The charged particles will enter at the top of the separator and will pass vertically through the electrostatic field. One important aspect of the separator design will be to provide baffles near the entrance of the separation chamber. This feature will provide laminar flow conditions between the electrodes, which is particularly important for separating fine particles. After passing through the separator, the clean coal and reject products will be discharged from the bottom of the separator through rotary air-lock valves. Secondary discharge of the fine clean coal and reject products will occur through gas discharge pipes connected directly to dust collectors. In addition, provisions have been made for the removal of "by-pass" material which passes through the electrostatic field without being separated. This material will be re-introduced into the coal pulverizer and recycled through the system until it becomes charged and/or separated. The entire triboelectrostatic test circuit will be operated under a net positive pressure by recirculating an inert gas via a blower system.

During the testing of the Carpco separator, several variables will be examined that have been previously determined to influence the efficiency of the triboelectrostatic separation process. These include, but are not limited to, particle size, solids concentration in the feed stream, velocity of the feed stream through the static mixer, static mixer design/configuration, and electrode potential. It is planned to investigate coarser feed sizes in the range of 50 to 100-mm top size. In addition, the effects of coal type will have to be examined. A statistical design of experiments will be used develop a test program for this phase of the work. The resultant test data will be evaluated using statistical techniques to establish clearly the significance of each variable and the degree to which it influences the performance of the triboelectrostatic separation of coal.

An important goal of the proposed work is to demonstrate the throughput capacity of the Carpco triboelectrostatic separator for coal applications. The unit proposed for the POC has a capacity that exceeds the stated feed rate of 200-250 kg/hr, and may in fact be capable of processing up to 1,000 kg/hr based on Carpco's experience with mineral separations. To establish the true design capacity, it is proposed to limit the width of the feed opening to the separator such that only a portion of the roll width is being utilized. This can be further refined by using vertical baffles which limit the separation width of the unit and confine the separation zone from top to bottom.

Scale-up of the triboelectrostatic separator is primarily a function of the separator width, i.e., mass rate of feed per unit of roller width. Thus, once the unit capacity (kg/cm) is established, the scale up to larger units is clearly established. The separation efficiency, on the other hand, will be a factor of other design features. One of the most important will be the path length for a particle in the separation zone (i.e., electrostatic field). In the proposed separator design, it will be possible to vary the length of the separation zone to optimize the separation efficiency. The initial design value for the separator length will be based on modeling predictions obtained from bench-scale test work. Another very important parameter, electrode voltage, will also be variable up to 50 kV on each electrode. This will yield a maximum total field intensity of 100 kV between the electrodes. Other operating parameters such as the solids loading in the gas stream, gas velocity, particle size, coal type, etc., will also be evaluated in the POC test program. It is anticipated that at least three different levels for each operating parameter will be evaluated during the course of the investigation.

CIRCUIT LAYOUT

The entire POC test circuit will be installed in the high bay area at the Coal Preparation Facility (CPF) at Virginia Tech. Modular design concepts will be employed to speed installation of the required circuitry. This approach will limit the impact of construction on existing facilities and will minimize the amount of time required to fully assemble and shakedown the test circuit.

The conceptual flowsheet of the POC facility is shown in Figure 4. Raw coal will be brought into the coal receiving area by truck. As required, the raw coal will be fed to a 25 HP Jeffery hammer mill for primary size reduction. The coal obtained from the primary mill will have a top size of approximately 3 mm. A 12-ft long flight conveyor will transfer the hammer mill product to a secondary hammer mill (Holmes 451) which will further reduce the particle topsize to 28 mesh. The product from the secondary hammer mill will drop directly into a vibrating feed storage bin. Material from the bin will be fed at the desired production rate to the triboelectrostatic test circuit by means of a programmable weighbelt feeder and screw conveyor configuration. Since the capacity of the primary and secondary hammer mills far exceeds the design capacity of the triboelectrostatic separator, this portion of the POC circuit will be operated intermittently to keep the vibrating bin filled.

The -28 mesh coal will be fed from the vibrating feed bin to a gas-swept impact pulverizer equipped with a rotary valve feeder. The pulverizer will be operated under a positive nitrogen pressure in closed-loop with the rest of the circuit. A Mikro-ACM (Model 10) pulverizer has been selected for final stage of grinding because of its ability to provide a pulverized coal grind at the desired capacity, low heat rise during operation, and capability for on-line adjustment of grind size. Depending on the mill operating conditions, a pulverized coal product between 200 to 400 mesh can be prepared using this unit.

The newly installed triboelectrostatic test module will occupy most of the available high bay area on the left side of the test facility. The triboelectrostatic separator will be located on the top floor of the test facility, while the fine coal pulverizer and air blower will be located on the bottom floor. After passing through the tribocharger, the charged particles pass downward through the electrostatic separator where the positively-charged coal particles are attracted to the negative electrode and the negatively-charged ash-rich and pyritic sulfur particles are attracted to the positive electrode. Electrode voltage will be varied from 10,000 to 60,000 volts on each electrode (maximum 120,000 volts between the electrodes). The products will be collected and discharged through air-lock valves in the bottom of the separator and transferred via flexible screw conveyors into separate dust collectors. The dust collectors will be mounted on the bottom floor, but will pass up through the second floor because of their physical height. The clean coal and refuse products from the dust collectors will be continuously discharged through rotary valves into collection drums.

A blower system has been selected over a conventional air compressor to provide the circulating flow through the POC test circuit. Since high pressure heads are not required, the blower system is more practical for large-scale installations due to its high reliability and very low capital, operating and maintenance costs. A centrifugal blower with radial blades is appropriate for this particular application. This type of blower is used in a variety of applications in both the mineral processing and coal preparation industries. The blower will be equipped with a variable speed drive so that on-line adjustments to the gas flow rate and pressure head can be made during operation. A total gas flow rate range between 0-1000 cfm can be studied using the proposed system. Appropriate duct work and valve control systems will be installed so that the gas flow rate through the pulverizer can be held constant with changes in the blower speed. This design will allow the ground coal to be passed through the static mixer tribocharger system at different pressures and gas/solids loadings without affecting the performance of the mill.

The entire POC circuit will be operated in an inert nitrogen atmosphere. The supply system for the nitrogen gas will be placed outside the main building for safety reasons. It will be necessary to recycle most of the gases in order to minimize the consumption of nitrogen gas. Gas recycling will be accomplished by connecting the dust collector air discharges to the blower that is connected to the manifold feeding the pulverizer and pulverizer by-pass to the static mixer. Provisions for adding fresh nitrogen directly to the separator will be provided as well as a bleed from the manifold feeding the system. Pressure relief valves and oxygen monitors will be provided as required to protect the equipment from over or under pressure situations. The nitrogen supply will also be connected to the dust collectors to operate the pulse cleaning required for the filter elements.

PROJECT PLANS

Future plans call for the completion of various subtasks related to the design, fabrication, installation and testing of the triboelectrostatic coal cleaning circuit. The most important of these tasks include (1) the design, fabrication and installation of all major unit process components and associated ductwork, electrical wiring, instrumentation, etc., as designated in the flowsheet approved by DOE/PETC, (2) the technical evaluation of the performance of the TES circuitry by conducting parametric studies as a function of key operating and design variables, (3) the validation of the steady-state performance of the optimized TES circuit by conducting long-duration test runs over a period of several days and by testing coals from other sources, and (4) the completion of economic feasibility studies to evaluate the commercialization potential of the TES technology for fine coal cleaning.

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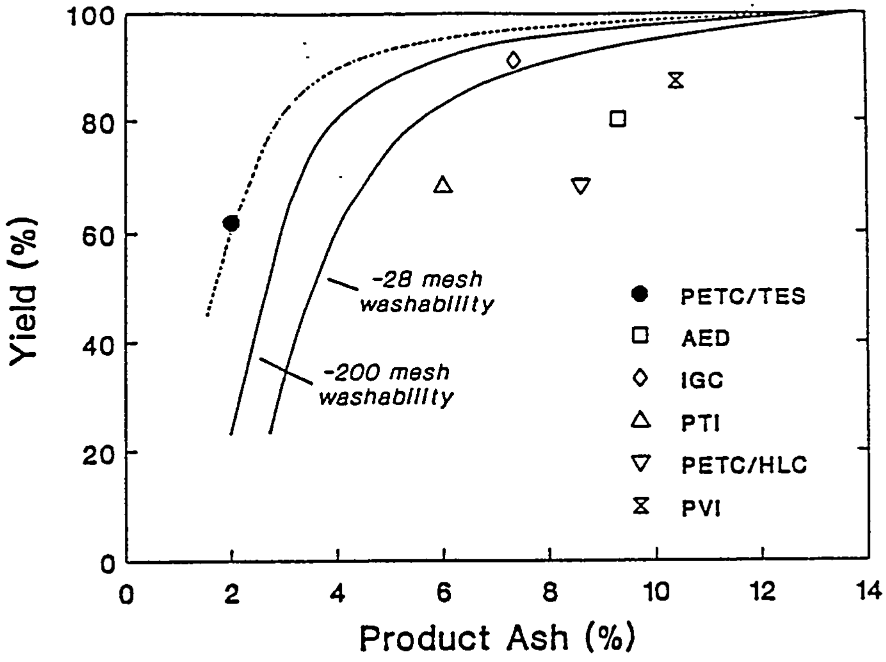

Figure 1. Results of round-robin tests conducted on an Illinois No. 6 coal comparing PETC's Triboelectrostatic Separator (PETC/TES), Advanced Energy Dynamics Electrostatic Separator (AED), Intermagnetics General Corporation Pseudo-Dense Media Separator (IGC), Process Tech's Heavy Liquid Cyclone (PTI), PETC's Heavy Liquid Cyclone (PETC/HLC) and Perfect View's Froth Flotation Chemical Pretreatment Process (PVI). (After Jacobsen *et al.*, 1989).

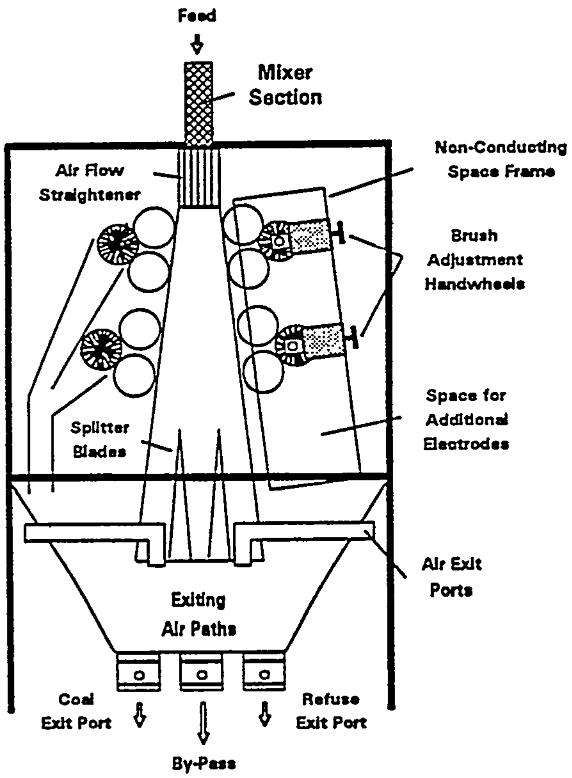

Figure 2. Schematic of Carpco's triboelectrostatic separator for fine coal cleaning.

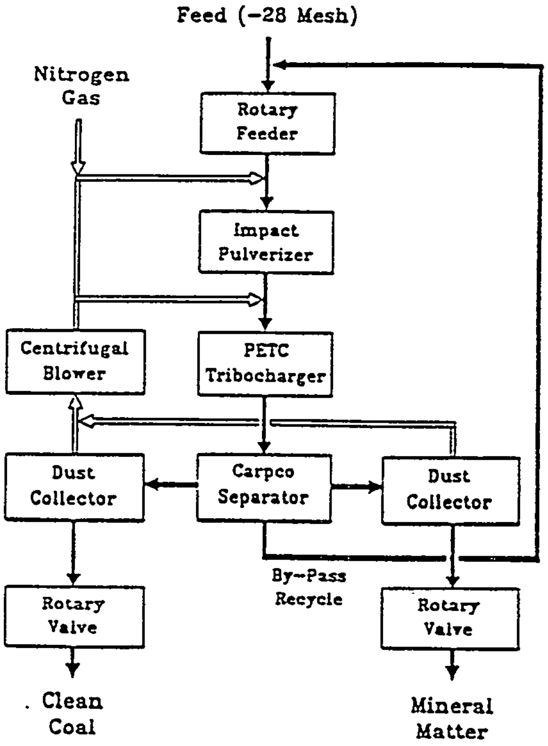

Figure 3. Conceptual block diagram for the triboelectrostatic separator test module.

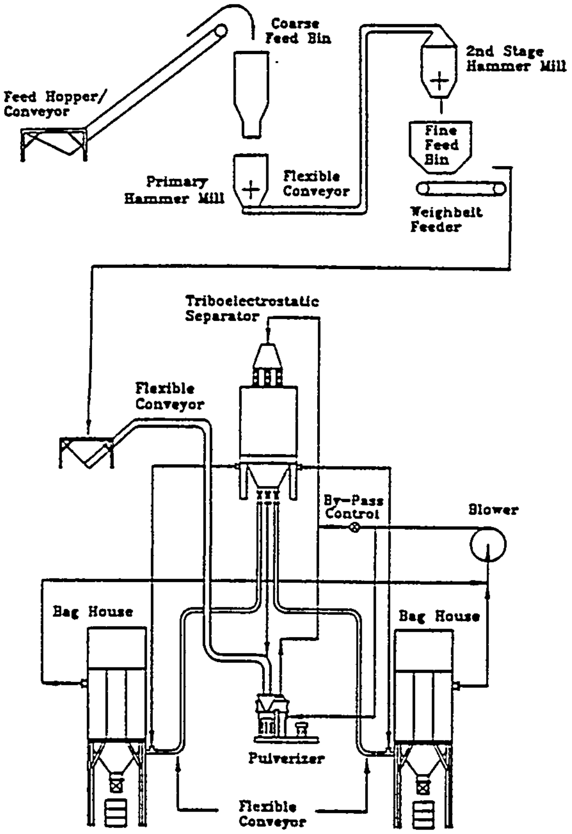

Figure 4. Process flowsheet for the proposed triboelectrostatic separator test circuit.

DEVELOPMENT, TESTING, AND DEMONSTRATION OF AN OPTIMAL FINE COAL CLEANING CIRCUIT

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Introduction

The overall objective of this project is to improve the efficiency of fine coal cleaning. The project will be completed in two phases: bench-scale testing and demonstration of four advanced flotation cells and; in-plant proof-of-concept (POC) pilot plant testing of two flotation cells individually and in two-stage combinations. The goal is to ascertain if a two-stage circuit can result in reduced capital and operating costs while achieving improved separation efficiency.

The plant selected for this project, Cyprus Emerald Coal Preparation Plant, cleans 1200 tph of raw coal. The plant produces approximately 4 million tonnes of clean coal per year at an average as received energy content of 30.2 MJ/Kg (13,000 Btu/lb).

Project Objectives

This project will test flotation units with features which have shown promise in improving the grade/recovery relationship for fine coal. The objectives in completing this project can be summarized as:

- Evaluate emerging flotation equipment and practices
- Develop optimal flotation circuit designs
- Test single and two stage circuit designs
- Improve flotation selectivity at maximum cell capacities.

The project will systematically evaluate the use of four advanced flotation machines individually and in two-stage configurations in order to develop the best processes for 100 mesh x 0 fines. The advanced flotation equipment and circuit combinations to be evaluated in this project are:

- Outokumpu Mintec HG Tank cell
- Jameson cell
- Open Column (Pyramid Resources)
- Packed Column (G&LV)
- Two stage combinations of either a Jameson cell or Outokumpu cell and an open column or a packed column.

The objective is to operate the column flotation equipment at its froth-limited capacity and to use the mechanical cells (Outokumpu and Jameson) to recover the remaining coal, either as a rougher or as a scavenger configuration. The selection of the optimal circuit configuration will depend on the particle size and flotation response of the coal fines and will be determined experimentally.

Project Methodology

The project work will be predominately experimental in nature. Coal samples from the preparation plant will be tested at bench and Proof-of-Concept (POC) scales to quantify flotation cell performance. Relevant aspects of the project approach include:

- Use of commercially available flotation equipment
- Develop an optimization function to help guide testing
- Optimize operation of each machine at bench scale
- Use a two step approach for bench scale tests
- Select two machines for POC testing
- Test single and two-stage circuits at POC-scale.

The optimization function will relate flotation cell(s) performance (grade and recovery) to economic benefit for the preparation plant. The existing plant configuration will be used as a basis for comparison. The optimization function consists of:

- Discounted cash flow analysis
- Flotation circuit variables
  - Yield
  - Ash, sulfur, and moisture
  - Btu recovery
- Plant variables
  - Yield
  - Ash, sulfur, and moisture
  - Btu recovery
- Costs
  - Capital costs
  - Operating costs

The existing preparation plant has been modeled with respect to coal quality and yield by circuit. Any changes in the fine coal circuit product quality will be compensated for by appropriate adjustments to the coarse coal heavy media circuit separation gravity such that the same overall plant clean coal energy content (as received basis) is achieved. This approach will insure that proper credit is given for flotation circuits that lower the fine clean coal ash content and/or increase the circuit Btu recovery. The evaluation will include costs related to increases in clarified water usage and plant space requirements. Preliminary analysis indicates that a net increase in plant Btu recovery of 0.5% to 1.0% can be achieved by improved fine coal cleaning.

Sample Characterization

Prior to the start of the bench scale test work, the coal fines were characterized. The proximate analysis and size consist are given in Table 1.

Table 1. Raw Coal Fines Sample Characterization Data

Size Consist, microns	Coal Analysis
d_{80} = 120	19.99% ash
d_{50} = 40	1.1% sulfur
d_{20} = 9	0.49% pyritic sulfur
	0.61% organic sulfur
	27.7 MJ/Kg (11,911 Btu/lb)

Conventional single-stage and two-stage (rougher-cleaner) batch flotation tests were also completed as part of this work as shown in Figure 1. The two-stage tests were completed to illustrate the improvement in clean coal ash by a reduction of entrained ash in the product via re-cleaning the first stage froth. These results suggest that a 5% ash product can be expected from the advanced flotation cells with high Btu recovery.

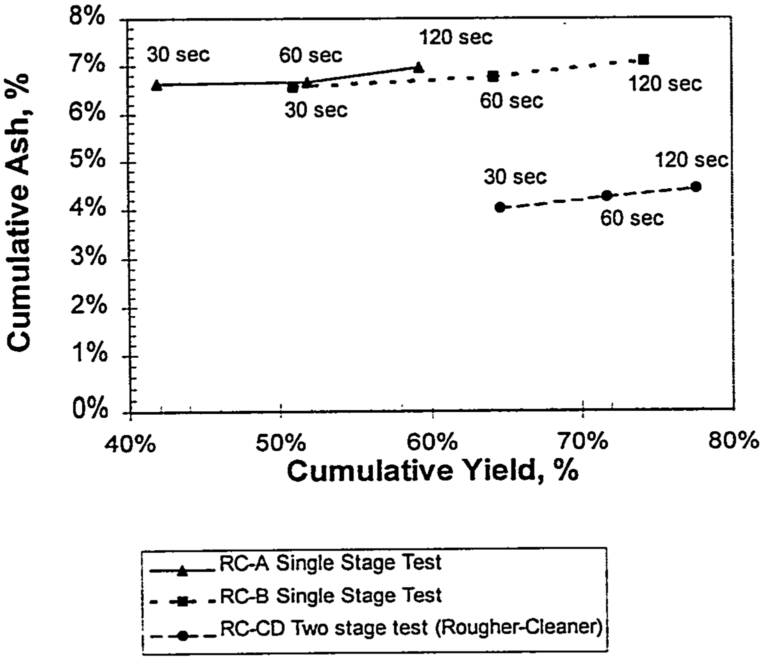

Figure 1. Conventional Batch Flotation Test Results

Bench Scale Test Work

A raw coal fines sample was collected from the preparation plant classifying cyclone overflow. A sample of the existing flotation circuit tailings was also collected after adjusting circuit operations to produce an ash content of approximately 40%. The tailings sample was collected to simulate a second stage feed stream.

Bench-scale work will first test each machine for single-stage operation using the raw coal fines sample. These tests will identify rate limiting conditions for high Btu recovery operation and low clean coal ash production. A series of tests will then be completed to establish a raw coal grade-recovery curve. Tailings samples (second-stage feed) will then be tested to determine conditions for efficient, high Btu recovery operations.

Bench Scale Test Analysis and Circuit Selection

Bench-scale test results will form the basis for selection of two flotation cells for in-plant POC testing. Analysis steps will include:

- Develop single and two-stage circuit material balances
- Use kinetic models to estimate second stage performance
- Extrapolate bench-scale results to full scale operation
- Determine full scale capital and operating costs
- Update economics.

The analysis will assume that the flotation circuit would be installed at the Cyprus Emerald preparation plant. The costs for consumables and utilities will be set to the average plant costs in the first quarter of 1995. Similarly, the value of additional raw coal recovery will be based on coal prices in the first quarter of 1995.

POC Design & Construction

A two-stage POC flotation circuit will be constructed at the Emerald coal preparation plant. Feed coal will be a taken as a slip stream from the classifying cyclone overflow at a nominal rate of 0.25 Kg/s (1.0 tph). The feed rate will be adjustable to facilitate determination of rate limiting conditions. The circuit design will incorporate features to measure mass flow rate and collect slurry samples for each process stream.

POC Operations

The POC test work will be completed in three phases:

- Single stage tests
- Two-stage tests
- Demonstration tests.

The POC tests will first replicate the optimal conditions determined during the bench-scale test program for verification of scale-up relationships. A series of parametric tests will then be run to optimize the process variables. Following the single stage optimization, two-stage tests will be run to determine the proper balance between first and second stage coal recovery for maximum capacity and separation efficiency. The demonstration phase will complete the two-stage optimization with regard to the following variables:

- System capacity and economics
- Product quality and yield
- Total reagent consumption and distribution between stages
- Process control
- Collection of data for system modeling and scale-up factors.

Final Technical and Economic Evaluation

The data collected during POC operations will be assimilated into process and economic models which will project the performance and costs of a commercial scale operation. Data reduction and process economics will be performed throughout the POC operation. Material balances will be calculated using raw and smoothed data as it becomes available. The final evaluation will encompass:

- Complete POC material balances as part of the test program
- Measurement of a grade/recovery relationship for each circuit
- Comparison of POC and Bench-scale test results
- Development of process models for scale-up
- Assessment of the controllability of the circuit
- Updated economics.

Project Status

The bench-scale test work is currently in progress. The results of these tests will be presented during the July 12-14, 1994 DOE contractors conference.

The following manuscript was unavailable at time of publication.

A FINE COAL CIRCUITRY STUDY USING COLUMN FLOTATION AND GRAVITY SEPARATION

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IMPROVING THE PERFORMANCE OF CONVENTIONAL AND COLUMN FROTH FLOTATION CELLS

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Introduction

Many existing mining operations hover on the brink of producing competitively priced fuel with marginally acceptable sulfur levels. To remain competitive, these operations need to improve the yield of their coal processing facilities, lower the sulfur content of their clean coal, or lower the ash content of their clean coal.

Fine coal cleaning processes offer the best opportunity for coal producers to increase their yield of high quality product. Over 200 coal processing plants in the U. S. already employ some type of conventional or column flotation device to clean fines. An increase in efficiency in these existing circuits could be the margin required to make these coal producers competitive.

To investigate potential improvements in existing froth flotation techniques, CQ Inc. engineers assessed the merits of high-speed, high-shear pre-treatment of conventional and column froth flotation feeds. This in-line device, which can be easily retrofit into existing circuitry, subjects the coal and flotation reagents to high-speed, high-shear mixing. While high-speed, high-shear mixing has been applied as part of oil agglomeration circuits, it has not been applied for improving conventional and column froth flotation. The purpose of this device is to totally disperse and coat the carbon particles in the froth cell feed with the collector chemicals. This assures better and more accurate bubble attachment for those carbon-bearing particles. With more accurate bubble attachment, the flotation process will reject more ash-forming and sulfur-bearing minerals while increasing clean coal yield and potentially reducing reagent consumption.

This project investigated the effect of high-speed, high-shear treatment of the feed to both conventional and column froth flotation cells at various collector rates using samples from two coal seams. The primary goal of the project was to determine the effects of high-speed, high-shear pre-treatment on flotation performance and reagent consumption. A secondary goal was to determine the effects of the pre-treatment on coal of different particle size ranges.

Fabrication of the High-Shear Mixer

CQ Inc. fabricated and tested a pilot/commercial model in-line, high-speed, high-shear mixing device, as shown in Figure 1 prior to installation. Slurry enters the bottom of the device and flows from the port near the top of the mixing chamber. Two blade types were tested. A Cowles-design C blade gives high shear, while a radial turbine blade gives more intense mixing. A variable speed drive allowed the testing of various levels of mixing. Conditions for the mixer were set based on a percentage of mixer speed. Values for rpm were measured at 50 and 100 percent:

Percent	Cowles C rpm	Radial rpm
50	584	615
100	1193	1178

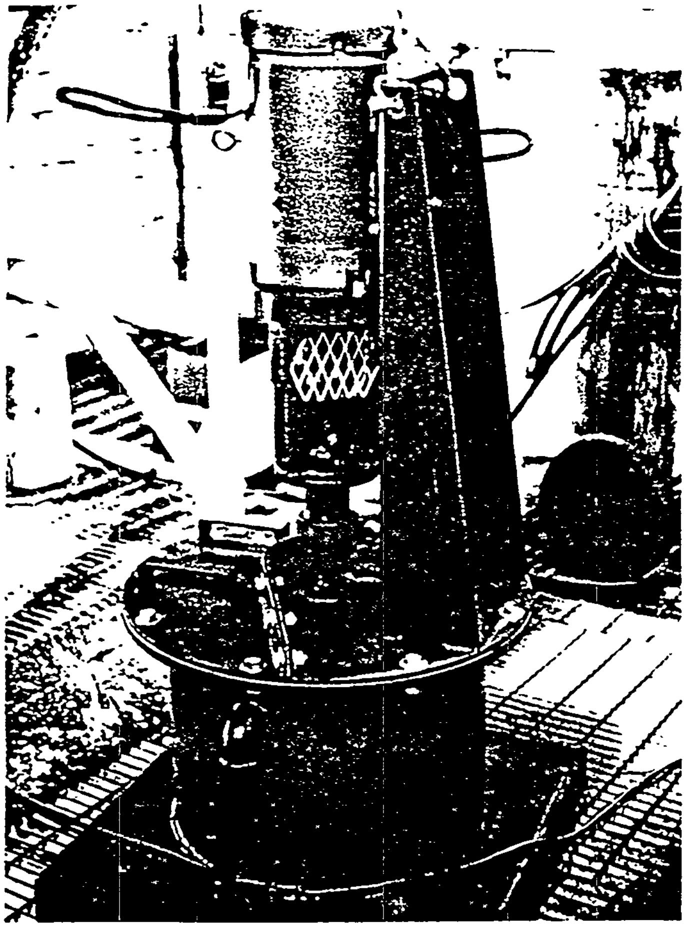

Figure 1. High-Shear Mixer

Testing Facilities

Tests were conducted at CQ Inc.'s Coal Quality Development Center (CQDC) in Homer City, Pennsylvania. The CQDC is a twenty ton per hour coal cleaning test facility, housing various fine coal cleaning devices and ancillary equipment for sizing, crushing, grinding, and dewatering coals. The facility houses the pilot-scale conventional and column continuous froth flotation circuits used in this project.

Coal Sources, Preparation Prior to Flotation Testing, and Test Matrix

Two coals were evaluated for this project. A Northern Appalachian coal from the Upper Freeport seam was obtained from the Rayne Mining Company in Indiana County, Pennsylvania. An Illinois Basin coal from the Illinois No. 6 seam was obtained from the Consolidation Coal Company's Rend Lake Mine near Sesser, Illinois. The Illinois No. 6 coal as-received at the CQDC was very wet and caused handling problems. The coal was first wet screened at 28 mesh to remove fine, clay material. The oversize was then prepared for flotation testing. The analyses of these coals are given in Table 1.

Table 1. Coal Characteristics

Analysis, Dry Basis	Upper Freeport As-Received	Illinois No. 6 As-Received	Illinois No. 6 Test Feed
Ash (Wt %)	22.47	40.41	21.99
Sulfur (Wt %)	1.10	0.93	1.22
Heating Value (Wt %)	11,925	7,780	11,092
lb SO_2/MBtu	1.84	2.30	2.20
Pyritic Sulfur (Wt %)	0.59	ND	0.56
Sulfatic Sulfur (Wt %)	0.01	ND	0.07
Organic Sulfur (Wt %)	0.50	ND	0.60

ND = Not determined

Prior to flotation testing, the coal--crushed to 1/4-in.--was conveyed to a 15-ton bin that discharged into a nominal one-tph ball mill. The coal was fed to the ball mill at a rate set to produce coal of the appropriate topsize, as measured by a Microtrac™ particle size analyzer. The slurry was then fed to a 15,000-gal agitated storage where percent solids was adjusted, if necessary.

In addition to adjustments in frother (methyl-isobutyl carbinol), collector (No. 2 fuel oil), and shear speed, tests were conducted with variations in cell type, particle size, and blade design as shown in Table 2.

Table 2. Test Matrix

Coal	Cell Type	Particle Size	Blade Design
Upper Freeport	Conventional	28 M x 0	Cowles Design C
		100 M x 0	Cowles Design C
		100 x 325 M	Cowles Design C
	Column	100 M x 0	Cowles Design C
			Radial Turbine
Illinois No. 6	Conventional	100 M x 0	Cowles Design C
			Radial Turbine

Note: Shear speed and reagent dosage were also varied during testing.

Results and Discussion

Upper Freeport Seam Coal. The Upper Freeport seam coal floated to good yields at low dosages of fuel oil collector. The results for the 28 mesh x 0 tests are given in Table 3. At the 0.15 lb/t dosage of fuel oil, a significant improvement in yield was noted with the addition of the high-speed, high-shear mixing. Yield increased from 50 without mixing to 81 percent with mixing in the high-speed, high-shear. However, at the higher dosage of fuel oil (0.26 lb/t), the increase in yield was relatively insignificant. This is probably because such a high energy recovery was already obtained without the high-speed, high-shear pre-treatment and there was little room for improvement.

Table 3. Upper Freeport Seam Conventional Flotation Results for 28 Mesh x 0 Feed

Conventional Flotation

MIBC 0.2 lb/t Cowles Design C Blade

Oil (lb/t)	Shear Speed (%)	Yield (Wt %)	Btu Rec (%)	Ash (Wt %)	Ash Rej (Wt %)	Sulfur (Wt %)	Sulf Rej (Wt %)
0.15	0	50	62	5.9	86	0.74	73
	50	68	82	6.4	79	0.77	59
	100	81	94	9.2	66	0.97	42
0.26	0	75	89	8.0	73	0.86	53
	0	81	95	9.2	66	0.95	44
	50	85	98	10.3	59	1.05	33
	50	84	97	10.4	60	1.04	36
	100	80	94	8.6	68	0.92	45

Ash and sulfur contents of the clean coal products all increased with increases in yields. It is interesting to compare the results of the 0.15 lb/t oil test with 100 percent mixing to the results of the 0.26 lb/t oil test with no mixing (second test). Both obtained an 81 percent yield with similar ash and sulfur results. The use of high-speed, high-shear mixing in this case would allow oil dosage to be reduced by half.

The results in Table 3 also show the reproducibility of the test results. At the 0.26 lb/t oil dosage and no mixing, the yield for the two tests differs by six percentage points. These tests were run on the same day but several hours apart. For the two tests with mixing at 50 percent, the yield only differs by one percentage point. These tests were run back-to-back.

Results for tests with the 100 mesh x 0 Upper Freeport seam coal are presented in Table 4. For both oil dosages presented, high-speed, high-shear mixing did not significantly improve the flotation yield or ash or sulfur rejection. For this easy-to-float coal, it appears that little improvement can be made to energy recoveries that are already 98 percent.

Tests with the deslimed 100 M x 325M Upper Freeport seam coal showed little improvement with mixing as this size fraction also floated to good yields with minimal reagents.

Table 4. Upper Freeport Seam Conventional Flotation Results for 100 Mesh x 0 Feed

Conventional Flotation MIBC 0.25 lb/t Cowles Design C Blade

Oil (lb/t)	Shear Speed (%)	Yield (Wt %)	Btu Rec (%)	Ash (Wt %)	Ash Rej (Wt %)	Sulfur (Wt %)	Sulf Rej (Wt %)
0.25	0	80	96	9.6	68	0.82	41
	33	82	98	10.0	66	0.87	38
	67	81	98	9.8	68	0.86	42
	100	81	98	10.0	67	0.86	43
22	33	82	98	9.6	67	0.85	38
	67	80	98	9.9	69	0.87	39
	100	79	98	10.1	69	0.91	41
	100	81	98	11.1	64	0.95	30

The 100 mesh x 0 Upper Freeport seam coal was also tested in the pilot-scale column flotation circuit at the CQDC. Table 5 gives the results of these tests. As with the 100 mesh x 0 conventional flotation tests, no improvement was observed with the application of the high-speed, high-shear mixer between tests with similar reagent dosages. However, there is a noticeable difference in yield between the tests with the Cowles C blade (top of table) and the radial blade (bottom of table). A higher yield was obtained for the radial blade tests. However, these differences also appear in the tests without the high-speed, high-shear mixer, giving rise to concerns with the feedrate through the mixer and into the column cell.

There were also observable differences between the froth characteristics between the two blades. The radial turbine was noted to produce larger bubbles in the froth and appeared to give a larger air holdup in the column than did the Cowles C blade. Though there are noticeable differences in the test results and the observed behavior of the froth between tests with the two different blades, no definite conclusions can be drawn from the column flotation data as to the differences in the blades.

Table 5. Upper Freeport Seam Column Flotation Results for 100 Mesh x 0 Feed

Column Flotation

MIBC/Oil (lb/t)	Shear Speed (%)	Yield (Wt %)	Btu Rec (%)	Ash (Wt %)	Ash Rej (Wt %)	Sulfur (Wt %)	Sulf Rej (Wt %)
2.0/0.5	0 (C)	68	79	8.6	72	0.76	58
	50 (C)	65	77	8.9	73	0.87	54
	100 (C)	67	79	8.8	73	0.81	58
1.4/0.3	0 (R)	79	92	9.3	67	0.90	46
	50 (R)	78	90	9.7	66	0.98	43
	100 (R)	77	91	9.3	68	0.94	45
	100 (R)	77	92	9.2	69	0.94	47

Note: C = Cowles Design C Blade, R = Radial Turbine Blade

Illinois No. 6. Some preliminary tests were conducted with the Illinois No. 6 seam coal (100 mesh x 0) in the column flotation cell. The high oil dosages required to float the Illinois No. 6 seam coal to good yield prohibited testing in the column. This is thought to be due to the build up of an oil film at the froth/pulp interface that prohibits bubble/particle movement into the froth. No further testing in the column was conducted.

The conventional froth flotation tests required significant quantities of fuel oil collector to achieve good yield. Table 6 shows these results as well as results comparing the Cowles C and radial turbine blades.

For the 0.33 lb/t MIBC plus 3.25 lb/t fuel oil tests, the addition of high-speed, high-shear mixing greatly improved the flotation yield. Yield improved from 27 percent to 45 percent. However, at the higher reagent dosages, the improvement in yield was quite insignificant.

The first 100 percent shear test preceded the no shear test and the other followed it, so that reproducibility should be within a few points of yield. These results are similar to the results reported for the Upper Freeport seam 28 mesh x 0 tests, where the low yield tests showed great improvement and the high yield tests showed no improvement.

Table 6. Illinois No. 6 Seam Conventional Flotation Results for 100 Mesh x 0 Feed

Conventional Flotation

MIBC/Oil (lb/t)	Shear Speed (%)	Yield (Wt %)	Btu Rec (%)	Ash (Wt %)	Ash Rej (Wt %)	Sulfur (Wt %)	Sulf Rej (Wt %)
0.33/3.25	0	27	35	6.0	93	1.15	73
	100(C)	45	57	6.3	88	1.17	57
0.5/8.0	0	68	85	7.2	79	1.13	36
	100(C)	71	89	7.5	78	1.14	32
	100(C)	70	88	7.1	79	1.14	33
0.5/7.0	0	59	76	6.7	84	1.12	43
	100(C)	61	79	7.2	82	1.11	42
	100(R)	64	81	6.8	82	1.11	39

Note: C = Cowles Design C Blade, R = Radial Turbine Blade

A comparison between the Cowles C and radial turbine blades for the Illinois No. 6 conventional flotation tests shows that a small improvement in yield could be possible with the radial turbine blade over the Cowles C blade. Remember that the Cowles C gives more shear while the radial turbine gives more mixing. These tests were run back-to-back.

Residence Time Considerations. The results show that improvements in clean coal yield are possible with high-speed, high-shear pre-treatment showing reductions in collector dosage of almost half. However, all of these tests were conducted with a residence time of approximately two minutes in the high-speed, high-shear mixer. Residence time is an important consideration in the application of shear and is an important consideration for scale-up to commercial scale. A two-minute residence time applied commercially would result in a mixer that would be very large and not easily retrofitted into existing plant circuits. Conventional froth flotation circuits have approximately three to four minutes of residence time, so that the mixer would need to have a volume equal to that of one or two flotation cells. Commercial flotation cells range in volume from about 300 to 1000 cu ft. Minimizing residence time (or mixer volume) is an important consideration in the economic potential of high-speed, high-shear pre-treatment.

These tests were all conducted at solids concentrations believed to be best for flotation (approximately 8 percent for the 28 mesh tests and approximately 5 percent for the 100 mesh tests). However, solids content has implications for residence time. If the solids content is higher (water lower), then the overall flowrate is lower for the same solids feedrate. This gives an increase in residence time for a constant volume according to the relationship:

$\tau = V / Q$

where τ = mean residence time (min)
V = volume (cubic feet)
Q = volumetric flowrate (cubic feet per min)

Blade Design. As shown in tables 5 and 6, blade design affects the flotation results. Blade design is also an important feature of the commercial high-speed, high-shear mixer. High shear (Cowles Design C blade) versus more intense mixing (radial turbine blade) must be further investigated.

Conclusions and Recommendations

From the previous discussion, it can be concluded that high-speed, high-shear pre-treatment can improve flotation yield at reduced collector requirements. However, these results also pose several other questions that must be answered. Residence time in the mixer and, therefore, mixer size must be further evaluated. And percent solids in the mixer must also be investigated as it also relates to residence time.

Before a more costly Phase II commercialization effort can begin, these additional questions should be answered by a second Phase I effort so that CQ Inc. and its potential industry partners can be assured that an economically viable product will be available for more extensive commercial testing under Phase II. A proposal for an additional Phase I project has been submitted under the 1995 DOE SBIR solicitation.

The following manuscript was unavailable at time of publication.

INTEGRATION OF THICKNER UNDERFLOW INTO THERMAL DRYER CIRCUIT

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POC-SCALE TESTING
OF AN ADVANCED FINE COAL DEWATERING EQUIPMENT/TECHNIQUE

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INTRODUCTION

Froth flotation technique is an effective and efficient process for recovering of ultra-fine (minus 74 μm) clean coal. Economical dewatering of an ultra-fine clean coal product to a 20 percent level moisture will be an important step in successful implementation of the advanced cleaning processes. This project is a step in the Department of Energy's program to show that ultra-clean coal could be effectively dewatered to 20 percent or lower moisture using either conventional or advanced dewatering techniques.

As the contract title suggests, the main focus of the program is on proof-of-concept testing of a dewatering technique for a fine clean coal product. The coal industry is reluctant to use the advanced fine coal recovery technology due to the non-availability of an economical dewatering process. In fact, in a recent survey conducted by U.S. DOE and Battelle, dewatering of fine clean coal was identified as the number one priority for the coal industry. This project will attempt to demonstrate an efficient and economic fine clean coal slurry dewatering process.

The cost-sharing program is for 36 months, which began October 1, 1994. The program will include laboratory, as well as pilot scale dewatering testing at a rate of 1 to 2 tons/hr of clean coal. The pilot scale studies will be conducted at the Powell Mountain Coal Company's Mayflower Preparation Plant located at St. Charles, VA.

This paper is the first public presentation on this program. It describes objectives and scope, and project plans of the program. Accomplishments of the first six months of the program are summarized.

OBJECTIVES AND SCOPE OF THE PROJECT

The main objective of the proposed program is to evaluate a novel surface modification technique, which utilizes the synergistic effect of metal ions-surfactant combination, for dewatering of ultra-fine clean coal on a proof-of-concept scale of 1 to 2 tph. The novel surface modification technique developed at the UKCAER will be evaluated using vacuum, centrifuge, and hyperbaric filtration equipment. Dewatering tests will be conducted using the fine clean coal froth produced by the column flotation units at the Powell Mountain Coal Company, Mayflower Preparation Plant in St. Charles, Virginia. The POC-scale studies will be conducted on two different types of clean coal, namely, high sulfur and low sulfur clean coal. The Mayflower Plant processes coals from five different seams, thus the dewatering studies results could be generalized for most of the bituminous coals.

PROJECT WORK AND MANAGEMENT PLANS

A highlight of the Project Work and Management Plans was prepared and submitted to DOE during the first quarter of the project. The plans will be revised annually.

Work Breakdown Structure

To accomplish the objectives, the project is divided into nine (9) tasks. As shown in Table 1, Work Breakdown Structure, many of the tasks are further divided into subtasks.

Project Organization

The University of Kentucky Center for Applied Energy Research (CAER) is the prime contractor for the project and most of the laboratory dewatering work will be performed at CAER. The Powell Mountain Coal Company is providing facilities and manpower at their Mayflower Preparation Plant for conducting pilot scale studies. Andritz Ruthner Inc. is providing their hyperbaric pilot unit and personnel to conduct high pressure dewatering tests. Each team member brings knowledge and experience in dewatering to accomplish the objectives of the program.

ACCOMPLISHMENTS

Currently in this program, Tasks 2, 3, 4, 5 and 6 are in progress.

Task 2. Sample Analysis and Laboratory Testing

The PMCC's Mayflower Preparation Plant processes high and low sulfur coal from five different seams. Samples of the column flotation products for the high and low sulfur coals were analyzed for particle size and ash distribution which are listed in Tables 2 and 3, respectively.

Table 1. Outline of Work Breakdown Structure

Task 1.	Project Work Planning	
	Subtask 1.1	Project Work Plan
	Subtask 1.2	Project Work Plan Revisions
Task 2.	Samples Analysis and Laboratory Testing	
	Subtask 2.1	Acquisition and Characterization of Samples
	Subtask 2.2	Laboratory Scale Testing
	Subtask 2.3	Optimization of Parameters
	Subtask 2.4	Analysis of Data
Task 3.	Engineering Design	
	Subtask 3.1	Conceptual Design Package
	Subtask 3.2	Final Design Package
	Subtask 3.3	Construction Schedule
Task 4.	Procurement and Fabrication	
	Subtask 4.1	Bid Packages
	Subtask 4.2	Fabricate/Assemble Components
	Subtask 4.3	Deliver POC-Scale Module and Install
	Subtask 4.4	Maintenance and Operating Manual
Task 5.	Installation and Shakedown	
	Subtask 5.1	Install and Tie-in Module
	Subtask 5.2	Startup Procedures/Shakedown
	Subtask 5.3	Operators Training
Task 6.	System Operation	
	Subtask 6.1	Test Coal No. 1
	Subtask 6.2	Test Coal No. 2
Task 7.	Process Evaluation	
Task 8.	Equipment Removal	
Task 9.	Reporting	
	Subtask 9.1	Monthly Reports
	Subtask 9.2	Project Final Report

Table 2. Particle size and ash distribution of high sulfur (non-compliance) clean coal froth slurry (% solids = 18.9)

Size (Mesh)	Weight (%)	% Ash	Ash Distribution
+100	8.96	6.30	6.65
-100+200	19.11	5.40	12.16
-200+325	16.91	6.20	12.36
-325+500	16.56	7.40	14.44
-500	38.46	12.00	54.39
Feed (Calc.)	100.00	8.49	100.00
Feed (Actual)		8.3	

Table 3. Particle size and ash distribution of low sulfur (compliance) clean coal froth slurry (% solids = 13.0)

Size (Mesh)	Weight (%)	% Ash	Ash Distribution
+100	7.77	3.00	3.06
-100+200	16.58	3.80	8.28
-200+325	16.39	4.80	10.34
-325+500	17.23	5.80	13.13
-500	42.04	11.80	65.19
Feed (Calc.)	100.00	7.61	100.00
Feed (Actual)		7.60	

Laboratory dewatering using the high pressure were conducted by Andritz using a 6.4 cm radius filter with a 125 sq. cm filter area. Tables 4 and 5 list the laboratory dewatering data for the high sulfur and low sulfur clean coal slurry, respectively. The dewatering efficiency index (DEI) for each test was calculated using the following formula

$$\textit{Dewatering Efficiency Index} = \frac{(\%\ \textit{dry solids recovery})\ (\%\ \textit{water in filtrate})}{\%\ \textit{moisture in product}}$$

For the high sulfur coal slurry filter cakes with moisture ranging from 21.3 to 24.5 percent and for low sulfur coal slurry filter cakes with moisture ranging from 20.7 to 22.5 percent were obtained. The DEI for high sulfur coal slurry was much higher than that of the low sulfur coal slurry.

Tasks 3, 4 and 5

The engineering and design of the POC-scale, procurement and fabrication task has been completed. The POC-scale unit for the hyperbaric filtration unit was successfully installed and tested at the Mayflower Preparation Plant.

Table 4. Laboratory hyperbaric filtration data for the high sulfur coal slurry.

Test No.	Filter Speed (rpm)	Pressure (bar)	Cake Formation Angle (degree)	Cake Thickness (mm)	% Moisture in Filter Cake	Dewatering Efficiency Index
HS-1	1.5	3	25	4.8	24.27	407.6
HS-2	0.5	3	25	14.3	21.31	466.7
HS-3	1.0	3	25	14.2	24.30	410.8
HS-4	1.0	3	85	17.3	23.57	422.8
HS-5	1.0	4	85	19.4	23.27	427.9
HS-6	1.0	5	85	21.4	22.89	435.2
HS-7	1.5	3	85	13.9	24.50	405.2
HS-8	1.5	4	85	15.2	22.60	440.7
HS-9	1.5	5	85	16.6	22.82	436.1
HS-10	2.0	3	85	13.0	24.43	406.5
HS-11	2.0	4	85	14.2	23.62	420.5
HS-12	2.0	5	85	15.6	23.72	419.8

Table 5. Laboratory hyperbaric filtration data for the low sulfur coal slurry.

Test No.	Filter Speed (rpm)	Pressure (bar)	Cake Formation Angle (degree)	Cake Thickness (mm)	% Moisture in Filter Cake	Dewatering Efficiency Index
LS-1	1.0	3	85	10.4	22.37	344.1
LS-2	1.0	4	85	11.4	21.55	361.9
LS-3	1.0	5	85	13.1	20.93	375.2
LS-4	1.5	3	85	8.7	22.70	337.5
LS-5	1.5	4	85	9.7	22.45	342.3
LS-6	1.5	5	85	10.6	21.38	365.1
LS-7	2.0	3	85	8.4	22.91	333.8
LS-8	2.0	4	85	9.5	22.51	341.3
LS-9	2.0	5	85	10.4	21.69	358.7

Task 6. System Operation

The first system tested for the program was the Andritz hyperbaric unit. The pilot hyperbaric unit has a disc of 1.4 meter (4.6 ft.) diameter with 2m^2 (22 sq. ft.) filtration area which is enclosed in a 2.5 meter (8.2 ft.) diameter pressure vessel. The trailer-mounted unit is self-sufficient and has its own feed pumps and air compressor. The unit requires 440 volts power to run.

Baseline Testing. The primary operating variables that were evaluated in baseline testing were cake formation angle (CFA), filter speed and pressure. The CFA refers to the angle of rotation, measured from the horizontal position where the rotating filter element enters the slurry, through which cake formation occurs and is analogous to the more common term 'cake formation time.' The filter speed simply refers to the rotation of the filter disc and is measured in revolutions per minute (rpm) while the pressure is the vessel pressure measured in bar (about 1 bar = 14.5 psi). Most of the tests were conducted at a feed rate of 50 gallons/minute (1.5 tons/hr dry solids) of slurry.

The effect of filter speed and cake thickness on cake moisture for the high sulfur clean coal froth product for 165° CFA is shown in Figure 1. The cake moisture increased with increasing filter speed as shown in Figure 1a. This was the case for both 1 and 2 bar pressures (1 bar = 14.5 psi). However, at 3 bar, cake moisture remained essentially constant at 23.5 percent moisture. Note, that increasing cake thickness from 10 to 20 mm, the filter cake moisture was lowered. This is very surprising, however, similar trends were observed in other tests conducted at different CFA. The lowest moisture of 23.2 percent was achieved using 2 and 3 bar pressures.

The effect of CFA on filter speed of 1.5 rpm is shown in Figure 2. As the CFA was increased from 85° to 165°, the cake moisture obtained at 1 bar pressure increased from 24.8% to 27% moisture. At higher pressure (3 bar), the cake moisture increased from 21% to 23.7% over the same range of CFA.

Air consumption and solids throughput are the two most important considerations in evaluating the performance of the hyperbaric filter. Figure 3 shows the air consumption requirements for tests conducted using various pressures and CFA. It shows that at a filter speed of 1.5 rpm and a CFA of 165°, the air consumption at 3 bar pressure was 460 scfm/ton. Figure 4 shows the dry solids throughput using the experimental conditions described above. The solids throughput at 1 bar pressure increased from 77 to 120 $lb/ft^2/hr$ as the CFA was increased from 85° to 165°. At 3 bar pressure, the solids throughput increased significantly from 110 to 165 $lb/ft^2/hr$ over the same range of CFA.

Before summarizing baseline testing results, it is important to recognize that while it is desirable to reduce cake moisture to the lowest levels possible, it is also desirable to obtain these results with minimum cost (i.e. minimize air consumption and maximize throughput). With these factors in mind, the baseline test conditions selected from these results to minimize moisture and air consumption while maximizing throughput were 3 bar pressure, 1.5 rpm filter speed and 165° CFA. These conditions produced a filter cake with 23.6% moisture and a cake thickness of 18 mm. These conditions resulted in a solids throughput of 165 $lb/ft^2/hr$ and an air consumption of 460 scfm/ton.

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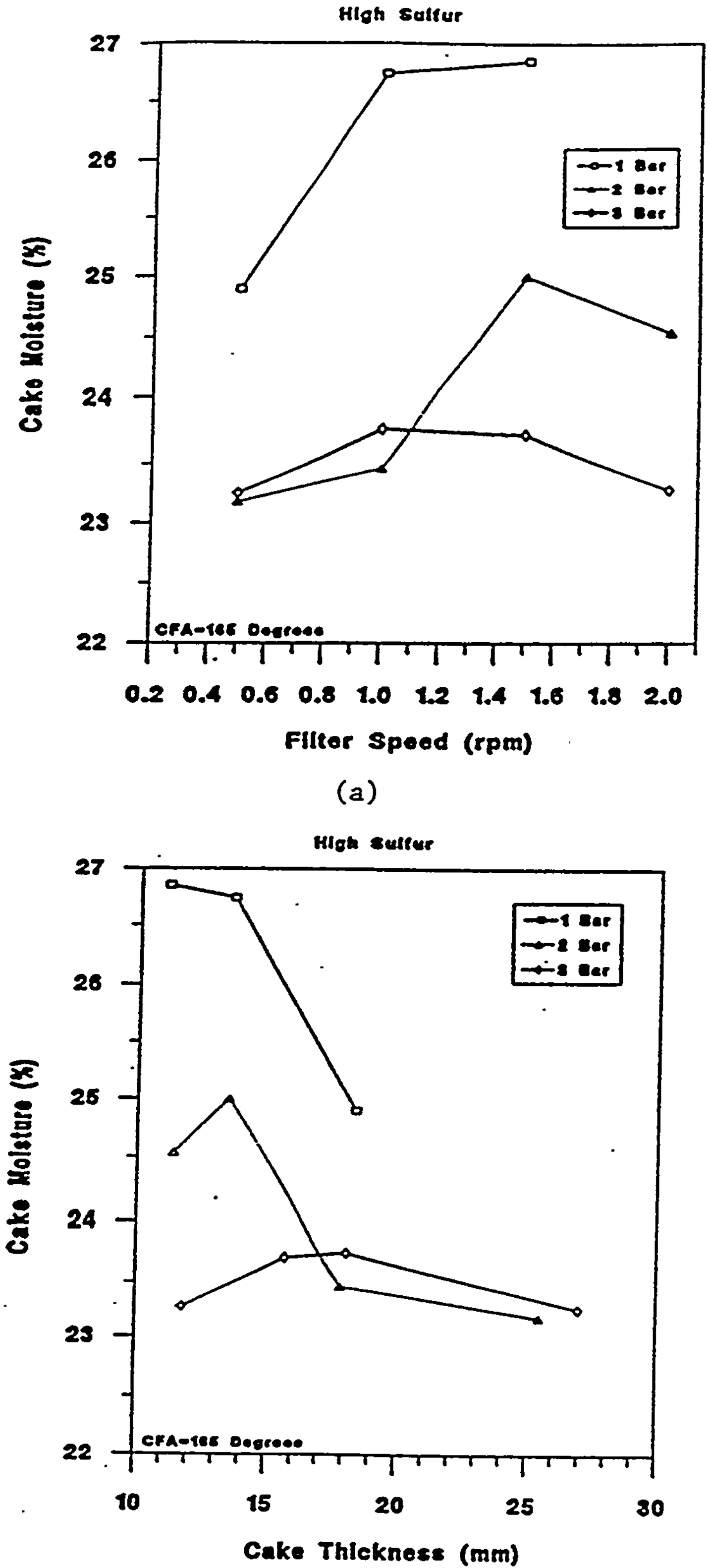


(a)

(b)

Figure 1. Effect of filter speed (a) and cake thickness (b) on filter cake moisture using 165° cake formation angle at various applied pressures

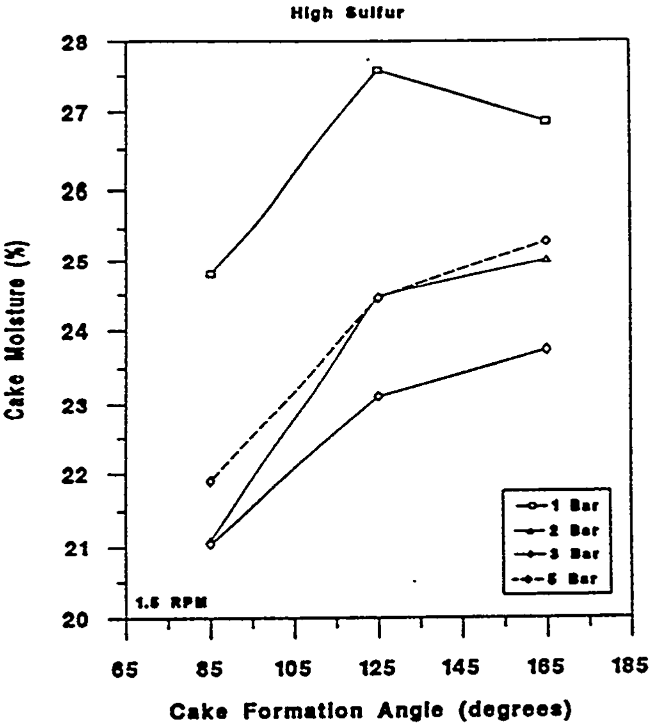
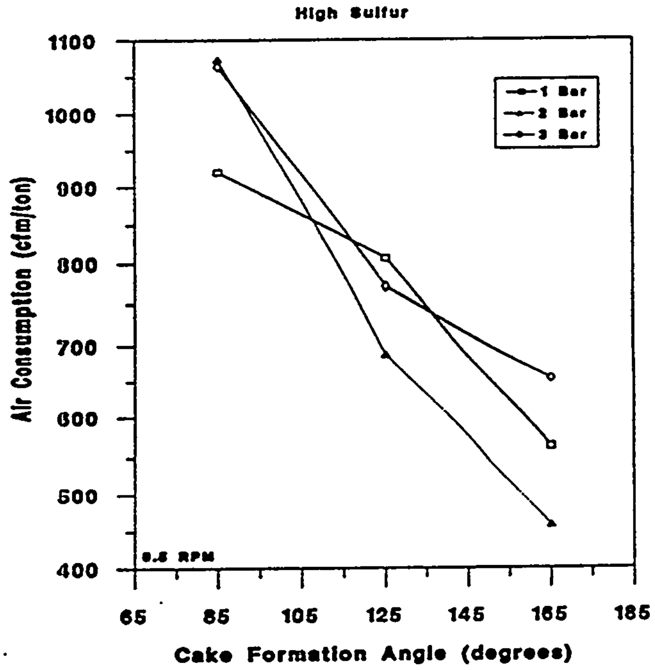


Figure 2. Effect of cake formation angle at various applied pressure on filter cake moisture obtained at 1.5 rpm filter speed

Figure 3. Effect of cake formation angle on air consumption for pressure filtration of high sulfur coal at 1.5 rpm filter speed and various vessel pressures



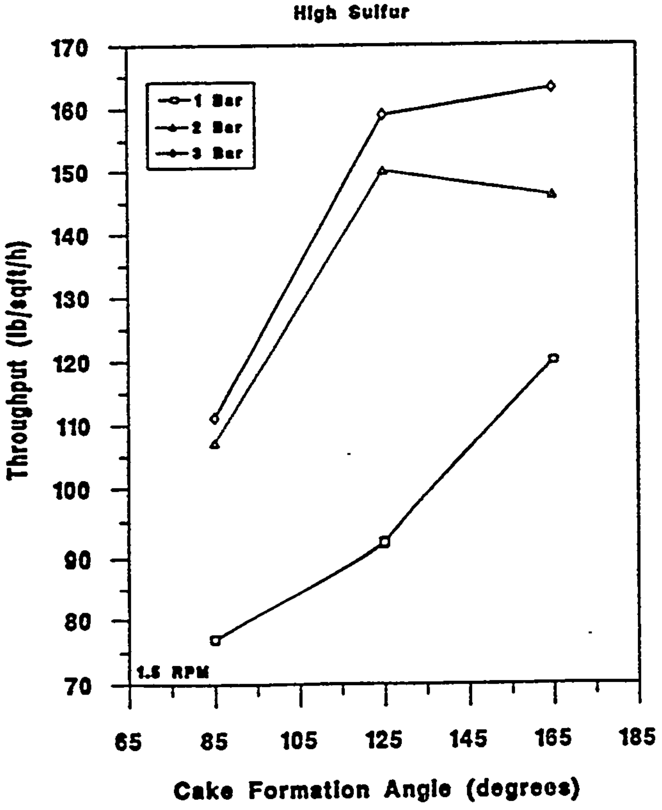


Figure 4. Effect of cake formation angle on throughput for pressure filtration of high sulfur coal at 1.5 rpm filter speed and various vessel pressures

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IMPROVEMENT OF STORAGE, HANDLING, AND TRANSPORTABILITY OF FINE COAL

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BENCH-SCALE TESTING OF THE GRANUFLOW PROCESS FOR FINE COAL DEWATERING AND RECONSTITUTION: RESULTS USING A HIGH-G SOLID-BOWL CENTRIFUGE

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CHARACTERIZATION OF AIR TOXICS FROM A LABORATORY COAL-FIRED COMBUSTOR AND UTILITY-SCALE POWER PLANTS

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CHARACTERIZING MERCURY EMISSIONS FROM A COAL-FIRED POWER PLANT UTILIZING A VENTURI WET FGD SYSTEM

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INTRODUCTION

Southern Research Institute (SRI) conducted a test program at a coal-fired utility plant from October 24 to October 29, 1994. The test schedule was chosen to permit us to collect samples during a period of consecutive days with a constant coal source. SRI collected the samples required to measured concentrations of anions and trace elements around two scrubber modules and in the stack. Anions of interest were Cl^-, F^-, and $SO_4^=$. We analyzed samples for five major elements (Al, Ca, Fe, Mg, and Ti) and 16 trace elements (As, B, Ba, Be, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, and V).

SRI made measurements across two scrubber modules, each treating nominally 20% of the total effluent from the boiler. Across one module we examined the effects of changes in the liquid-to-gas ratio (L/G) on the efficiency with which the scrubber removes trace elements and anions from the flue gas. Across another module we examined the effects of slurry pH on the removal of trace elements and anions from the flue gas. Measurements in the stack quantified emissions rates of anions and trace elements.

Special emphasis was placed on measurements of mercury concentrations. SRI sampled with two methods designed to measure mercury in flue gases -- EPA Method 29, and a proprietary modification to EPA Method 101A developed by Ontario Hydro Technologies.

Plant Features

Features of the plant that affect emissions of the chemical substances of interest are:

1) The coal is beneficiated by washing to remove a substantial fraction of mineral matter and sulfur.
2) The coal is burned in a cyclone furnace, with the attendant high temperature of combustion and the emission of a high concentration of nitrogen oxides, but the emission of a lower fraction of the ash than occurs with wall or tangential firing.
3) The fly ash evolved from the boiler is first subjected to collection in an ESP.

4) The residual fly ash at the outlet of the ESP and the SO_2 are subject to capture in a venturi scrubber with limestone as the basic reactant. Design specifications of the scrubber are particulate collection of 94% and SO_2 reduction of 84%.

The scrubber consists of six venturi modules. Normally, five scrubber modules are in service, and one is in maintenance. Customarily four of the active modules are operated at "high" pH and the fifth is operated at "low" pH. During this test the high pH was typically 5.7 and the low pH was typically 5.1. Scrubber sorbent is prepared at the plant by pulverizing limestone in a wet ball mill. Additional water is added to this slurry to maintain a solids concentration in the recycle tanks around 12%. The actual feed rate of limestone is governed by the pH of the recycle tanks. Fresh limestone slurry is supplied only to the high-pH modules; spent slurry from the high-pH modules performs the scrubbing in the low-pH module. Fresh limestone slurry is added at Ca/S mole ratio of about 1.05, or perhaps sometimes as high as 1.10. The scrubber is operated with forced oxidation to produce a waste product in which gypsum rather than calcium sulfite is dominant. Waste liquor and solids from the recycle tanks are pumped to an effluent tank and then to an ash pond.

The main constraint placed on the plant by our test program was the exclusive use of coal from one seam of one mine. Gross generation was kept within 0.5% of full load throughout our sampling periods. In addition to holding the load constant, soot blowing of air heaters was suspended during our sampling times to eliminate the effect of this erratic ash loading from our flue gas measurements.

Test Program

Our test program called for three operating conditions in the scrubber. We tested across a scrubber module at the normal liquid-to-gas ratio (L/G) and at a higher L/G each day of our test. The adjustment in L/G was made by reducing the flue gas flow through a scrubber module (identified as Module X) while maintaining the slurry feed rate. The flue gas flow was reduced by closing a louver-type damper at the inlet to the module. We also tested across another scrubber module operated at low and high pH levels on alternate days. The change in scrubber pH was made over night on another module (identified as Module Y). Module Y operated at low pH on the first and third days of our test, and high pH on the second and fourth test days.

Other than the operational changes in the scrubber modules and the restrictions on sootblowing, the boiler and scrubber systems operated during our test program as they would normally operate. The operators maintained very stable conditions during our test periods.

Samples taken during this program were comprised of both flue gas and process liquids and solids. Flue gas samples were taken at four locations over a four-day period:

1) Inlet to Scrubber Module X — 4 samples at normal L/G and 4 at high L/G
2) Outlet of Scrubber Module X — 4 samples at normal L/G and 4 at high L/G
3) Outlet of Scrubber Module Y — 2 samples at low pH and 2 at high pH
4) Stack — 4 samples.

The sampling methods we used for flue gases were as follows:

- Major metals and trace metals (including mercury) in both particulate and vapor forms were sampled using EPA Draft Method 29.
- Mercury was also collected as the single analyte by an impinger train developed by Dr. Keith Curtis of Ontario Hydro Technologies. The Ontario Hydro mercury train is a modification to the EPA Method 101A sampling train.
- Anions were sampled by use of the Method 5 train in which solids on the filter as well as sodium carbonate/bicarbonate impinger solutions were retained for analysis.
- Samples collected for metals analysis in three ranges of particle size were taken using teflon-coated cyclones I and II of the SRI/EPA Five Series Cyclone sampling system.

RESULTS

The emphasis in this paper is on the results of measurements of mercury concentrations, which was the main emphasis of the test program.

Mercury Concentrations in Coal

We determined mercury in the as-fired (washed) coal to assess the plausibility of the mercury concentrations measured in the flue gas. We had reason to believe the mercury value reported by analytical subcontractor Galbraith Laboratories (GL) for the cleaned coal was low. We had some samples of cleaned coal analyzed by Brooks Rand, Ltd. (BR). For the period October 25-28, the concentrations of mercury in the washed coal average 0.0837 µg/g in the analyses at BR, but only 0.0578 µg/g in the analyses at GL. We believe the reason for this difference is the use of different sample digestion procedures by the two labs. GL used a standard microwave digestion technique for sample preparation (based on Application Note MS-6 for coal digestion by CEM Corporation, manufacturer of the microwave oven). The BR sample preparation procedure employs perchloric acid to accomplish complete dissolution of the sample. Only the higher concentrations reported by BR could have produced the highly consistent flue-gas concentrations that were measured. The consistency of results of the BR analyses is shown below:

	µg/g
October 25	0.0781
October 26	0.0840
October 27	0.0883
October 28	0.0844
AVERAGE	**0.0837**
Std. Deviation.	0.0042

The average mercury concentration in the washed coal was 0.0837 µg/g, which for this coal would yield 9.7 µg/Nm^3 in the flue gas. (In our usage, Nm^3 is the dry flue gas volume in cubic meters corrected to 20°C, 1 atm pressure, and 3% O_2 content.) This concentration agrees very well with the measured concentrations of mercury in the flue gas, assuming that all mercury contributed by the coal was entrained in the flue gas.

Mercury Concentrations in Flue Gases

We used two different sampling methods to determine the concentration of mercury in flue gases. Both methods, Method 29 and the modified Method 101A (MM101A), ostensibly provide distinct measures of two ionic species of mercury — Hg(II) and Hg(0).

Analyses of filter solids were performed for SRI by Galbraith Laboratories, Inc. (GL). Both SRI and GL analyzed the impinger solutions. All impinger solutions were prepared for mercury determinations by EPA Method 7470. Mercury was determined primarily by CVAAS as per EPA Method 7470. But SRI's CVAAS instrument is also equipped for simultaneous determinations by atomic fluorescence spectrometry (AFS), which offers lower detection limits than CVAAS. Hence, those few samples in which the mercury levels were below the detection limit of the CVAAS technique were analyzed by CVAFS.

The Method 29 permanganate-containing impinger solutions and both types of MM101A impinger solutions were prepared and analyzed for mercury essentially in accordance with EPA Method 7470. At SRI, the Method 29 peroxide-containing impinger solutions were prepared for mercury determinations by a slightly modified version of EPA Method 7470. At the point where potassium permanganate was added to the solutions, we added solid potassium permanganate, after first adding the permanganate solution specified in the method, to minimize the increase in sample volume that is associated with this step. But GL encountered problems in their attempts to follow this protocol for peroxide-containing samples. Specifically, they found that their samples generated too much heat on addition of the solid permanganate. Indeed, the solution temperatures actually reached the boiling point on certain occasions, which raised concerns that certain volatile elements could be lost by evaporation.

It was later discovered that, in an attempt to attain the lowest possible detection limits for mercury, GL had used a lower sample-dilution ratio than we did. Thus, their samples had contained more of the original hydrogen peroxide than ours, and their peroxide-neutralization reactions were thus more intensely exothermic than ours. But in the absence of this knowledge, GL carried out a microwave digestion of these samples (i.e., the EPA Method 29 protocol for Method 29 impinger liquids) prior to any further preparation or analysis, in hopes of circumventing the problem altogether. Unfortunately, their mercury measurements on these samples correlated poorly with ours; their results were generally much lower and more variable. We can only speculate that they somehow experienced losses of mercury during their microwave sample-preparation step. Note that, if they had decomposed the hydrogen peroxide in the microwave oven, then portions of the ionic mercury could have been reduced to the neutral elemental form, leading to losses of elemental mercury vapor on opening the microwave vessels.

Although we did not attempt to speciate mercury in solid matter, it seems plausible that the mercury in this state is ionic (perhaps as the compound HgO), not elemental. The percentage of the total mercury found in the particulate state was 1% or less of the total, confirming the expectation that mercury would occur mainly in the vapor state. At the scrubber inlet the solid phase mercury was 0.8% of the total. At the stack it was 0.5% of the total.

The average mercury concentrations in the vapor state are tabulated below for ready comparison. These averages were produced disregarding the scrubber L/G or pH, which was inconsequential as described later. Thus, there were eight individual measurements represented in the averages at Module X inlet for Method 29, seven individual measurements at Module X inlet for MM101A, eight measurements at Module X outlet for both sampling methods, and four measurements for each method at Module Y outlet and the stack. The concentrations are in the units μg/Nm^3; the percentages of the two forms of mercury are shown in parentheses:

	Method 29	Modified Method 101A
Inlet, Module X	μg/Nm^3	μg/Nm^3
Ionic	7.39 (74.3%)	4.74 (48.1%)
Elemental	2.56 (25.7%)	5.12 (51.9%)
Total	9.95	9.86
Outlet, Module X	μg/Nm^3	μg/Nm^3
Ionic	1.15 (20.8%)	0.56 (9.3%)
Elemental	4.37 (79.2%)	5.56 (90.7%)
Total	5.52	6.13
Outlet, Module Y	μg/Nm^3	μg/Nm^3
Ionic	-	0.51 (8.5%)
Elemental	-	5.54 (91.5%)
Total	-	6.06
Stack	μg/Nm^3	μg/Nm^3
Ionic	1.35 (22.6%)	0.52 (7.9%)
Elemental	4.63 (77.4%)	6.13 (92.1%)
Total	5.98	6.66

The more important observations from the above tabulation are as follows:

1. The two methods were in good agreement on the total concentration at each location where both methods were used. The differences range only from 0.1 to 0.6 μg/Nm^3.

2. Both methods indicate that the scrubber removed most of the ionic mercury. Either method shows good agreement between the outlet of Module X and the stack; MM101A also shows good agreement between the outlets of Modules X and Y.

3. The methods differ substantially on the proportions of mercury in the ionic and elemental states. At each sampling location Method 29 gave the higher percentage in the ionic state. Moreover, Method 29 seemed to show that part of the ionic mercury at the scrubber inlet was converted to the elemental form at the outlet.

The explanation for the difference in speciation cannot be explained unequivocally. It may have to do, however, with the lack of specificity of the peroxide impinger in Method 29 for capturing the ionic form of mercury. The combination of hydrogen peroxide and nitric acid in the so-called peroxide impinger surely has the oxidizing potential for converting part of the elemental mercury to the ionic state. The suggestion that ionic mercury shifts from the ionic state to the elemental state across the scrubber is contrary to the predictions of thermodynamics. Therefore, these data suggest Method 29 did not accurately differentiate the species of mercury.

Mercury Concentrations in Scrubber Solids and Liquids

Concentrations of mercury in streams associated with the scrubber are listed below:

Sampling Occasion	INPUT STREAMS		OUTPUT STREAMS	
	Make-up Water, ng/mL	Dry Limestone, µg/g	Recycle Slurry, µg/g	Discharge Slurry, µg/g
Oct. 25 AM	<0.010	0.0120	-	0.0248
PM	<0.010	<0.010	0.0295	0.0248
Oct. 26 AM	<0.010	<0.0087	0.0084	0.0248
PM	0.036	0.0150	0.0279	0.0248
Oct. 27 AM	<0.010	0.0100	0.0283	0.0240
PM	0.003	<0.00097	0.0289	0.0240
Oct. 28 AM	0.005	<0.0066	0.0303	0.0237
PM	<0.010	<0.010	0.0324	0.0237

It is to be noted that the concentrations in the liquid components of all slurries were in the units ng/mL, whereas those in the solids were in the units µg/g. Thus, there was a 1000-fold difference in the mercury concentrations in the two phases of the slurries.

The concentrations in the input water and limestone were often below the detection limits. The data can be conservatively summarized by the statements that in the water the value was always below 0.04 ppb and that in the limestone (where the detection limit was much higher) always below 0.02 ppm. The mercury entering the scrubber in the limestone slurry was far below that entering in the flue gas. In other words, the limestone slurry was responsible for only a small fraction of the total mercury.

The mercury in both liquid and solid phases leaving the scrubber as the recycle slurry or the discharge slurry was much enriched over the level entering in liquid and solid forms. As may be reasonably inferred, the increase was due to the uptake of mercury from the flue gas. There was some variability from sample to sample, but in either slurry composite the calculated mercury concentration was approximately 0.02-0.03 ppm. The composite analyses of the two slurries agree satisfactorily, in general.

Mass Balances

Coal vs. Scrubber Inlet

The plan of the investigation did not include collection of samples of bottom ash or ESP ash. Moreover, the plan did not include measurement of the proportions of ash leaving the boiler as bottom ash and fly ash or the measurement of ash removal in the ESP. The only task relevant to these general considerations that can be undertaken is a comparison of the concentrations of substances flowing in the duct leading to Module X against the concentrations that would have been observed if all of these substances originally in the coal had been entrained uniformly in the inlets to all five operating modules.

The average metal concentrations based on the coal analysis were compared with the averages found at the Module X inlet. For the major metals recoveries range approximately from 23-32%. For fly ash at the inlet of Module X, the recovery might be expected to fall somewhere within this range. It is consistent with what we know about this plant: 1) fly ash makes up about 30% of the total ash, and 2) the efficiency of the ESP is at most 40%.

The recovery of mercury was 105%. The result for this metal is highly gratifying. As we have said, over 99% of the total mercury was in the vapor phase. So we expected essentially all of the mercury in the coal to be present at the scrubber inlet.

Scrubber Module X Inlet vs. Outlet

We were able to calculate a mass balance around the scrubber Module X. Values fixed at the outset of calculations at 100% were recoveries for calcium, sulfate, and water. These assumptions were required in the absence of measured flow rates for scrubber slurries. We achieved a very gratifying balance of 99% for heat across the scrubber with these assumptions, which is to a degree independent of the assumed closure for water.

The percentage of mercury in the scrubber inlet streams that was accounted for in the scrubber outlet streams was 91% — an excellent mass balance. The inlet flue gas dominates input, and the outlet flue gas contains the majority of the output. All of the mercury data having to do with flue gas used in this calculated balance were based on Method 29.

Effects of Scrubber Operation

Measurements at the inlet and outlet of Module X provided data at two L/G ratios: the customary value around 85 gal/acf and an increased value of about 100 gal/acf. The data on mercury based on Method 29 or based on the modification of Method 101A lead to the same conclusion — that mercury removal in the scrubber is not altered by changing L/G.

Concentrations of mercury at the outlet of Module Y when scrubbing occurred at recycle pH values of 5.7 and 5.1 are not decisive enough to show any difference due to pH. A tabulation is given below for mercury concentrations in µg/Nm^3:

	Higher pH	Lower pH
Ionic	0.67, 0.50	0.37, 0.50
Elemental	4.75, 5.70	6.45, 5.26

Removal Efficiencies and Emissions Factors

The average reduction of mercury across scrubber Module X was 45% based on data from Method 29; the reduction was 38% based on data from modified Method 101A. As the data presented previously show, the removal of ionic mercury was very efficient across the scrubber. Method 29 results indicate 82% reduction of ionic mercury, and modified Method 101A indicates 89% reduction in ionic mercury. The speciation results from modified Method 101A data are more credible, for reasons discussed above.

The emissions factor for mercury was determined from the average concentration of mercury in the stack gas, gas volume per unit mass of coal, and coal calorific content. The emissions factor is 1.85 g/10^{12} J , or 4.30 lb/10^{12} Btu.

ACKNOWLEDGMENTS

This work was funded by DOE Contract No. DE-AC22-93PC93254. Dr. Michael J. Baird serves as the DOE Project Manager. We appreciate the cooperation of the host utility. Galbraith Laboratories, Inc. and Brooks Rand, Ltd. conducted some of the analyses reported in this paper. We appreciate the excellent work of Wynema Kimbrough of SRI in performing the mercury measurements at SRI.

A STUDY OF TOXIC EMISSIONS FROM A COAL-FIRED GASIFICATION PLANT

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Abstract

Toxic emissions were measured in the gaseous, solid and aqueous effluent streams in a coal-fired gasification plant. Several internal process streams were also characterized to assess pollution control device effectiveness. The program, consisted of three major phases. Phase I was the toxics emission characterization program described above. Phase II included the design, construction and shakedown testing of a high-temperature, high-pressure probe for collecting representative trace composition analysis of hot (1200°F) syngas. Phase III consisted of the collection of hot syngas samples utilizing the high-temperature probe. Preliminary results are presented which show the emission factors and removal efficiencies for several metals that are on the list of compounds defined by the Clean Air Act Amendments of 1990.

Background

The Louisiana Gasification Technology, Inc. (LGTI) project was selected by the U.S. Department of Energy (DOE) to demonstrate the Dow gasification process as part of the DOE Innovative Clean Coal Technology (ICCT) program. The primary goal of the DOE ICCT program is to demonstrate the technical readiness of clean coal technologies and to provide design and operating data that can be used in commercially developing these processes. The environmental performance of each of the demonstrated clean coal technologies is a critically important factor in determining their commercial readiness and endorsement.

During the LGTI demonstration program, the environmental characteristics of some streams, particularly the discharge streams, have been regularly monitored. However, with the passage of the Clean Air Act Amendments (CAAA) in 1990, it has become very important to define the fate of currently unregulated hazardous air pollutants (HAPs) within and from the LGTI process. Most of the HAPs have not yet been measured at the demonstration facility. For that reason, the DOE and the Electric Power Research Institute (EPRI) retained Radian Corporation to measure selected HAPs in the discharge streams and in most of the major internal process streams of the LGTI demonstration plant.

Within the last few years, EPRI and DOE have both implemented programs to measure HAPs in the process and discharge streams of conventional fossil-fueled power plants. Sampling and analytical methods for measuring HAPs in these streams have been identified and/or developed as a part of these programs. However, many of these methods are not be applicable for coal gasification systems, which differ considerably in both process conditions and process complexity from those of conventional systems. The gas matrix found at the turbine exhaust stacks (and to a lessor extent at the incinerator stack) is comparable to that found at most conventional coal-fired power plants. Internal streams in a gasifier are typically reducing environments, with major gas components being hydrogen, carbon monoxide and carbon dioxide. Sulfur is present as primarily hydrogen sulfide and lessor amounts of other reduced sulfur species. Nitrogen is present, not as NO_x, but as ammonia and hydrogen cyanide. Trace elements may not be oxides, but rather hydrides or carbonyls.

It is not surprising then, that EPA Reference Methods often do not yield accurate results when applied to internal gasification streams. Unfortunately, reference methods do not exist for testing gasification process streams and any test methods that are used are subject to interpretation. During this test program, Radian used alternate test methods to augment analytical data from the EPA Method 29 multi-metals sampling train. The approach to the test program and results from alternative method testing are described in the following section.

The Process

LGTI (Louisiana Gasification Technology Inc.), a subsidiary of DESTEC Energy Inc., operates the coal gasification plant at the Dow Louisiana Division chemical complex in Plaquemine, Louisiana. The syngas project began operations in 1987 as the Dow Syngas Project. The gasification unit produces medium Btu synthesis gas (syngas) for consumption by gas turbine power generating units at the Louisiana site.

At full capacity, the LGTI Plant produces 30,000 MM Btu of equivalent syngas per day from approximately 2,200 tons per day of western subbituminous coal from the Rochelle mine in the Powder River Basin in Wyoming. The power unit produces the equivalent of 160 MW of net power considering both electricity and steam production.

Figure 1 is a block flow diagram of the LGTI gasification facility at Plaquemine. The block diagram includes the coal preparation, gas production, particulate removal, moisture removal, acid gas cleanup, power production, wastewater stripping, acid gas treatment, sulfur production, and tail gas incineration.

The coal is ground and slurried with water recycled from the process and pumped to the gasifier where it is mixed with oxygen and steam. The oxygen feed rate is carefully controlled to maintain the reactor temperature within a narrow range. Sulfur in the coal is almost totally converted to H_2S and small amounts of COS, while nitrogen is efficiently converted to NH_3 and trace amounts of cyanide and thiocyanate.

The raw gas passes through the heat recovery train where steam is produced. The partially cooled gas then passes through a venturi scrubber where particulate matter is removed. The gas is further cooled before it passes through sulfur (acid gas) removal in the Selectamine™ unit. Water, condensed from the gas during cooling, is sent to the sour water stripper and then to the water treatment unit. Over 97% of the sulfur species are captured in the sulfur removal process. The concentrated acid gases (primarily H_2S and CO_2) are sent to sulfur recovery.

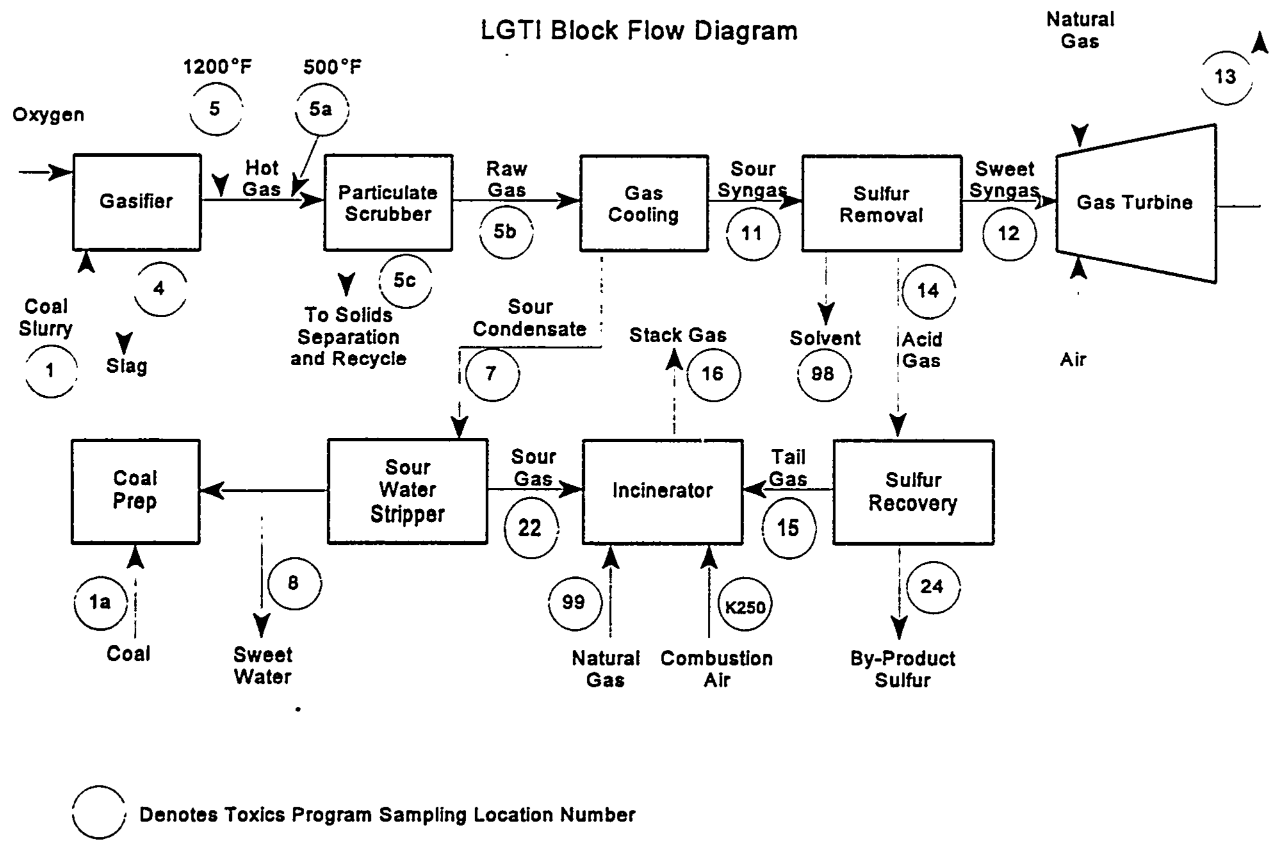


Figure 1. LGTI Block Flow Diagram

The Selectox™ process is used to recover sulfur from the acid gas produced in the Selectamine™ unit. This process is identical to the Claus process reactions, but the combustion furnace of the Claus process is replaced by a fixed bed of Selectox™ catalyst. Liquid sulfur produced from the process is sold as by-product. The sweetened syngas is sent by pipeline to Dow's Power II facility where it is mixed with natural gas and fired in two large combustion turbines. During the HAP's test program, approximately 60% of the fuel to the turbine tested was from syngas.

The sour water condensed from the product gas as it cools is directed to the wastewater treatment system which includes filtration and stripping. Stripped sour water (sweet water) from the treatment system is recycled to the coal preparation area. Excess sweet water is discharged to the Dow plant water system for further treatment. The Dow plant-wide water treatment system includes activated sludge and clarification. The gas which is stripped from the sour condensate is referred to as sour gas, and it is routed to the tail gas incinerator.

The incinerator receives tail gas from the Selectox™ unit, sour gas from the sour water stripper, and combustion air (including vapors from the tank vents). All are combusted in the natural gasfueled incinerator for efficient destruction of combustibles. The incinerator stack discharges its exhaust at a height of approximately 200 feet.

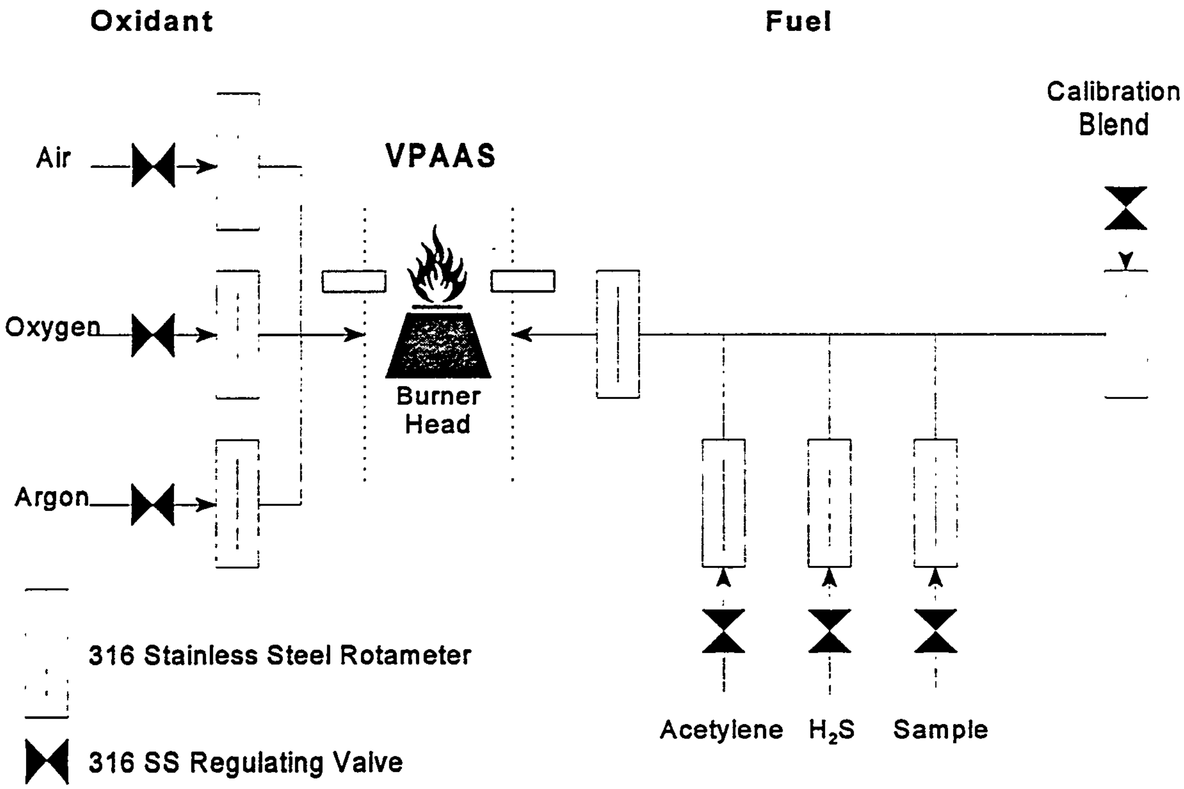
Testing

The measurement of HAPs at the LGTI plant was one of the most comprehensive ever performed at a coal gasification facility, and was conducted in three phases. Phase I included the majority of the toxics characterization. Phase II involved the design, manufacture and shakedown testing, of a probe for collecting gas samples from high-temperature, high-pressure process locations. During Phase III, the hot (1200°F) syngas was characterized for trace metal composition of the particulate and vapor phase syngas utilizing the high temperature probe.

As stated earlier, the majority of the program was performed as part of Phase I. The actual test effort required approximately two weeks to complete with a field crew of as many as 20 scientists and engineers. The two week test effort was conducted as three test periods. Each test period focused on the characterization of the process streams associated with a specific control device(s). The first test period encompassed the Selectamine™, gas turbine, and Selectox™ units. The sour water stripper and incinerator stack were testing during Period II, and the gasifier, venturi scrubber, and gas cooling sections were part of Period III testing. In all, samples were collected from 20 locations throughout the gasification and turbine blocks.

In previous test efforts conducted by Radian on gasification systems, results have indicated that EPA Reference Method 29 for trace elements did not yield accurate results. In general, the sampling and analytical methodologies that were used on this program were consistent with those used by EPRI during the Field Chemical Emissions Monitoring (FCEM) program[1]. However, Method 29 (for the internal process streams) was modified to try to compensate for the reducing gas matrix. The nitric/peroxide impingers were boosted to 10% nitric/30% peroxide and the potassium permanganate impingers were not used as the $KMnO_4$ is rapidly consumed by the H_2S in the syngas. In addition to Method 29, syngas was passed through quartz tubes containing specially prepared coconut-based charcoal. These tubes were subsequently digested in nitric acid and analyzed by either ICP-AES, GFAAS, or CVAAS for trace elements. Detection limits for elements determined by the charcoal adsorption technique are nominally in the range of 1 $\mu g/Nm^3$.

The sour syngas and the sweet syngas were also sampled for trace elements using an on-line vapor-phase atomic absorption spectrophotometer (VPAAS), developed by Radian. The AAS was modified to accept a syngas sample stream as part of the fuel supply going to the nebulizer mixing chamber and flame. In the flame, vapor-phase trace elements are atomized and absorb light energy from an element-specific light source just like aqueous samples in conventional AAS. The sample gas, fuel gas, and air supplies are regulated and monitored to determine the syngas component going to the flame, and ultimately the elemental concentration in the gas sample stream. Absorbance and concentration are related by Beer's law and gas concentration are determined by comparison with standard curves generated from aqueous standards. A simplified schematic of the VPAAS setup is shown in Figure 2.



Calibration Blend:

35% H_2
42% CO
23% CO_2

Figure 2. VPAAS Schematic

The second part (Phase II) of this program was done in parallel with Phase I. Design and manufacture of the hot gas probe was completed in December 1994. Performance and safety audits with LGTI engineers were done in the early spring of 1995 and the shakedown test was completed in May. The shakedown test was performed at a low temperature location (500°F) and was directed at operation (insertion and extraction) of the probe.

The probe was designed to operate at a maximum gas temperature of 1200°F, and a pressure of nominally 400 psig. Gas/particle separation takes place "in stack" at process conditions. The probe and filter assembly are inserted into the process gas stream via a double ball valve and packing gland arrangement. A constant nitrogen purge is maintained in the area of the packing gland so that any gas leakage during insertion or removal of the probe will be nitrogen and not syngas. Vapor phase samples can be collected from a slipstream of the sampled gas. Nitrogen can also be mixed with the sampled syngas as needed to either quench the gas temperature or to dilute the overall gaseous sample and effectively lower the gas dew point. At the completion of testing, the probe is withdrawn from the process and collected solids are allowed to cool (in a nitrogen atmosphere) before being exposed to the air. Following the successful shakedown test, the probe was moved to the 8th level of the gasifier structure for testing of the hot syngas.

Hot syngas testing represents Phase III of the toxics program. This testing is scheduled to occur during the final week in May 1995. Gas phase samples will be collected for the analysis of trace elements, cyanide, ammonia, chloride and fluoride. In addition, collected particulate will be analyzed for trace elements.

Results

Preliminary results from the toxics emission testing program indicate the emissions are extremely low for most metals. Volatile metals which were present in the syngas as vapor phase compounds such as hydrides or carbonyls are found in the turbine exhaust in about the same range as that of a conventional coal-fired power plant. The results are presented graphically in Figure 3. Only cadmium and mercury had elemental reductions that were less than 90 percent.

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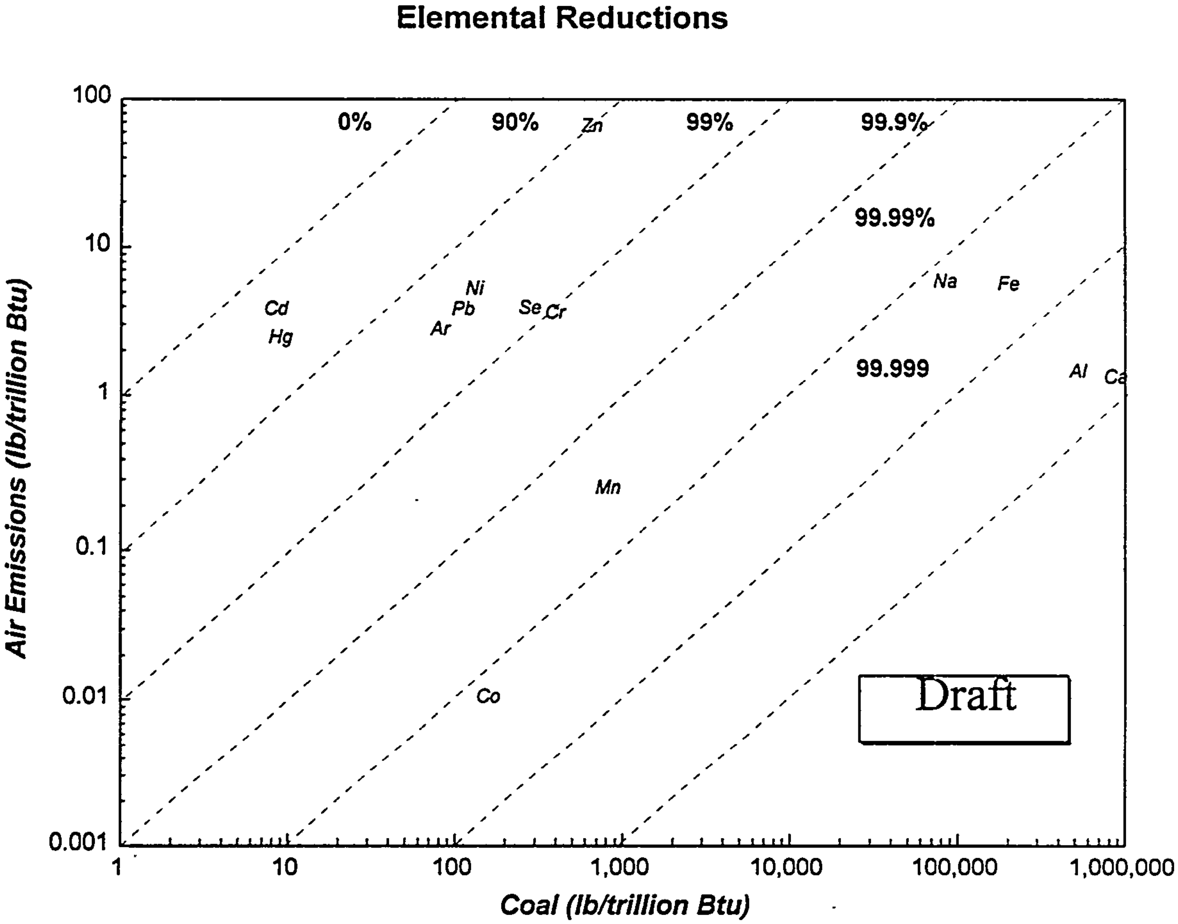

Figure 3. Elemental Emissions and Reductions

AUDITING OF SAMPLING METHODS FOR AIR TOXICS AT COAL-FIRED POWER PLANTS

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Summary

Advanced Technology Systems, Inc. (ATS) with subcontract assistance from International Technology Corporation (IT) has provided external audit activities for Phase II of the Department of Energy-Pittsburgh Energy Technology Center's air emission test program. The objective of the audits is to help ensure that the data obtained from the emission tests are precise, accurate, representative, scientifically sound and legally defensible.

This paper presents the criteria that were used to perform the external audits of the emission test program. It also describes the approach used by ATS and IT in performing their audits.

Examples of findings of the audits along with the actions take to correct problems and the subsequent effect of those actions on the test data are presented. The results of audit spikes performed at the Plant 1 test site are also discussed.

Background

The U.S. Department of Energy is currently funding research to characterize hazardous air pollutants (HAPs) from coal-fired power plants. These studies, along with other current research being conducted by the U.S. Environmental Protection Agency (EPA), the Electric Power Research Institute (EPRI) and others, are required as part of the Clean Air Act Amendments (CAAA) of 1990.

In 1991, the Department of Energy's-Pittsburgh Energy Technology Center (DOE-PETC) commissioned five primary contractors to conduct emission studies at eight different coal-fired electric utilities. Prior to the initiation of this study, very little documented data on coal-fired utility HAPs emissions were available. In addition, the methods of sampling and analyzing the emissions required modifications and refinements in order to characterize HAPs emissions from coal-fired power plants. As a result, a critical concern to the sampling program was that the collection and analysis of HAPs were accurate, precise, representative, scientifically sound and legally defensible.

To ensure that these data quality objectives were met, the DOE contracted independent Quality Assurance/Quality Control auditors to provide oversight for the air emission tests and other applicable test criteria for the emission testing program.

During Phase I of the testing program, Research Triangle Institute (RTI) was contracted as the independent auditor. Advanced Technology Systems, Inc. (ATS) with subcontract assistance from IT Corporation (IT) has been contracted to provide audit oversight for Phase II of the program.

Evaluation of the sampling and analytical methodologies requires both internal and external Quality Assurance/Quality Control. Suggested Quality Assurance/Quality Control criteria can include the following items: 1) Evaluation of the efficiency of the sampling procedures; 2) Performance evaluations of sampling and analytical equipment; 3) Determination of the robustness of the calibration procedures and practices and 4) The use of outside intervention (auditors) to pick out the non-obvious errors and problems.

The efficiency of the sampling procedures depends on two factors: 1) the ability of the sampling and subsequent analytical methods to collect and analyze the desired analyte and 2) the ability of the sampling and analytical crew to perform their assigned tasks. The sampling and analytical methodology can be evaluated by examining the precision and accuracy of the sample test results and by examining the precision and accuracy of the audit spikes. Data precision can be evaluated through the use of duplicate samples, duplicate spike samples and standard deviations or relative standard deviations for multiple sets of samples. Data accuracy can be evaluated using the recovery of matrix spikes, surrogate spikes, duplicate matrix spikes and internal audit spikes using certified standards. The closure of material balances is another tool often employed.

An evaluation of the performance of the sampling and analytical personnel is, of course, more subjective. The sampling and analytical personnel should be carefully observed, by both internal and external auditors, during the performance of their sampling or analytical activities. The auditor should evaluate the sampling teams on their organization and apparent knowledge of the sampling procedures and experience. Sampling train preparation, operation and recovery should be observed to determine if the correct protocol for the sampling method is followed. In addition the auditor should note if the sampling equipment was handled carefully and properly. Changes from the normal procedures for the sampling method being observed should be recorded so that its effect on the resulting data, if any, can be verified. In addition any deviations in the sampling procedures from the final sampling plan should be discussed with the sampling coordinator.

Furthermore, the auditor should check to see if the sampling data sheets are properly completed and if the appropriate chain-of-custody procedures are followed.

The performance of the sampling and analytical equipment also can be evaluated using the precision and accuracy of the sampling data and audit spikes. As with the sampling procedure evaluation, duplicate samples and matrix spikes, duplicate matrix spikes and audit samples can be used to evaluate sampling and analytical equipment performance.

Calibration check audits using critical orifices of known diameter and electronic signal generators can be performed on the sampling control boxes to evaluate their performance. EPA approved calibration quality objectives should be used in evaluating the control box performance. Failure to meet these objectives should be discussed with the sampling coordinator.

The analysis of certified standards can also be used to evaluate the performance of analytical equipment. As with the sampling control boxes, EPA approved data quality objectives for precision and accuracy should be used to evaluate the performance of analytical instruments. Failure to meet these objectives should be discussed with the analytical supervisor and may require the recalibration and/or repair of the instrument.

The quality of laboratory instrument calibrations can be checked by reviewing laboratory records. Calibration curves which do not meet laboratory or DOE data quality objective criteria should be rejected and new calibration curves should be generated.

Introduction

ATS, with subcontract assistance from IT Corporation, was contracted to provide external audit activity for Phase II of the DOE-funded test program. ATS audited the sampling activities of Southern Research Institute who were conducting a multi-pollutant field study to characterize toxic emissions from a coal-fired power plant burning pre-combustion cleaned bituminous coal (Plant 1). SRI performed sampling for multi-metals, acid gases, particulates and mercury . Sampling for mercury was performed using both EPA Method 29 and the Ontario Hydro Method. SRI's sampling program was coordinated with stack and helicopter plume sampling for mercury using the Bloom Method.

IT assisted with the auditing of two other sampling programs. One program was a multi-pollutant field study conducted by Battelle to collect and characterize toxic emissions from coal-fired utility boilers operating at different combustion intensities. The sampling site was the Sammis power plant near East Liverpool, Ohio. Battelle sampled for particulates, multi-metals, acid gases and mercury. The sampling program emphasized the relationship between the particle size range and pollutant concentration and the effect of dilution and cooling on pollutant composition.

The other sampling program audited by IT was the validation of EPA Method 29, by the Energy and Environmental Research Center (EERC) located at the University of North Dakota, for the assay of mercury from a pilot-scale combustor.

IT's efforts included review of the experimental plans, on-site observation of the testing activities, the preparation of performance audit samples and laboratory performance review. ATS also performed the above activities and oversaw IT's audit.

Audit Program Approach

The audit program employed consists of the following key elements:

- Pre-audit site visit and/or conference calls
- Review of sampling, analytical and QA/QC plans and problem resolution/recommendations
- Field and laboratory audits
- Final test report review

Within each key element, the evaluation criteria include:

1. Pre-audit site visit and/or conference calls
    - Gain knowledge of the plant layout and the condition of the sampling sites.
    - Observe plant operating conditions.
    - Obtain input on QA/QC matters.
    - Learn safety and security concerns and operating constrains at the site.
    - Determine the needed logistics such as the route to the site, nearest airport, lodging, rental car availability, FedEx and UPS locations, etc.

2. Review of sampling, analytical and QA/QC plans (project specific)
    - Determine the intended data use and the applicability of the selected test methods to that use.
    - Evaluate the experimental design for flaws or deficiencies.
    - Learn Quality Assurance/Quality Control objectives, the internal QA/QC activities planned and the corrective measures that will be implemented if needed.

3. Field and Laboratory Audits
    - Follow EPA audit guidelines.
    - Technical system audits - Review, observe and document the sampling and analytical practices, scrutinize the data reduction and review and the reporting activities. Also, examine the contractor facilities and equipment.
    - Performance evaluation audit - Spikes and performance evaluation audit samples are used to evaluate compliance.

4. Final test report review
    - Examine data validity.
    - Determine the credibility of the conclusions.
    - Evaluate data comparability

ATS visited the Plant 1 site one month prior to the start of sampling activities to establish the logistics previously discussed. No pre-audit site visits were made for the EERC and Sammis sites but the necessary logistical information was obtained from conference calls.

Experienced ATS and IT personnel reviewed each sampling plan. For each plan review, a document was prepared describing all questions, concerns and perceived plan deficiencies. These issues were discussed with the contractors until all parties were satisfied with the quality of the plan.

ATS and IT used a field check list to review each sampling procedure. The list was used to document the type of equipment used, the materials of construction, equipment and personnel performance and specific handling problems. The sample recovery and handling procedures were observed to ensure that the test samples were handled in a clean environment, with complete documentation of sample identity and chain-of-custody.

Equipment audits were performed using a critical orifice to verify the calibration of the dry gas meter and an Omega Instruments millivolt signal generator to check the accuracy of the digital temperature readouts. EPA data quality objectives were used to determine the ability of the sampling control boxes to meet calibration specifics. The thermocouples were audited using ASTM grade thermometers. The field barometers were evaluated by comparison to an independently calibrated field barometer supplied by the auditor. Spot checks of selected nozzle diameters were made using calipers supplied by the auditors.

Laboratory performance audits were also performed. The auditors observed sample receiving, handling and analytical procedures and reviewed laboratory practices for chain-of-custody, data review and documentation, sample numbering, and report procedures. Instrument calibration procedures and maintenance practices were also examined.

Spiked samples, including field spikes and laboratory audit samples were also a part of the audit program. Spiked samples or audit samples were left at the sampling site or sent to the analytical laboratory on return from the sampling activity. All spike samples were NIST materials or NIST-certified materials.

Results and Discussion

Field audit reports were prepared to document all findings. Battelle, EERC and SRI sampling programs were performed in accordance with the approved test plans. All studies are expected to yield acceptable data.

However, minor problems occurred with all of the sampling programs Many of these problems were corrected on site. The other problems should have only negligible affect on the data quality. Examples of these problems are presented below.

- At the Plant 1 tests, the initial samples for the recycle slurry process stream were taken at the wrong scrubber module. The problem was rectified after the first afternoon sample and all subsequent samples were taken from the correct module stream. The effect of the error on the data should be negligible because the metals concentrations in the scrubber recycle slurry should be sufficiently constant such that the two correct samples can represent the entire sampling effort.

- Sampling of the course refuse stream at the Plant 1 coal preparation plant originally included only the refuse screen oversize and not both the screen oversize and undersize. Upon recommendation, the sampling point was moved to a location where the entire refuse stream could be sampled. This change in the sampling location made the subsequent samples more representative of the course refuse stream. Only the samples obtained after the change in sampling location were used as refuse stream samples. The effect of this problem on the data should be minimal because the concentration of metals in the coal refuse stream should be consistent throughout the sampling period. As such the samples obtained after the sampling location change should represent the entire sampling period.

- The original process stream samples for magnetite, frother and anionic polymer at the Plant 1 Coal Preparation Plant were obtained in dirty mason jars with metallic lids. These samples were rejected by ATS because of possible contamination from the jars or lids. A second set of samples was obtained one day later using clean sterile sample jars. The second set of samples was accepted. This action improved the quality of the samples for these process streams by removing obvious sources of contamination that compromised the integrity of the first set of samples.

- The February 28, 1995 HEST test at the Sammis plant failed to pass the final leak test. As a result the test was voided by Battelle and their subcontractor, TRC Environmental Corporation, resulting in no effect on the data.

Blank spikes were performed at the Plant 1 site by ATS and IT sent laboratory check standards to EERC and Battelle to verify the accuracy of laboratory calibration materials. The results (triplicate averages) of the Plant 1 spikes are shown in Table 1.

Mercury spike results for the Ontario Hydro Method (modified Method 101A) were very good. The spike recoveries ranged from 87.74% to 102.69% with an average recovery of 94.79 ± 7.51%.

The filter and recovery solutions for the front-half acid wash and peroxide impingers of an EPA Method 29 train were spiked with a metals mixture. The permanganate impinger recovery solution of the same train was spiked for mercury. The analytical results for these spiked samples were examined for arsenic, cadmium, lead, selenium and mercury ($KMnO_4$ impingers) and the percent recoveries of these analytes were calculated. Average spike recoveries for arsenic, cadmium, lead and selenium in all EPA Method 29 train samples were within ± 25% of the spiked values.

Lead had an average recovery of 88.50 ± 15.40% and cadmium had an average recovery of 76.77 ± 13.58%. Average recoveries for arsenic and selenium were 79.88 ± 13.75% and 76.94 ± 13.38% respectively. The average percent recovery of these four analytes from the filter was 80.69 ± 12.40%. Average recoveries from the front-half acid wash and H_2O_2 impingers were 69.33 ± 4.53% and 91.55 ± 10.67% respectively. The average recovery of mercury from the $KMnO_4$ impingers was 98.74 ± 1.80%.

No recovery data was obtained for the anion spikes because the blank values were larger than those obtained for the spiked samples. The results of the EERC and Sammis audit samples were not available when this paper was written.

Conclusions

The programs observed were well planned and executed research projects conducted by experienced field sampling and laboratory personnel. In spite of this, numerous questions and concerns with the test plans arose and were discussed in advance of the program. In addition, internal and external audits resulted in corrective actions to improve and/or enhance data quality.

The results from the spiked sample analyses (Plant 1) are testimony to the high quality of both the sampling and analytical expertise employed in these emission studies.

The value of the ongoing audit program is its ability to identify problems in the sampling program while corrective action can still be made. The continuation of this audit and report review program will ensure that the results of the air toxic studies under the direction of the DOE are legally and technically defensible and usable in a standards-setting process.

Acknowledgements

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Table 1 Results for the Audit Spikes at the Plant 1 Test Site.

Test Method	Absorbent	Spike Conc.	Observed Conc.*	Percent Recovery
Ontario Hydro	Front-half Wash	501.5 ug Hg	471.3 ug Hg	93.98
	Back-half Wash	1003 ug Hg	1030 ug Hg	102.69
	KCl Imp.	1003 ug Hg	880 ug Hg	87.74
	$KMnO_4$ Imp.	1003 ug Hg	1010 ug Hg	100.70
EPA Method 29	Filter	40 ug As	30.6 ug As	76.50
		20 ug Cd	13.0 ug Cd	65.00
		10 ug Pb	9.1 ug Pb	91.0
		40 ug Se	36.1 ug Se	90.25
	Front-half Wash	80 ug As	54.5 ug As	68.13
		40 ug Cd	29.5 ug Cd	73.68
		20 ug Pb	14.4 ug Pb	72.00
		80 ug Se	50.8 ug Se	63.50
	H_2O_2 Imp.	160 ug As	152 ug As	95.00
		80 ug Cd	73.3 ug Cd	91.63
		40 ug Pb	41.0 ug Pb	102.50
		160 ug Se	123.3 ug Se	77.06
	$KMnO_4$ Imp.	501 ug Hg	494.6 ug Hg	98.74

* Average of triplicate analyses

EVALUATION OF ACTIVATED CARBON FOR CONTROL OF MERCURY FROM COAL-FIRED BOILERS

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INTRODUCTION

The ability to remove mercury from power plant flue gas may become important because of the Clean Air Act Amendments' requirement that the U.S. Environmental Protection Agency (EPA) assess the health risks associated with these emissions. One approach for mercury removal, which may be relatively simple to retrofit, is the injection of sorbents, such as activated carbon, upstream of existing particulate control devices. Activated carbon has been reported to capture mercury when injected into flue gas upstream of a spray dryer baghouse system applied to waste incinerators or coal-fired boilers.[1,2] However, the mercury capture ability of activated carbon injected upstream of an electrostatic precipitator (ESP) or baghouse operated at temperatures between 200° and 400°F is not well known.

A study sponsored by the U.S. Department of Energy and the Electric Power Research Institute is being conducted at the University of North Dakota Energy & Environmental Research Center (EERC) to evaluate whether mercury control with sorbents can be a cost-effective approach for large power plants. Initial results from the study were reported last year.[3] This paper presents some of the recent project results. Variables of interest include coal type, sorbent type, sorbent addition rate, collection media, and temperature.

EXPERIMENTAL APPROACH

Baseline and sorbent injection tests were conducted at the EERC with a pulverized coal (pc)-fired combustor known as the particulate test combustor (PTC) and a pulse-jet baghouse. A complete description of the PTC and baghouse was given in a previous report.[4]

The tests were conducted with three coals: Powder River Basin subbituminous coals from the Absaloka mine, a similar coal from the Belle Ayr mine (Comanche), and a bituminous coal from the Pittsburgh No. 8 seam, Blacksville mine. Since the level of mercury in the coals ranged from 59 to 85 ppb, and the coal feed rate to the combustor is about 60 lb/hr, the required sorbent add rate is only about 2–20 g/hr to achieve sorbent-to-mercury ratios of 1000–10,000. Steady sorbent injection at the required low feed rate was accomplished by using a Model 3410 Dry Powder Disperser (DPD), manufactured by TSI Inc. This instrument is designed to disperse dry bulk powders into their original particle-size distribution in a carrier gas, with precise control over the feed rate. For all sorbent tests, the additive was injected with the DPD into the flue gas duct just upstream of a pulse-jet baghouse operated at an air-to-cloth ratio of 4 ft/min. The two primary carbon-based sorbents used in this study included a lignite-based activated carbon (LAC), commercially available from American Norit Co, Inc., and an activated carbon impregnated with an iodine compound (IAC) obtained from Barnebey & Sutcliffe Corp.

Simultaneous inlet and outlet mercury sampling was conducted according to EPA (Draft) Method 29, also known as a multimetal sampling train method. Method 29 does not claim to speciate between oxidized and elemental mercury, but bench- and pilot-scale results indicate that oxidized mercury will be trapped in the peroxide impingers and elemental mercury in the permanganate impingers.[3,5,6,7] However, further research is being conducted at the EERC to evaluate the mercury speciation ability of Method 29.[8] In this paper, the fraction of mercury collected in the peroxide impingers is referred to as "oxidized" mercury, and the fraction collected in the permanganate impingers is called "elemental" mercury. Mercury analyses were completed with a Leeman PS200 cold-vapor atomic absorption analyzer.

RESULTS AND DISCUSSION

The inlet sampling location was upstream from the sorbent injection port, which allowed combining the inlet data for each coal. Average inlet mercury data for the Comanche coal are shown in Figure 1. Inlet data for the other coals were previously reported.[3] The total mercury measured by Method 29 includes mercury retained on the filter, mercury collected in the peroxide impingers, and the mercury collected in the permanganate impingers. Total inlet mercury concentrations were fairly constant from test to test as indicated by the error bars which represent plus or minus one standard deviation. A significant amount of mercury was retained on the filter, ranging from about 10% at 400°F to 60% at 200°F. The filter temperature of the Method 29 train was adjusted to the same temperature as the baghouse for each test.

Baseline tests without sorbent addition and tests in which activated carbon was injected just upstream of the baghouse were conducted with the pilot combustion system. Baghouse temperature ranged from 200°–400°F. Sorbent type included mainly LAC and IAC, but two tests were conducted with a mixture of LAC and IAC, and one test was run with a bituminous-based activated carbon (PC-100). Fabric type included Ryton and GORE-TEX® Membrane on GORE-TEX Felt. Most tests were completed over a continuous 2-day period and included 4 pairs of simultaneous inlet–outlet Method 29 measurements. The mercury removal results for the Comanche coal tests are shown in Figure 2. Values reported are based on the total inlet and total outlet mercury concentrations. Total mercury for both inlet and outlet included filter, oxidized, and elemental mercury. However, the baghouse particulate collection efficiency was typically about 99.99%, so very little fly ash was collected on the outlet sampling filter. In all cases, any mercury collected on the outlet filter was below detection limits, so the total measured outlet mercury consisted only of vapor-phase oxidized and elemental mercury. From Figure 2, a general trend is seen toward better mercury control at 200°F compared to 300°F. However, at 300°F a wide range in mercury removal was observed depending on the sorbent type and concentration. Perhaps the most surprising result for the Comanche coal tests was the ineffectiveness of the IAC, which showed no improvement in mercury removal over the baseline tests. Previous tests with Absaloka coal showed that IAC was highly effective at total mercury removal, removing essentially all of the elemental mercury. The mercury speciation data for the Comanche coal tests also indicate very little elemental mercury at the outlet. However for these tests, an equivalent increase in oxidized mercury was evident at the outlet with no improvement in total mercury removal. Examination of all of the pulse-jet baghouse tests with IAC shows that it removes much more elemental than oxidized mercury, but some of the elemental mercury is apparently converted to oxidized mercury by the IAC. This effect was especially significant for the Comanche coal tests at 300° and 400°F, but was also noticeable with Blacksville and Absaloka coals at temperatures of 350°F and greater. The Comanche coal test with IAC using the GORE-TEX fabric at 300°F also shows this conversion effect, which indicates it is a direct result of the IAC and not the result of an interaction among the fabric, sorbent, and mercury. The exact mechanism by which this occurs is not clear but could involve initial collection of the elemental mercury, the forming of mercury(II) iodide in the iodine-impregnated activated carbon, and then subsequent desorbing of mercury(II) iodide. Any mercury(II) iodide would most likely be collected in the hydrogen peroxide impingers and, therefore, be measured as oxidized mercury. The reason this effect appears to be much more significant for the Comanche coal than for the Absaloka coal is unknown, but could be related to the lower sulfur content of the Comanche coal or differences in ash composition. A comparison of the effectiveness of IAC for the three coals is shown in Figures 3 and 4. While the total mercury removal data (Figure 3) should be considered the most reliable, there is additional confidence in the conclusions if the vapor-phase data (Figure 4) show the same results. Since varying amounts of mercury were captured on the inlet sampling filters, mainly because of temperature differences, the mercury vapor concentration at the baghouse inlet was more variable than the total inlet mercury concentration. Nevertheless, both the total and vapor-phase mercury data show that IAC was much more effective at mercury removal for the Absaloka coal than for the other two coals. The ineffectiveness of IAC with Blacksville coal is not surprising, since it had very little elemental mercury.

The effectiveness of the LAC also appears to be somewhat coal dependent as shown in Figures 5 and 6. Data on the total mercury removal indicate that the LAC works well for all three coals at temperatures lower than 250°F; however these data may be somewhat misleading, since they don't account for the amount of mercury that might be removed naturally at lower temperatures. The highest baseline mercury removal was observed with Absaloka coal, which explains why the total mercury removal with LAC was highest for Absaloka coal, while the highest vapor-phase mercury removal was observed with the Comanche coal. From the vapor-phase data, the conclusion is that the LAC is most effective with the Comanche coal. However, caution should be used when interpreting these data because of the low inlet vapor-phase mercury concentrations if a significant amount of mercury is retained on the sampling filter, and subsequent greater uncertainty in calculating the vapor-phase removal.

Another surprising effect observed in bench-scale tests with simulated flue gas was an interaction between the mercury and Ryton fabric. Results showed that mercury(II) chloride is absorbed by Ryton fabric and may be converted to elemental mercury and then to offgas at a later time. Initially, this effect was thought to be caused by exposed stainless steel surfaces; however, after coating surfaces with Teflon, the effect remained unchanged. When similar bench-scale tests were conducted with an all-PTFE (polytetrafluoroethylene) fabric, no evidence of this absorption and conversion was observed. Because of this observation, additional pilot-scale tests were conducted with an all-PTFE fabric (GORE-TEX Membrane on GORE-TEX Felt). The comparative results with the GORE-TEX fabric are shown in Figure 7. With the LAC, the mercury removal using the GORE-TEX fabric was somewhat higher than with Ryton fabric, but this is most likely the result of a higher sorbent add rate. For the baseline tests, the mercury removal was better with the GORE-TEX fabric at 300°F and slightly poorer at 200°F. Whether this difference lies within experimental variability is not clear. The more significant fabric effect with the IAC, however, suggests a possible interaction between the Ryton fabric and IAC. This result needs to be confirmed before a conclusion can be drawn. Whether the fabric effect is a short-term phenomenon that would disappear in tests longer than the completed 100-hour tests is not known.

From these results, temperature, coal-type, sorbent type, and possibly fabric type all appear to affect mercury removal significantly, at least under some conditions. EPA bench-scale test results showed much better elemental mercury removal for PC-100-activated carbon compared to the LAC used in our tests. Subsequently, tests were conducted with the PC-100 sorbent to see if it was superior to the LAC. Our results, shown in Figure 8, indicate no significant difference in total mercury removal and only a small difference in vapor-phase mercury removal between the LAC and the PC-100 bituminous-based activated carbon. The EPA results are partially in agreement with ours, since both showed somewhat better elemental mercury removal for the PC-100 (71% compared to 61% for the LAC). Our results, however, showed significantly poorer oxidized mercury removal for the PC-100 (53% compared to 82% for the FGD LAC). The bench-scale tests were conducted in a stream of pure nitrogen with elemental mercury, and the results may not be good indicators of sorbent performance with real flue gas that includes both oxidized and elemental mercury.

SUMMARY

- Inlet mercury speciation for the three coals was significantly different and was highly dependent on the Method 29 filter temperature.
- Iodine-impregnated activated carbon provided effective mercury control at 300° and 400°F with one subbituminous coal but was ineffective for a second subbituminous coal.
- Iodine-impregnated activated carbon was highly effective at reducing the outlet elemental mercury concentration for all three coals; however in some cases, the elemental mercury was apparently converted to oxidized mercury and was not captured.
- Lignite-based activated carbon provided some mercury control at lower temperatures for all three coals but appeared to work best for the Comanche coal.
- Mercury may interact with the Ryton fabric under some conditions to affect mercury speciation and control effectiveness.
- Bench-scale screening tests may not be good indicators of sorbent effectiveness unless flue gas conditions are adequately simulated.

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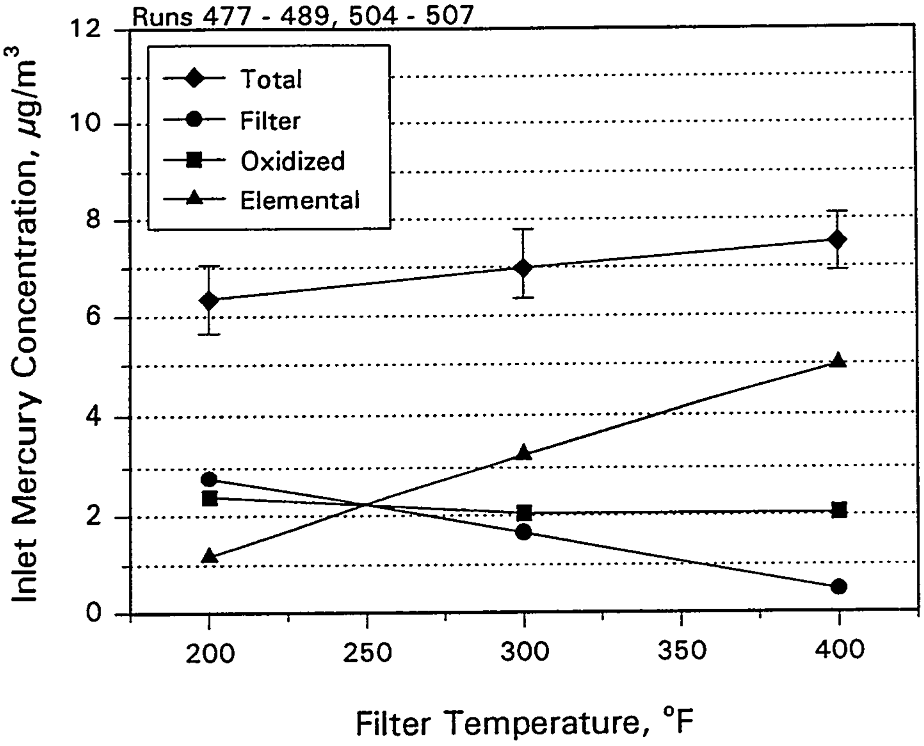

Figure 1. Average inlet mercury concentrations for Comanche subbituminous coal. Error bars represent plus or minus one standard deviation.

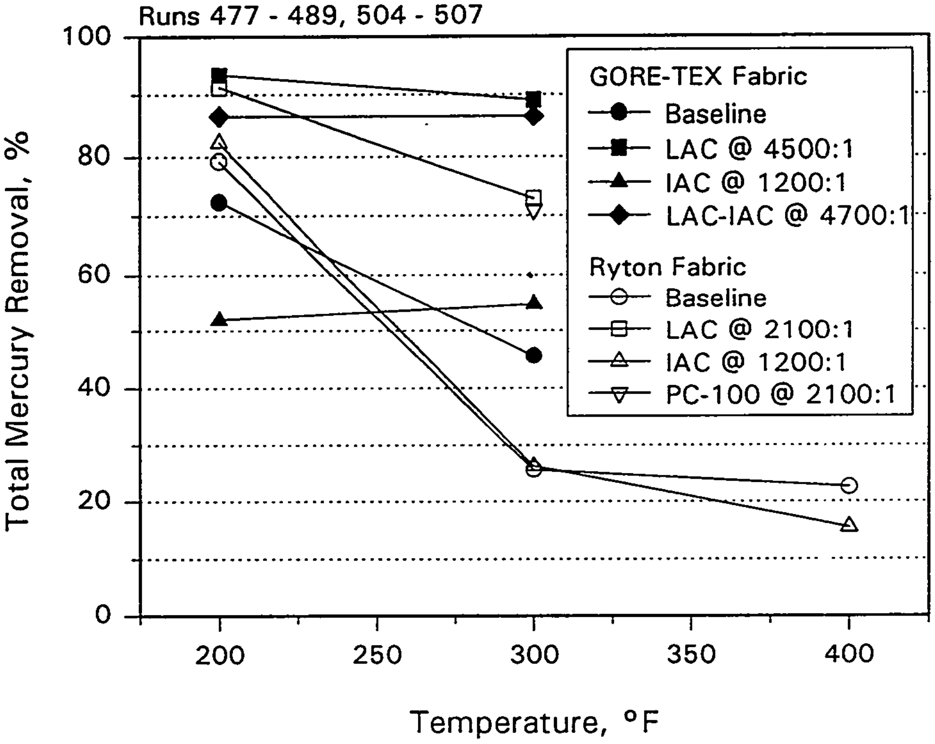

Figure 2. Total mercury removal across the baghouse for Comanche coal tests.

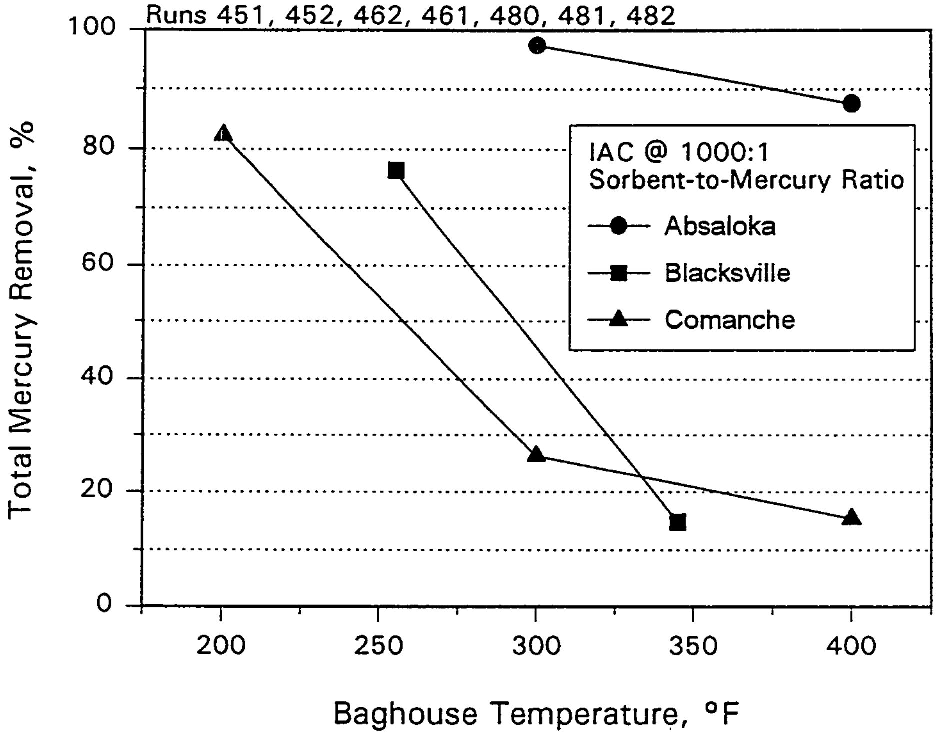

Figure 3. Effect of coal type on total mercury removal across the baghouse with iodine-impregnated activated carbon.

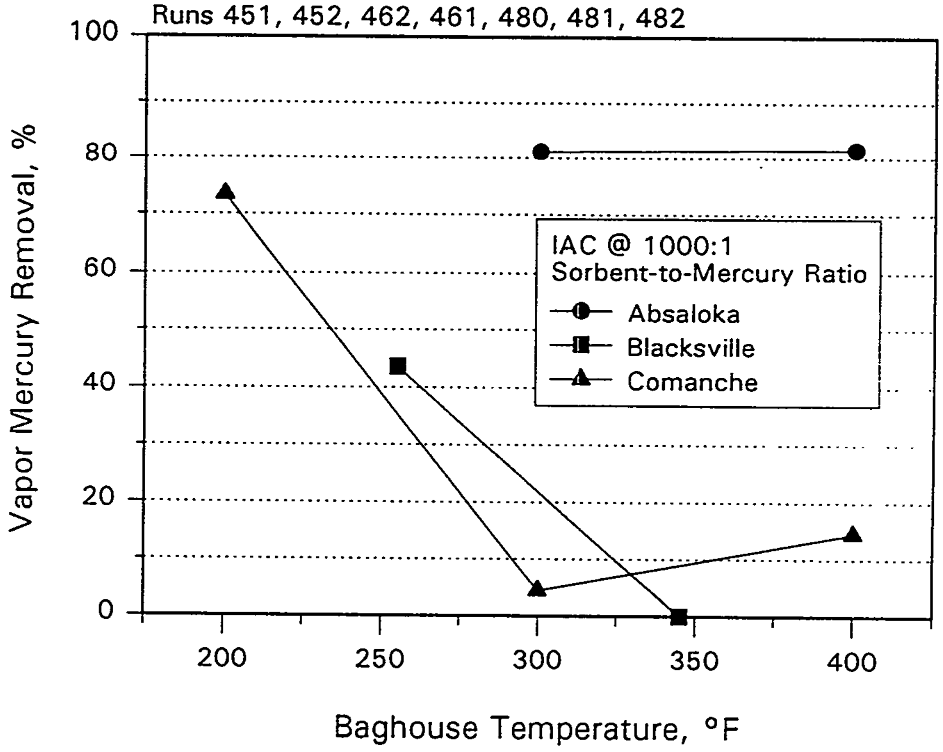

Figure 4. Effect of coal type on vapor-phase mercury removal across the baghouse with iodine-impregnated activated carbon.

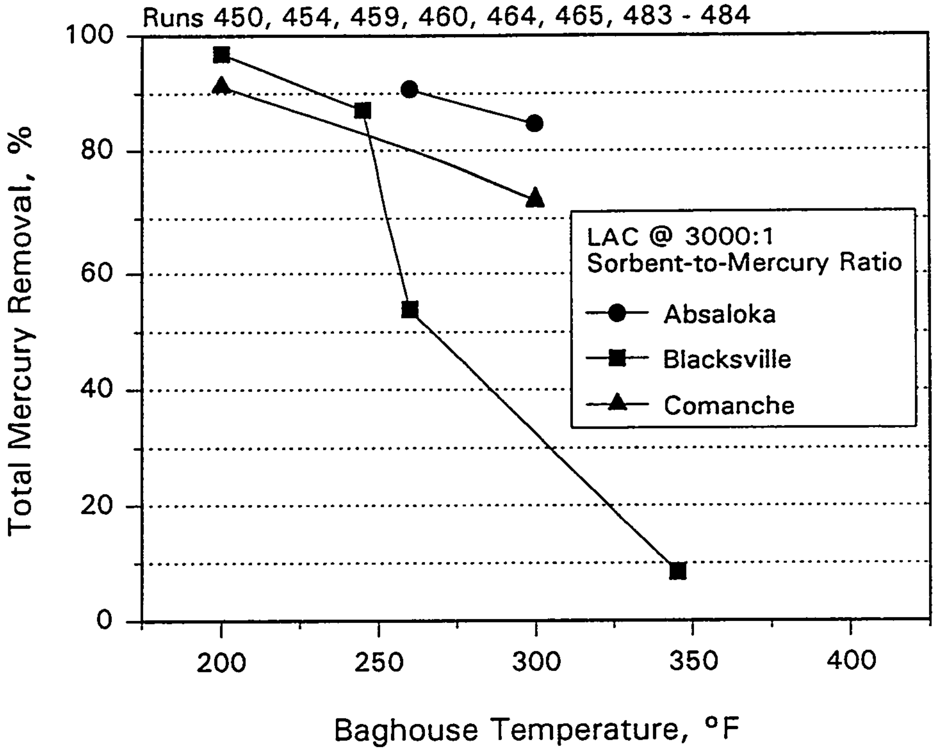

Figure 5. Effect of coal type on total mercury removal across the baghouse with lignite-based activated carbon.

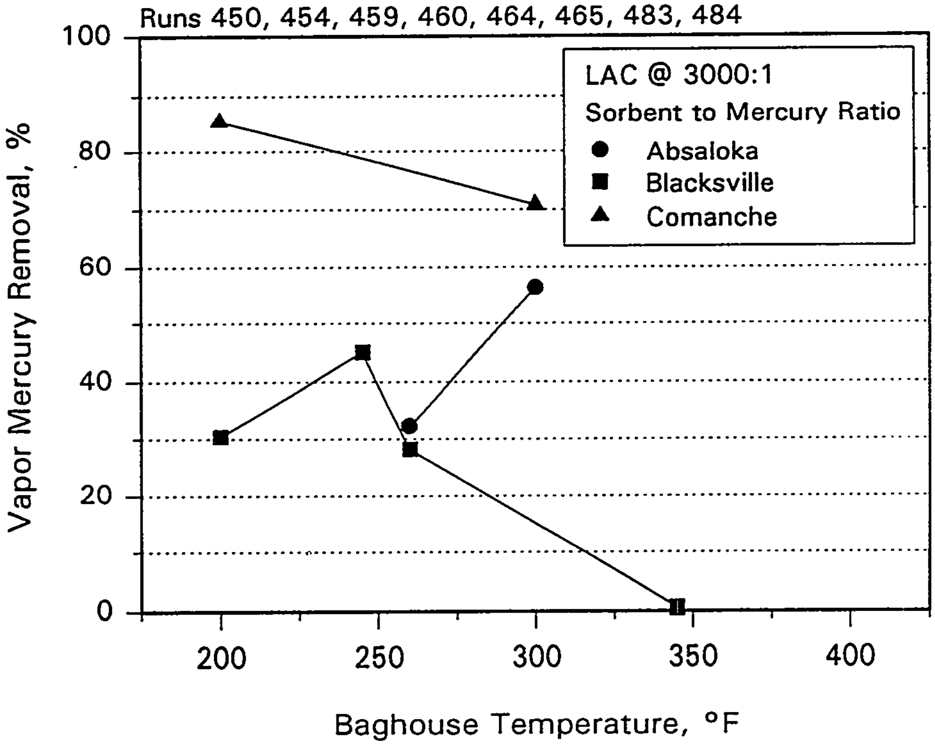

Figure 6. Effect of coal type on vapor-phase mercury removal across the baghouse with lignite-based activated carbon.

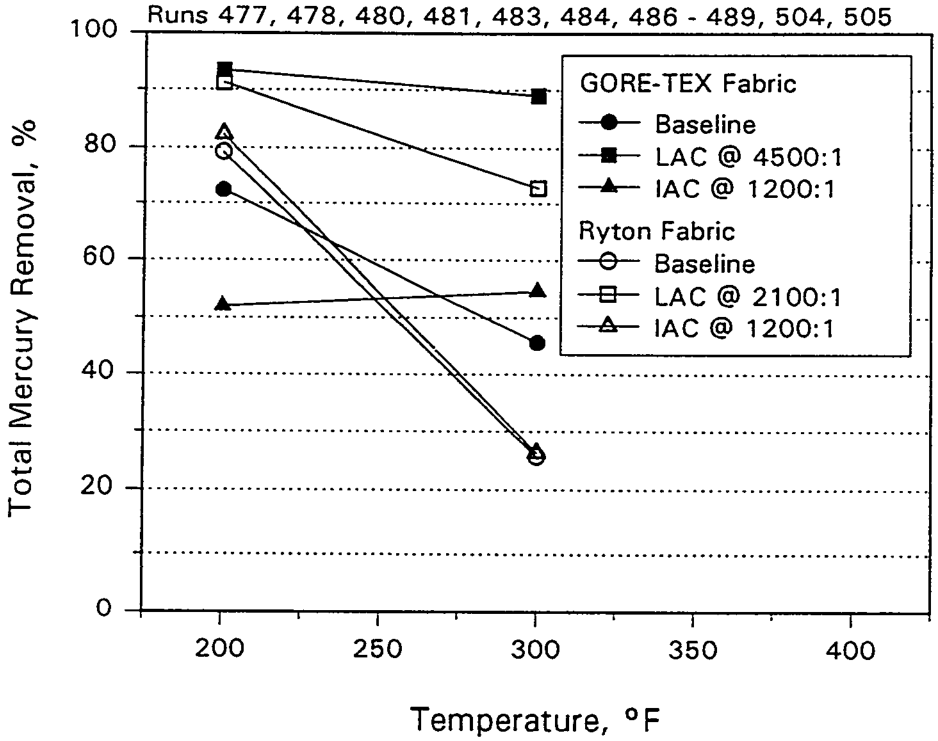

Figure 7. Effect of fabric type on total mercury removal for Comanche coal tests.

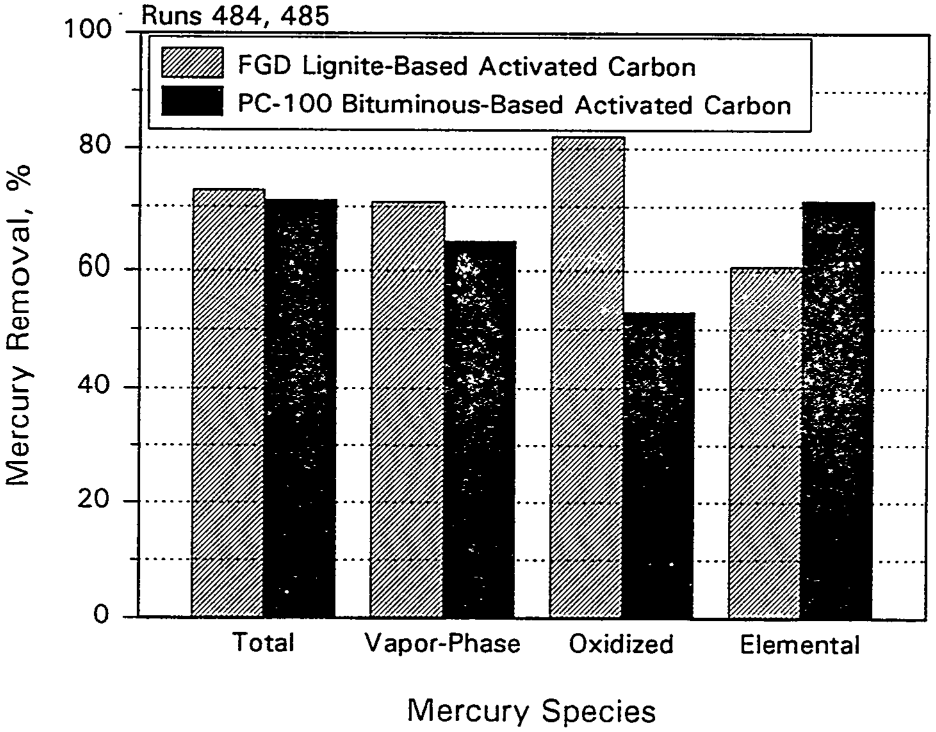

Figure 8. Effect of activated-carbon type on mercury species removal using Comanche coal.

REAL-TIME ANALYSIS OF

TOTAL, ELEMENTAL, AND TOTAL SPECIATED MERCURY

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ABSTRACT

ADA Technologies, Inc., is developing a continuous emissions monitoring system that measures the concentrations of mercury in flue gas. Mercury is emitted as an air pollutant from a number of industrial processes. The largest contributors of these emissions are coal and oil combustion, municipal waste combustion, medical waste combustion, and the thermal treatment of hazardous materials. It is difficult, time consuming, and expensive to measure mercury emissions using current testing methods. Part of the difficulty lies in the fact that mercury is emitted from sources in several different forms, such as elemental mercury and mercuric chloride. The ADA analyzer measures these emissions in real time, thus providing a number of advantages over existing test methods: 1) it will provide a real-time measure of emission rates, 2) it will assure facility operators, regulators, and the public that emissions control systems are working at peak efficiency, and 3) it will provide information as to the nature of the emitted mercury (elemental mercury or speciated compounds). This update presents an overview of the CEM and describes features of key components of the monitoring system--the mercury detector, a mercury species converter, and the analyzer calibration system.

THE NEED FOR A MERCURY CEM

Future strategies for controlling hazardous air pollutants will involve the use of continuous emissions monitoring systems. These systems provide a real-time measure of pollutants being emitted from sources and are needed in terms of assuring compliance with emissions regulations. They can also be used to help facilities operate pollution control equipment at peak efficiencies.

Mercury is a pollutant that has been receiving much attention in terms of monitoring and control strategies. The toxicity of mercury has prompted industry and regulators alike to develop means to control its release to the environment. Emissions monitoring systems will play a key role in assuring that emissions of this hazardous material are minimized.

Mercury is emitted from industrial sources in a variety of chemical forms depending on the specific process and flue gas conditions. For example, mercury is known to exist as elemental mercury [Hg^o] and as mercuric chloride [$HgCl_2$] in most industrial flue gases that contain mercury. A knowledge of the relative concentrations of mercury between its different forms will be required for air pollution control devices to operate effectively. An example of this principle is given in Table I for coal-fired power plants.

Table I. Mercury Removal Under Different Process Conditions

Plant	Ash Loading to Spray Dryer	Coal Cl	**% Mercury Removed**
A	High	Low	**14**
B	High	Low	**23**
C	High	Low	**6**
G	High	Low	**16**
E	Low	High	**55**
H	Low	High	**44**
F	Medium	High	**89**
D	High	High	**96**

Current standard testing techniques rely on manual "grab samples" where flue gas is drawn through filters and traps to collect mercury. The collected samples need to be analyzed in a chemistry laboratory using complex techniques and instrumentation. These field sampling and analytical techniques are cumbersome, labor intensive, and expensive. A 1-week comprehensive sampling program can cost in the range of $25,000-$50,000.

A continuous mercury monitoring system addresses the following needs:

- Since mercury control depends on the specific chemical form of the mercury, an analyzer that can distinguish between the chemical forms is needed to assure effective operation of the APCD.
- An analyzer will assure that the APCD is working properly.
- An analyzer can be used to control the feed rate of a process generating the mercury emission.
- An analyzer will help assure the public and regulatory agencies that emissions limitations are being complied with.

DESCRIPTION OF CEM

In response to the need for monitoring mercury emissions in real-time, ADA Technologies has developed a continuous emissions monitoring system that is capable of measuring total mercury, elemental mercury, and (by difference) total speciated mercury. The system features a sensitive mercury detector, a mercury species converter, and a calibration system. Figure 1 shows the components in a typical CEM arrangement.

The "converter" is used to change speciated mercury compounds to elemental mercury. When the sample gas is placed through the converter, a measure of the total mercury content of the flue gas is obtained. When the converter is bypassed, only elemental mercury is measured in the gas sample. The difference between the two measurements is the concentration of total speciated mercury content.

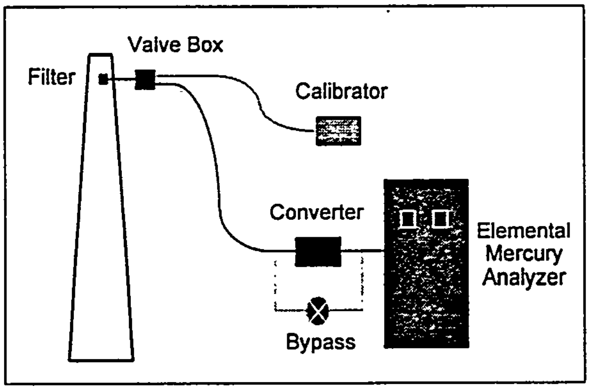

Figure 1. Mercury CEM arrangement.

A non-reactive sample transport line is used to convey the gas sample to the analyzer. Calibration gas is introduced to the end of the sample line in order to assure that the entire sampling system and the analyzer are calibrated as a single unit.

DESCRIPTION OF COMPONENTS

Mercury Detector

The analyzer uses a unique ultraviolet absorption spectrometer to measure the mercury. Proprietary optical components are incorporated that provide a measurement sensitivity below 1 $\mu g/m^3$ (less than approximately 0.1 ppb v/v). The analyzer has a linear response to a concentration of greater than 100$\mu g/m^3$. The optical design of the analyzer also eliminates the effects of interfering gases such as sulfur dioxide.

Figure 2 shows the analyzer response when elemental mercury was introduced at a concentration of 4.2 µg/m^3 (0.7 ppb v/v). Also shown in the figure is the signal when zero gas was introduced into the analyzer. Based on the peak-to-peak noise level observed, a minimum level of detection (defined as 2x noise level) of 0.2µg/m^3 (27 ppt v/v) is calculated.

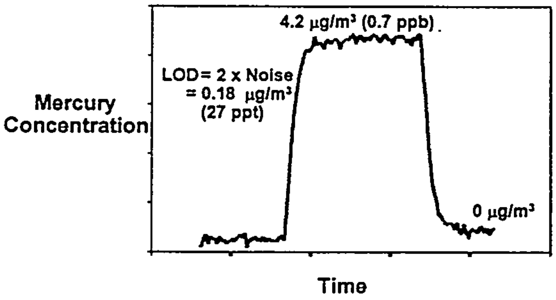

Figure 2. Response of the analyzer to 4.2 µg/m^3 of mercury.

The ADA analyzer incorporates a unique optical design that eliminates the effects of interfering gases such as sulfur dioxide. Figure 3 shows the response of the detection system when measuring mercury at a concentration of 10 µg/m^3 in the presence of sulfur dioxide at a concentration of 500 ppm.

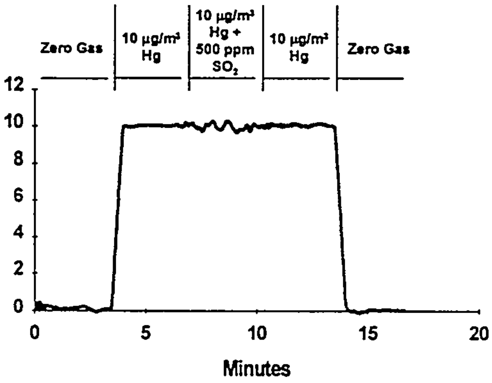

Figure 3. Mercury detector response when measuring mercury in the presence of sulfur dioxide.

Figure 4 shows the response of the analyzer over a concentration range of 0 to 6 ppb (v/v). This range is expected to cover most concentrations expected in coal-fired and municipal solid waste generated flue gases. A dilution probe is used on the analyzer where high concentrations of mercury are expected, such as when monitoring uncontrolled emissions ahead of an APCD.

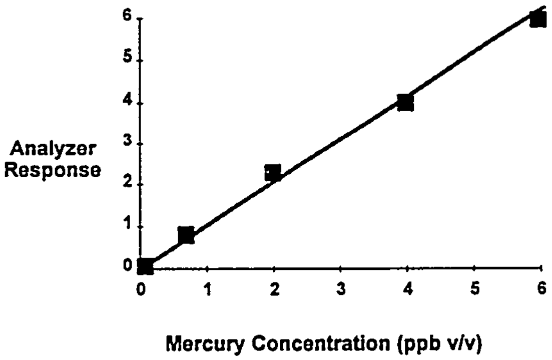

Figure 4. Linearity of the mercury detector.

Converter

A mercury species converter is another key component of the CEM system. The converter is used to distinguish between concentrations of elemental and"total" mercury found in the flue gas. Since the mercury detector measures elemental mercury alone, a converter is needed to change any speciated forms of mercury to elemental mercury for measurement. Total mercury is, therefore, measured by passing the flue gas sample through the converter. Elemental mercury concentrations are measured by the CEM when the flue gas sample bypasses the pre-conditioning converter. Total speciated mercury is then determined as the difference between the measured total mercury concentration and the elemental mercury concentration.

The converter uses unique design features that eliminate the need for wet chemicals or other expendable chemicals.

Figures 5 and 6 show the response of the analyzer when two surrogate speciated mercury compounds were input--mercuric chloride and dimethyl mercury. The test sequence followed the pattern of placing the mercury species through the converter, then the bypass valve was actuated to circumvent the converter. This sequence was followed for a number of cycles to establish the fact that the mercury compounds were being converted to elemental mercury.

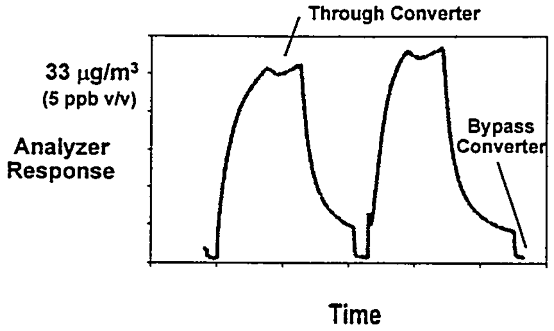

Figure 5. Mercuric chloride being converted to elemental mercury.

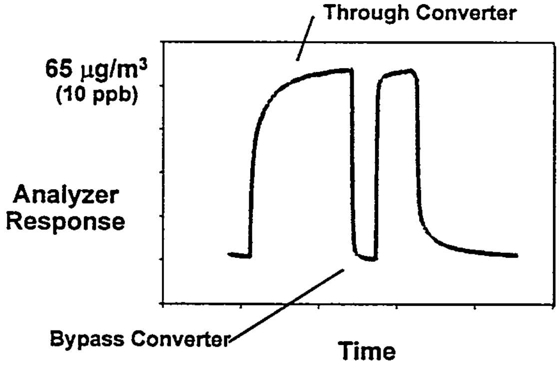

Figure 6. Dimethyl mercury being converted to elemental mercury.

Calibrator

ADA Technologies developed a calibrator for use with the mercury CEM. The calibrator is based on the use of permeation tubes to provide known and accurate concentrations of elemental mercury and mercuric chloride. These devices are considered primary standards for calibrating continuous monitors and they are used to calibrate ambient air analyzers. ADA developed a two-channel calibrator--one channel is used to calibrate the elemental mercury detector and the other is used to calibrate the converter.

EVALUATION OF MERCURY SPECIATION BY EPA (DRAFT) METHOD 29

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INTRODUCTION

The 1990 Clean Air Act Amendments require that the U.S. Environmental Protection Agency (EPA) assess the health risks associated with mercury emissions. Also, the law requires a separate assessment of health risks posed by the emission of 189 trace chemicals (including mercury) for electric utility steam-generating units. In order to conduct a meaningful assessment of health and environmental effects, we must have, among other things, a reliable and accurate method to measure mercury emissions. In addition, the rate of mercury deposition and the type of control strategies used may depend upon the type of mercury emitted (i.e., whether it is in the oxidized or elemental form).

It has been speculated that EPA (Draft) Method 29 can speciate mercury by selective absorption; however, this claim has yet to be proven. The Electric Power Research Institute (EPRI) and the U.S. Department of Energy (DOE) have contracted with the Energy & Environmental Research Center (EERC) at the University of North Dakota to evaluate EPA (Draft) Method 29 at the pilot-scale level. The objective of the work is to determine whether EPA (Draft) Method 29 can reliably quantify and speciate mercury in the flue gas from coal-fired boilers.

SCOPE OF WORK

Pilot- and bench-scale tests are being performed to statistically evaluate the ability of EPA (Draft) Method 29 to speciate mercury emissions. The bench-scale tests are designed to initially establish parameters that may affect mercury speciation, while the pilot-scale tests are designed to follow the verification criteria established in EPA Method 301. The pilot-scale tests are being completed using the particulate test combustor (PTC) which is a 550,000-Btu/hr pulverized coal (pc)-fired boiler designed to generate flue gas and fly ash representative of that produced in a full-scale utility boiler.

In accordance with EPA Method 301, quadtrain sampling with six quadtrain replicates was conducted. Since the EPA (Draft) Method 29 and the Method 301 criteria were designed for large ducts, some modifications were necessary to adapt the procedure to the EERC pilot-scale PTC. The most important modification is the probe location for the quadtrains. Since the pipe internal diameter is only 5.25 in. at the sampling locations, the system could not meet the 5% area criterion of Method 301. The alternate sample probe configuration used for this project (discussed with the EPA) has the nozzles 90° from each other and 1 in. apart, as shown in the photograph in Figure 1.

For EPA (Draft) Method 29, a total of seven impingers are included in the sampling train. Impinger 1 is empty and is intended to remove most of the moisture. Impingers 2 and 3 contain acidified hydrogen peroxide solution. It is in these impingers, it is speculated, that the oxidized mercury will collect. Impinger 4 is empty to prevent any mixing of the two types of trapping solutions. The mercury that passes the two peroxide impingers is thought to be elemental mercury and is subsequently captured in a solution of acidified permanganate in Impingers 5 and 6. Finally, Impinger 7 contains silica gel to ensure the flue gas is thoroughly dried before it leaves the impinger train. After the sampling is completed, the solutions are prepared and then analyzed for mercury using cold-vapor atomic absorption spectroscopy.

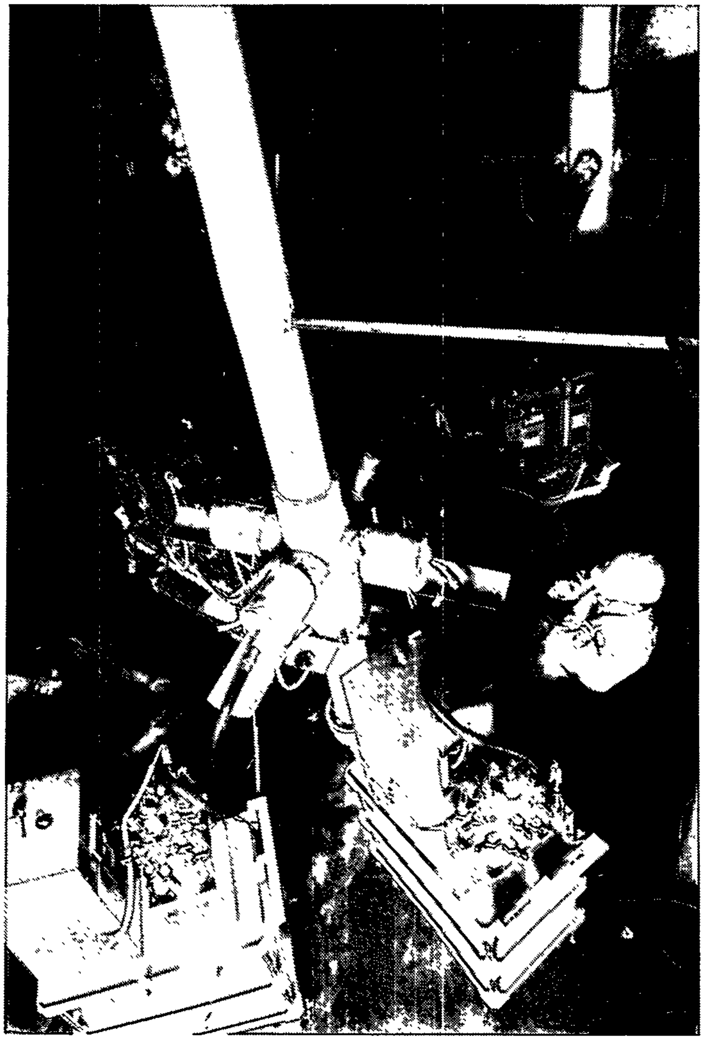

Figure 1. Photograph of EPA (Draft) Method 29 quadtrain setup.

A bench-scale test unit, shown in Figure 2, was designed and built to simulate flue gas conditions. Known quantities of elemental mercury vapor and mercury(II) chloride ($HgCl_2$) vapor were introduced into the system by flushing nitrogen around calibrated permeation tubes. The quantity of mercury vapor released into the gas stream was determined by its vapor pressure at a specific temperature. The temperature of the permeation tubes was maintained and controlled using a straight-tube condenser and water bath. The simulated flue gas consisted of 5% O_2, 10% water vapor, 15% CO_2, and 1000 ppm SO_2, with N_2 as the balance. For several of the tests, hydrogen chloride (HCl) was also added as a process variable.

Four pilot-scale tests have been completed to date. Details of the pilot-scale test combustor have been described in a previous report.[1] The conditions for each of these tests are shown in Table 1. Three of the four completed tests included six replicate quadtrains (four EPA [Draft] Method 29 sampling trains operated simultaneously at essentially the same point), resulting in a total of 24 EPA (Draft) Method 29 samples per test in accordance with EPA Method 301. The other test was designed to compare EPA (Draft) Method 29 results directly to those of Method 101A (total mercury measurement); this test was to help act as a quality control check.

Although direct spiking of the impinger solutions and filter is needed to determine the analytical uncertainty, it was also necessary to determine the uncertainty of the entire sampling train. Therefore, an important part of the overall test program was to spike the flue gas stream with mercury. A schematic of the mercury injection system is shown in Figure 3. The quantity of elemental mercury injected into the flue gas stream is controlled by changing the nitrogen flow rate through the condensers.

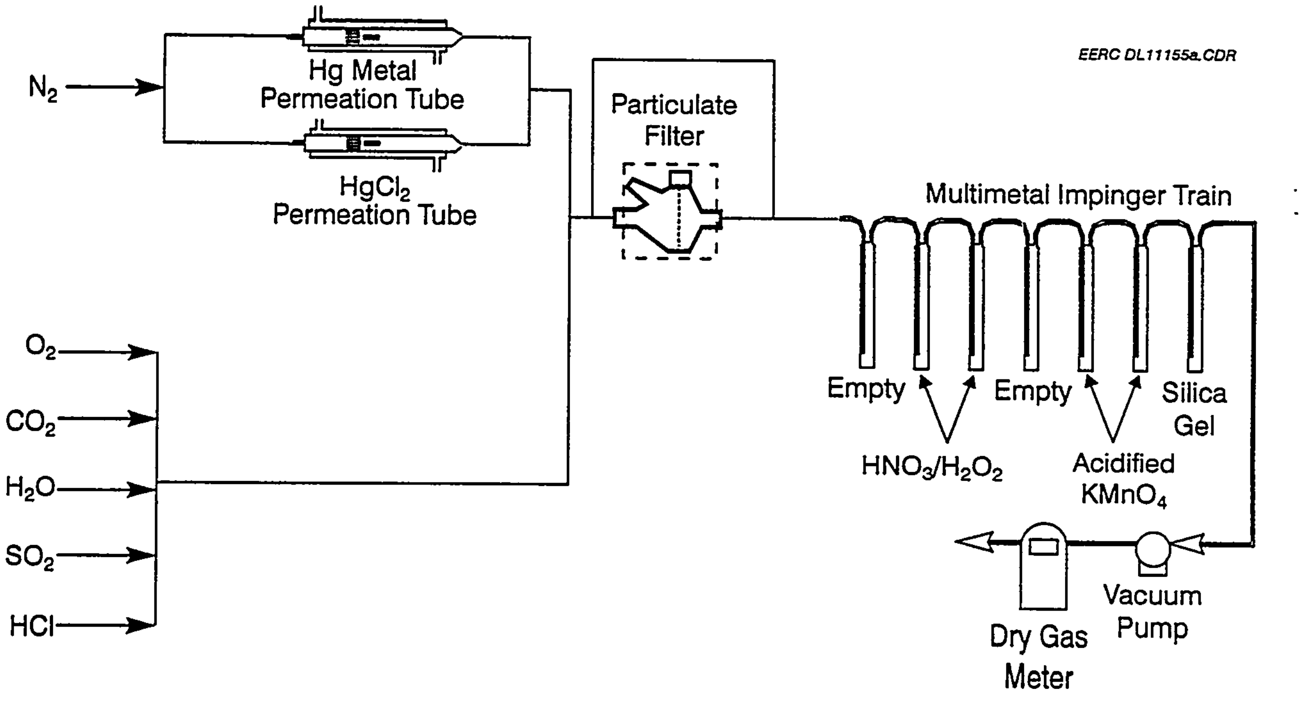

Figure 2. Schematic of bench-scale test system.

TABLE 1

Completed Pilot-Scale Test Matrix

Test No.	Fuel	Sampling Method	Sample Location (relative to the baghouse)	Spike Location[1]
1	Blacksville[2]	All Method 29	Inlet + outlet	None
2	Blacksville	All Method 29	Inlet	Inlet
3	Blacksville	All Method 29	Outlet	Outlet
4	Blacksville	Method 29 + Method 101A	Inlet + outlet	None

[1] Spike sample is the inlet Hg concentration plus enough mercury vapor to bring the flue gas concentration to 20 $\mu g/m^3$.

[2] Pittsburgh No. 8 bituminous coal.

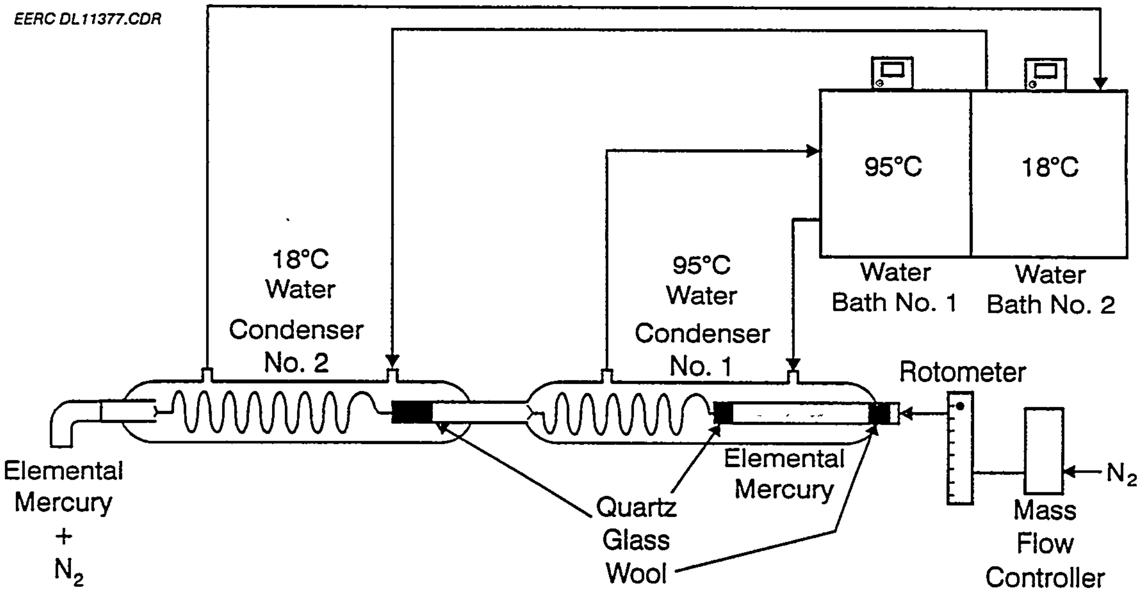

Figure 3. Schematic of elemental mercury spiking system.

RESULTS

Bench-Scale Tests

The first bench-scale tests were completed with only nitrogen as a carrier gas to determine whether EPA (Draft) Method 29 had any chance of speciating mercury. When elemental mercury was injected, almost all of the mercury was captured in the permanganate solution (>99%), and when $HgCl_2$ was injected, almost all of it was captured in the peroxide solution (96%). Since these results were encouraging, the remaining tests were then completed with simulated flue gas.

When $HgCl_2$ was added to the simulated flue gas without HCl present, about 90% was captured in the peroxide. The 10% captured in the permanganate may have been a result of sampling variation, and/or elemental mercury contamination in the $HgCl_2$ used to make the permeation tube. The data indicates little or no effect of the HCl on $HgCl_2$ speciation.

When elemental mercury was added to the simulated flue gas, with or without HCl, 90% of the mercury was captured in the permanganate solutions, and 10% was captured in the peroxide solutions. The data indicated that there was no clear effect from HCl addition. The data for both speciation tests are shown in Figure 4. As described later, pilot-scale tests at EERC have shown that some type of conversion of elemental mercury may occur in the flue gas stream, and it appears that the conversion may be related to the SO_2 concentration in the flue gas. For the bench-scale test completed to date, the SO_2 concentration was maintained at 1000 ppm. This level is compared to 1500–2000 ppm SO_2 in the flue gas for the pilot-scale tests firing Blacksville bituminous coal. Future bench-scale tests are planned to help determine the effect of SO_2 concentration on mercury speciation using EPA (Draft) Method 29.

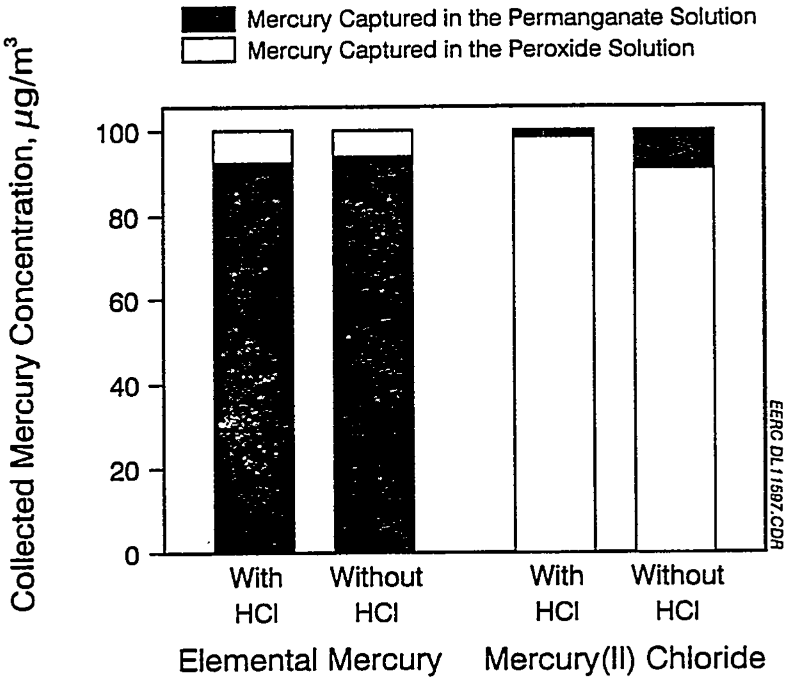

Figure 4. Mercury speciation by EPA (Draft) Method 29 as a function of HCl in bench-scale tests using a simulated flue gas.

Pilot-Scale Tests

During the shakedown testing, sampling was completed to determine if the flue gas flow rate and dust loading were the same at each of the ports of the quadtrain setup. A port analysis showed that the flue gas flow rate and dust loadings were within 10%. The most interesting result from the tests completed to date is that a substantial portion of the spiked elemental mercury collected in the peroxide solutions. When the baseline mercury concentrations, as determined from previous EPA (Draft) Method 29 tests, are compared to the tests with flue gas mercury spiking, approximately 60% of the spiked elemental mercury was collected in the peroxide solution, as is shown in Figure 5. The question, then, is whether EPA (Draft) Method 29 is speciating the mercury correctly, or some type of conversion of the elemental mercury is occurring in the flue gas stream prior to sampling. The original test matrix is being changed to allow future tests to be designed to help resolve this question.

The statistical analyses for the four tests are shown in Tables 2-5. From these tables, it can be seen that the data appear to be consistent and statistically valid. The spike recoveries are close to 90% in most cases, and the correction factors and relative standard deviations are low. The overall results show very good precision and low analytical bias.

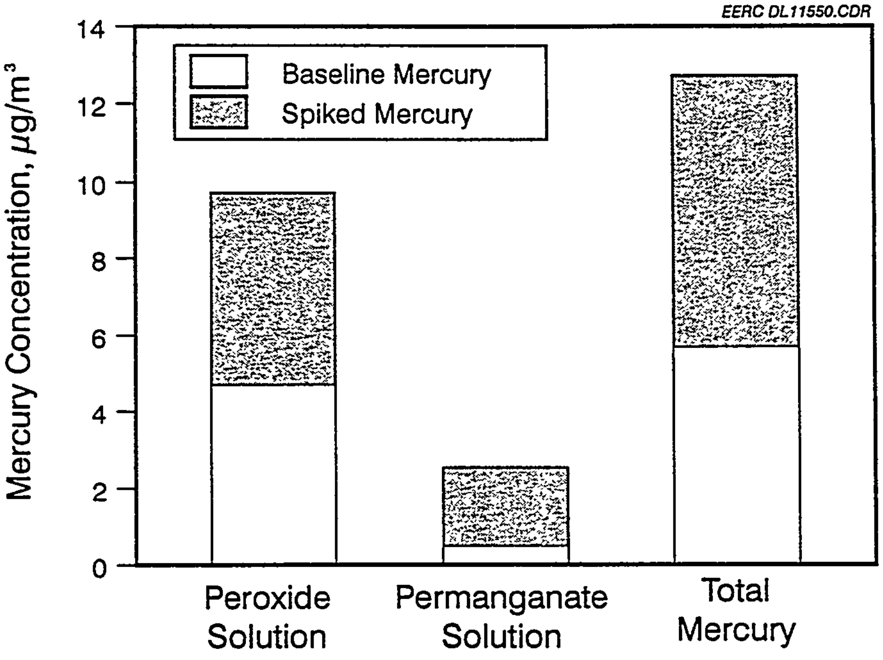

Figure 5. Speciation of the flue gas elemental mercury spike as determined by EPA (Draft) Method 29.

TABLE 2

Statistical Analysis for Test 1 of Pilot-Scale Test Matrix

	Corrected Values		
	Peroxide Solution, $\mu g/m^3$	Permanganate Solution, $\mu g/m^3$	Total Mercury, $\mu g/m^3$
Analyte Spike	0	0	----
Average	6.39	0.51	6.82
Analyte Spike	5.05	5.05	----
Average (with spike subtracted)	6.50	0.49	6.99
*Spike Recovery, %	93.9	96.1	---
Correction Factor	1.07	1.04	---
Relative Std. Dev., %	12.5	35.8	12.2

*Spike recoveries are based on the analytical data comparing the spiked and unspiked sample.

TABLE 3

Comparison of EPA (Draft) Method 29 to EPA Method 101A (Tests 1 and 5)

Test No.	Average, µg/m³	Relative Standard Deviation, %
Test 1 (Method 29)	6.49	12.2
Test 4 (Method 29)	6.14	14.8
Test 4 (Method 101A)	5.79	9.6

TABLE 4

Statistical Analysis for Test 2 of Pilot-Scale Test Matrix

	Corrected Values			
	Filter Ash, µg/m³	Peroxide Solution, µg/m³	Permanganate Solution, µg/m³	Total Mercury, µg/m³
Analyte Spike	0	0	0	----
Average	0.37	12.43	3.14	15.94
Analyte Spike	----	6.45	6.45	----
Average (with spike subtracted)	0.41	12.44	3.14	15.98
*Spike Recovery, %	102.7	80.0	89.9	---
Correction Factor	1.00	1.25	1.11	---
Relative Std. Dev., %	53.7	4.4	12.5	3.1

*Spike recoveries are based on the analytical data comparing the spiked and unspiked sample.

TABLE 5

Statistical Analysis for Test 3 of Pilot-Scale Test Matrix

	Corrected Values		
	Peroxide Solution, µg/m³	Permanganate Solution, µg/m³	Total Mercury, µg/m³
Analyte Spike	0	0	----
Average	10.17	4.00	14.17
Analyte Spike	6.81	6.81	----
Average (with spike subtracted)	10.29	4.04	14.32
*Spike Recovery, %	89.2	93.1	---
Correction Factor	1.12	1.07	---
Relative Std. Dev., %	9.4	13.9	4.8

*Spike recoveries are based on the analytical data comparing the spiked and unspiked samples.

PRELIMINARY OBSERVATIONS

- On the bench scale, HCl does not appear to influence mercury speciation by EPA (Draft) Method 29 when either injecting elemental or oxidized mercury.
- At the pilot-scale level, very precise mercury measurements with little bias can be obtained with EPA (Draft) Method 29.
- When elemental mercury is spiked into a flue gas stream while firing a medium-sulfur bituminous coal, a substantial portion is collected in the peroxide impingers.
- Additional tests are necessary to determine if a problem is associated with EPA (Draft) Method 29, and/or if some type of conversion of the elemental mercury is occurring in the flue gas stream.

FUTURE WORK

In addition to the completed pilot-scale test, three more tests are planned. The primary purpose of these tests is to compare other mercury sampling methods with EPA (Draft) Method 29 to try and establish whether elemental mercury is converted in the gas stream, or a problem exists with the premise of EPA (Draft) Method 29. The following four different mercury sampling methods will be tested.

- Mercury Speciation Absorption Method (Bloom Method)
- Conventional EPA Method 29
- The Keith Curtis Method which uses a solution of KCl instead of the peroxide solution of conventional EPA Draft Method 29
- Use of an acetate buffer as a first solution in EPA (Draft) Method 29

REFERENCE

1. Miller S.J.; Laudal D.L. "Pulse-Jet Baghouse Perfomance Improvement with Flue Gas Conditioning," EPRI Project No. RP-3083-9, October 1992.

The following manuscript was unavailable at time of publication.

MEASUREMENT OF MERCURY AND OTHER TRACE METALS IN COMBUSTION GASES

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Please contact author(s) for a copy of this paper.

LABORATORY-SCALE EVALUATION OF VARIOUS SAMPLING AND ANALYTICAL METHODS FOR DETERMINING MERCURY EMISSIONS FROM COAL-FIRED POWER PLANTS

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Summary

Comparative bench-scale mercury sampling method tests were performed at the Advanced Technology Systems, Inc (ATS) laboratories for EPA Method 101A, EPA Method 29 and the Ontario Hydro Method. Both blank and impinger spiking experiments were performed.

The experimental results show that the ambient level of mercury in the ATS laboratory is at or below the detection limit (10 ng Hg) as measured by a cold vapor atomic absorption spectrophotometer (CVAAS) which was used to analyze the mercury samples. From the mercury spike studies, the following observations and findings were made.

a) The recovery of mercury spikes using EPA Method 101A was 104%.

b) The Ontario Hydro Method retains about 90% of mercury spikes in the first absorbing solution but has a total spike retention of 106%. As a result, the test data shows possible migration of spiked mercury from the first impinger solution (KCl) to the permanganate impingers.

c) For the EPA Method 29 solutions, when only the peroxide impingers were spiked, mercury recoveries were 65.6% for the peroxide impingers, 0.1% for the knockout impinger and 32.8% for the permanganate impingers with a average total mercury recovery of 98.4%. At press time, data was still being obtained for both the peroxide and permanganate impinger solution spikes. This and other data will be available at the presentation.

Background

Title III of the 1990 Clean Air Act Amendments requires the measurement and inventory of a possible 189 hazardous air pollutants (HAPs) from any stationary source producing more than 10 tons per year of any one pollutant or more than 25 tons per year of total pollutants. Coal-fired power plants are included on this list of potential emission sources requiring such inventories and possible regulation.

doeatspp

In 1991, the Department of Energy's-Pittsburgh Energy Technology Center (DOE-PETC) commissioned five primary contractors to conduct emission studies at eight different coal-fired electric utilities. The eight sites represented a cross section of feed coal type, boiler designs, and particulate and gaseous pollutant control technologies. The major goal of these studies was to determine the sampling and analytical methodologies that could be used to perform these emission tests while producing representative and reliable emission data. The successful methods could then be recommended to the EPA for use as compliance testing methods for the regulation of air toxic emissions from coal-fired power plants.

A secondary purpose of the testing was to determine the effectiveness of the control technologies in reducing target hazardous air pollutants.

The CAAA regulations did not identify the sampling and analytical methods that were to be used in performing the emission tests. As such, one of the challenges facing the primary contractors was to identify methods, previously used for other applications, that could be used for emission tests at coal-fired power plants to gather accurate HAPs emission data. A second challenge was to identify criteria that could be used to determine the efficacy of the selected sampling and analytical methods in performing their intended purpose.

The five primary contractors were Battelle, Energy and Environmental Research Corporation, Radian, Roy F. Weston, and Southern Research Institute. The eight locations at which the emission tests were performed were: Ohio Edison's Niles Station and Cooperative Power Association's Coal Creek Station (Battelle), Ohio Power Company's Cardinal Station (Energy and Environmental Research Corporation), Tucson Electric Power Company's Springerville Station and Northern Indiana Public Service Company's Bailly Station (Southern Research Institute), Illinois Power Company's Baldwin Station and Minnesota Power Company's Boswell Station (Roy F. Weston) and Georgia Power Company's Plant Yates (Radian Corporation).

The contractors tested for major and trace metals, mercury, total particulates, volatile organic compounds, semi-volatile organic compounds, aldehydes, acid gases (HF, HCl, HBr, F_2, Cl_2 and Br_2), ammonia, cyanide, phosphates, sulfates and radionuclides. Mercury testing was performed using EPA Method 29 and usually either the HEST or the Bloom methods. Most of the sampling and analytical methods employed were based on existing EPA-approved methodologies or modifications of methods that had previously been approved for other applications.

Advanced Technology Systems, Inc. (ATS) as a secondary DOE contractor on this project, has assessed the sampling and analytical plans and the emission reports of the five primary contractors to determine how successful the contractors were in satisfying their defined objectives. To accomplish this task ATS examined the precision and accuracy of the emission test results, the emission levels of the target hazardous air pollutants (HAPs), the precision and accuracy of the audit sample results and the closure of material balances for individual processing steps and for the overall combustion process.

doeatspp

As a result of these efforts, ATS identified several problem areas where the sampling and analytical methodologies applied were not able to adequately measure the concentration of the target analytes in the flue gas streams of coal-fired power plants. These areas included but were not limited to the measurement of mercury and other volatile metals such as arsenic and selenium, and the measurement of semi-volatile metals such as antimony, cadmium, lead, boron and molybdenum. Other areas of concern include the sampling and analysis of volatile organic compounds such as benzene and toluene and the sampling and analysis of acid gases such as HCl and Cl_2.

Introduction

As a result of the identification of deficiencies in the methods detailed above, ATS' assignment from DOE was to rectify the shortcomings in the sampling and analytical methodologies applied to flue gas sampling at coal-fired power plants by method improvement and/or method development. Consequently, ATS is presently involved in an intensive program of method development studies. These studies are being conducted in the laboratory with subsequent tests planned for selected pilot plant and power plant test sites.

ATS' approach to these method development studies has been to first test the existing methods under ideal laboratory conditions. The philosophy behind this approach is that if the methods cannot perform as designed under ideal laboratory conditions, there is little chance that they would produce desired performance results at a plant site environment.

The initial focus is on mercury. Five mercury sampling methods have been selected for testing at ATS laboratories. These methods are EPA Method 101A, EPA Draft Method 29, the Ontario Hydro Method, The Hazardous Element Sampling Train (HEST) Method and the Bloom Method. This paper will discuss the experimental results from tests with the first three methods. The findings from tests with the HEST and Bloom Methods will be discussed in later presentations.

Experimental

A. Design of Experiments.

Sampling performance evaluation tests were conducted for each method under investigation. These tests consisted of both blank and mercury spiking tests. The blank runs were performed to determine if the sampling method was collecting any mercury contamination that might be present in the laboratory environment. Once blank baseline mercury concentrations were established, mercury was introduced into the sampling train by spiking directly into the impinger solutions with a known concentration of mercury in the form of mercuric chloride. To provide for statistical evaluation of the data obtained, five spiked mercury replicates were performed for each test.

The sampling tests were performed using Nutech 2010 Stack Samplers. The sampling trains were assembled in accordance with the EPA methodology guidelines. Filter weights, and the weights and volumes of the impingers and their contents were recorded before and after a sampling run. A sampling run consisted of collecting 108 cubic feet volume of ambient laboratory air. The time required to collect the required volume was approximately 3 hours. In addition, temperatures and vacuum pressures were carefully monitored and recorded every 30 minutes.

Upon completion of the sampling run, the train was disassembled, and the filter and impinger solutions were recovered as per appropriate EPA methodology. The impinger solutions were analyzed for mercury as per EPA Method 7470. Briefly, this method involves reducing the mercury collected (in the mercuric form) to elemental mercury, which is then aerated from the solution into an optical cell and measured by atomic absorption spectrophotometry. Mercury analysis was performed using a Bacharach Model MAS-50B CVAAS Mercury Analyzer System. Calibration of this unit was based on a five point calibration curve.

i) Blank Runs.

Blank tests were performed for each sampling method evaluated. Initially, five blank tests were performed for EPA Draft Method 29. The analytical results for these tests showed that the ambient level of mercury in the laboratory was below the detection limits of the analytical instrument. As a result only spot check blank tests were performed for the other two methods.

ii) Spiked Runs.

Mercury spiking experiments were performed for each method tested. These tests were performed by introducing known volumes of a mercuric chloride standard solution directly into the impingers using a repeater pipette. The mercury spike concentrations were based on the volumes of the recovery samples and the optimum working range of the CVAAS. After the impingers were spiked, the train was assembled, leak-checked and 108 cubic feet of laboratory air was drawn through the train. When the desired volume of air had been collected, the filter and impinger solutions were recovered as per EPA methodology for the method being tested and the impinger solutions were analyzed for mercury following EPA Method 7470 procedures.

The EPA Method 101A spiking tests were performed by spiking 5,000 ng of mercuric chloride into the second and third permanganate impingers then assembling the sampling train, performing the test and recovering the train as described above. This would theoretically produce a Hg level of 10,000 ng/L in the recovered samples.

The spiking scheme for the Ontario Hydro impinger mercury spiking tests was as follows. The first KCl impinger was spiked with 5000 ng of mercury and the first $KMnO_4$ impinger was spiked with 5000 ng of mercury. The filter was not spiked for this series of tests. A Hg level of 10,000 ng/L would be expected in the recovered samples.

Two series of spiking tests were performed for EPA Draft Method 29. In the first series of impinger spiking tests only the peroxide impingers were spiked. In these tests, the first peroxide impinger was spiked with 3,000 ng of mercuric chloride. In the second series of tests, the first peroxide impinger was spiked with 3,000 ng of mercuric chloride and the first permanganate impinger was spiked with 4,000 ng of mercuric chloride. For all of these experiments the expected level of mercury in the recovery samples was 10,000 ng Hg/L.

Results and Discussion

The analytical results from the blank and mercury impinger spiking tests are presented in Tables 1 and 2. The results are shown in total ug for the blank tests and in both total ug and percent recovery for the impinger spiking tests. Both individual test results and average results are shown. Where appropriate, standard deviations are also presented.

The blank test results shown in Table 1 indicate that the level of mercury present in the laboratory is at or below the detection limit of the analytical instrument. These results demonstrate that only nominal amounts of mercury are present in the air sampled for the series of mercury spiking tests. As a result, all of the mercury present in the recovery samples from the mercury spiking tests can be considered to originate from the mercury spikes.

Previously, analysis of the Method 101A blank runs had yielded detectable mercury in concentrations ranging from 17.2 ng to 388 ng. It was presumed that the procedure for cleaning the glassware was insufficient in removing residual mercury from the sampling train glassware. Laboratory glassware was scrupulously cleaned between each sampling run in accordance with the EPA Method 29 guidelines. Cleaning the glassware consisted of a soapy (Citranox) wash and rinse followed by a 10% nitric acid soak for a minimum of 4 hours. The glassware was then triple-rinsed with deionized water and oven dried. As a precaution to prevent further contamination of blank runs, separate impingers and glassware were purchased to be used exclusively for the blank analysis of sampling methods. The current blank data was obtained with such glassware.

Table 2 shows that the EPA Method 101A mercury spike test results range from 103.24% recovery (tests 1, 3 and 5) to 107.88% recovery (test 2). The average recovery was 104.23% with a standard deviation of 2.04%. The precision and accuracy of these results are very good. As such, these results indicate that EPA Method 101A can serve as a standard against which the recovery results of all the other mercury spiking tests in this study can be compared.

Table 2 also shows that the experimental results for the Ontario Hydro Method ranged from 84.09% to 91.64% recovery of mercury for the first absorbing solution and 110.51% to 131.26% recovery for the permanganate absorbing solution. Total mercury recovery for the Ontario Hydro Method ranged from 98.24% to 111.45% The average percent recoveries of mercury were 88.11 ± 3.23 for the first absorbing solution, 124.47 ± 8.5 for the permanganate solution and 106.49 ± 4.88 for total recovery. These results show that the precision of mercury recovery for each impinger solution type and for total recovery are good. However, there is a reproducible portion of the mercuric chloride that appears to migrate from the first absorbing solution impingers to the $KMnO_4$ impingers where it is retained. To investigate this migration effect, the experiment will be repeated with mercury spiking into only the first absorbing solution impingers.

The bottom half of Table 2 shows the experimental results for the peroxide impinger spiking tests performed using EPA Draft Method 29. The results from this series of tests indicate that the average recovery of mercuric chloride spikes into the peroxide impingers was only 65.6%. Recovery of mercury from the knockout impinger and from the permanganate impingers, which were not spiked, were 0.1% and 32.8% respectively. Total spiked mercury recovery was 98.4%. These results seem to indicate that the peroxide impinger solutions did not totally retain mercuric chloride species under the conditions of the test and that migration of the spiked mercuric chloride to the permanganate solutions occurred. A second series of tests is currently underway with spiking into both the peroxide and permanganate impingers. Results from this study will be available at the conference presentation.

Conclusions

The experimental results show that the ambient level of mercury in the ATS laboratory is at or below the detection limit for the cold vapor atomic absorption spectrophotometer used to analyze the mercury samples. The results also showed that, under the test conditions, the recovery of the mercury spikes using EPA Method 101A is complete within experimental error. This implies that Method 101A can serve as a control or standard for comparison with all of the other methods tested and those that will be tested in the future.

The results also showed that the Ontario Hydro Method retains about 90% of mercury spikes in the first absorbing solution and has a total spike retention of around 100%. As a result, migration of mercury spikes from the first impinger solution into the permanganate impingers is suspected. Further tests will be performed to verify if migration actually occurs.

In addition, the experimental results showed that the peroxide impingers were not able to totally retain oxidized mercury species spiked directly into them under ideal laboratory conditions. These results cast doubts on the ability of the method to perform correctly under more rigorous field conditions. Further tests are in progress to confirm this finding along with determining recoveries from both peroxide and permanganate impingers each spiked with equivalent amounts of mercury species.

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Table 1. Concentration of Mercury in the Recovery Samples for the Blank and Mercury Spiking Tests.

Sample	Mercury Level (ug)					
	Test 1	Test 2	Test 3	Test 4	Test 5	Ave/*SD*
EPA Method 101A						
• Blank Test	0.053	-	-	-	-	0.053
• Spiking Tests	10.320	10.790	10.320	10.360	10.320	10.420/*0.206*
Ontario Hydro Method						
• Blank Test	ND	-	-	-	-	-
• Spiking Tests						
• KCl Impingers	4.393	4.299	4.581	4.204	4.550	4.405/*0.161*
• $KMnO_4$ Impingers	6.132	5.525	6.563	6.405	6.500	6.225/*0.424*
• Total Mercury	10.525	9.824	11.144	10.609	11.050	10.630/*0.525*
EPA Method 29						
Blank Tests						
• Front-half	ND	0.011	ND	ND	ND	0.011
• H_2O_2 Impingers	ND	0.011	ND	ND	0.018	0.015
• Knockout	ND	ND	ND	0.018	ND	0.018
• $KMnO_4$ Impingers	0.030	ND	ND	ND	0.030	0.030
• $KMnO_4$ Wash	ND	ND	ND	ND	ND	
H_2O_2 Spiking Tests						
• H_2O_2 Impingers	1.988	2.259	1.956	2.041	1.591	1.967/*0.241*
• Knockout	ND	ND	ND	ND	ND	ND
• $KMnO_4$ Impingers	0.977	1.092	0.820	1.012	1.013	0.983/*0.100*
• Total	2.965	3.351	2.776	3.053	2.604	2.950/*0.284*

ND - Non-detected at a detection limit of 0.010 ug.
- Not determined.

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Table 2. Percent Recovery of Mercury from Mercury Spiking Tests.

Sample	Percent Recovery					
	Test 1	Test 2	Test 3	Test 4	Test 5	Ave/*SD*
EPA Method 101A	103.2	107.9	103.2	103.6	103.2	104.2/*2.0*
Ontario Hydro Method						
• KCl Impingers	87.7	86.0	91.6	84.1	91.0	88.1/*3.2*
• $KMnO_4$ Impingers	122.4	110.5	131.3	128.1	130.0	124.5/*8.5*
• Total Mercury	105.2	98.2	111.4	106.1	110.5	106.5/*4.9*
EPA Method 29						
H_2O_2 Spiking Tests						
• H_2O_2 Impingers	66.6	75.3	65.2	68.0	53.0	65.6/*8.1*
• Knockout	0.0	0.1	0.1	0.1	0.1	0.1/*0.0*
• $KMnO_4$ Impingers	32.6	36.4	27.4	33.7	33.8	32.8/*3.3*
• Total	98.8	111.8	92.6	101.8	86.9	98.4/*9.4*

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COMPARING AND ASSESSING DIFFERENT MEASUREMENT TECHNIQUES FOR MERCURY IN COAL SYNTHESIS GAS

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ABSTRACT

Three mercury measurement techniques were performed on synthesis gas streams before and after an amine-based sulfur removal system. The syngas was sampled using 1) gas impingers containing a nitric acid-hydrogen peroxide solution, 2) coconut-based charcoal sorbent, and 3) an on-line atomic absorption spectrophotometer equipped with a gold amalgamation trap and cold vapor cell. Various impinger solutions were applied upstream of the gold amalgamation trap to remove hydrogen sulfide and isolate oxidized and elemental species of mercury. The results from these three techniques are compared to provide an assessment of these measurement techniques in reducing gas atmospheres.

INTRODUCTION

The U.S. Department of Energy (DOE), the Electric Power Research Institute (EPRI), and Louisiana Gasification Technology, Inc. have sponsored a comprehensive assessment of toxic emissions from the integrated gasification combined cycle (IGCC) process located at Dow Chemical-Louisiana Division's facility in Plaquemine, Louisiana. Radian Corporation performed this assessment which included the measurement of vapor phase trace elements from various syngas streams and other reducing gas matrices in addition to the emission sources.

Reducing gas matrices containing reactive substances such as hydrogen sulfide adversely affect the ability of conventional gas sampling techniques (e.g., EPA Draft Method 29) to collect some vapor phase metal species. In this paper, vapor phase substances are defined as those elements collected in traps or impingers after particulate removal. For example, acidic potassium permanganate solutions typically used to oxidize and collect mercury in flue gas are quickly reduced by hydrogen sulfide, rendering the solution ineffective. In addition, metal carbonyls, hydride-forming compounds like arsenic, mercury, and other uncharacterized metal species are not efficiently collected in the nitric acid impinger solutions used for oxidized gas streams.

EXPERIMENTAL

Radian Corporation used three different sampling approaches to overcome the limited application of Method 29 on two internal process streams sampled during this test. First, the EPA Draft Method 29 impinger technique was modified by increasing the strength of the hydrogen peroxide component from 10% to 30% and the permanganate solutions were not used. Parallel with Method 29 sampling, sample tubes containing coconut-based charcoal were used to collect mercury and other vapor phase metals. In addition, direct analysis of the gas with an atomic absorption spectrophotometer (AAS) was performed for mercury and a selected set of trace elements. The sour and sweet syngas streams were sampled to characterize the product gas before and after the sulfur removal system. The concentration of hydrogen sulfide is the primary difference between these two process streams.

Nitric Acid/Hydrogen Peroxide Impinger Sampling

EPA Draft Method 29 (M-29) consists of a filter media, which removes particulate matter, and a series of impingers. It is often assumed that substances collected in the impinger exist in the vapor state. This method uses two impingers containing a 5% HNO_3/10% H_2O_2 solution, followed by two impingers containing a 4% $KMnO_4$/10% H_2SO_4 solution for total mercury collection. Current research is attempting to determine the speciation capabilities of M-29. It is commonly believed that oxidized forms of mercury preferentially report to the nitric/peroxide impingers and elemental mercury can only be trapped in the permanganate impingers. When this method is applied to syngas or other reducing gas matrices containing hydrogen sulfide (H_2S), the permanganate impinger solution is quickly reduced so it is ineffective at collecting mercury. The standard nitric acid solution (5% nitric/10% peroxide) has also been shown to be ineffective in syngas applications for the collection of mercury and other trace elements.

In an effort to enhance the collection efficiency of the nitric acid impingers for other vapor phase metals in syngas, the concentrations of nitric acid and hydrogen peroxide were increased to 10% and 30%, respectively. Although the oxidation potential of this solution is enhanced, it does not effectively trap H_2S. The low pH of the impinger solution keeps the H_2S equilibrium shifted towards the gas phase. As such, H_2S does not dissociate and, therefore, oxidation and removal do not occur. Consequently, permanganate impingers were not used in the sampling trains for the sweet and sour syngas. Therefore, the potential to collect elemental mercury in this M-29 configuration is minimal.

To measure the analytical bias of the mercury measurements in this matrix, duplicate syngas samples were spiked with aqueous mercury standards before sample digestion and analysis. These spikes were recovered at 99 and 104 percent. The analytical results for the enhanced nitric acid/hydrogen peroxide matrix are considered acceptable and accurate.

Adsorption on Charcoal Sorbent

Some industrial processes utilize charcoal sorbents in guard beds to protect catalysts from metal poisoning. Using the same principle, charcoal has also been demonstrated as a suitable sorbent for the collection of mercury in flue gas.[1,2] Coconut-based charcoal was aggressively cleaned using concentrated nitric acid followed by an ultra-pure deionized water rinse then dried over night. The cleaning procedure required five days to complete. The charcoal was then loaded into precleaned quartz tubes.

Two charcoal tubes were placed in series for sample collection using Teflon® tubing and plastic connectors. A total of 100 L of syngas was sampled through the tubes at ambient temperature at a maximum flowrate of 1 L/min. After sample collection, the charcoal tubes were sealed with plastic caps and sent to the laboratory for analysis. The charcoal sorbent was digested with nitric acid in a closed microwave digestion vessel to minimize losses of volatile elements. This digestate was analyzed for mercury by cold vapor atomic absorption spectrophotometry (CVAAS).

To assess the quality of mercury recovery from the charcoal, blank charcoal media was spiked before digestion with a commercially-prepared aqueous standard solution. Duplicate spikes (1 μg) were recovered at 52 and 62 percent. Duplicate analytical spikes introduced in the sweet syngas sample digestates were recovered at 77 and 81 percent. Blank media was analyzed to provide a measure of background concentrations for correction of the sample results. Three blanks were analyzed with concentrations ranging from 0.08-0.10 μg mercury per tube. Based on these quality control results, mercury data from the charcoal tube sampling method may be biased low.

Direct Analysis by Cold Vapor Atomic Absorption Spectrophotometry

Mercury analyses of the process stream were carried out on a semi-continuous basis using a cold vapor atomic absorption method.[3] The field apparatus, depicted in Figure 1, consisted of an impinger sampling train, a gold amalgamation unit, the CVAAS instrument, and units to clean and measure the volume of the sampled gas.

The gas stream temperature was controlled to avoid water condensation within the lines. A continual gas flow was maintained by by-passing the gas upstream of the impinger train when sampling was not being performed.

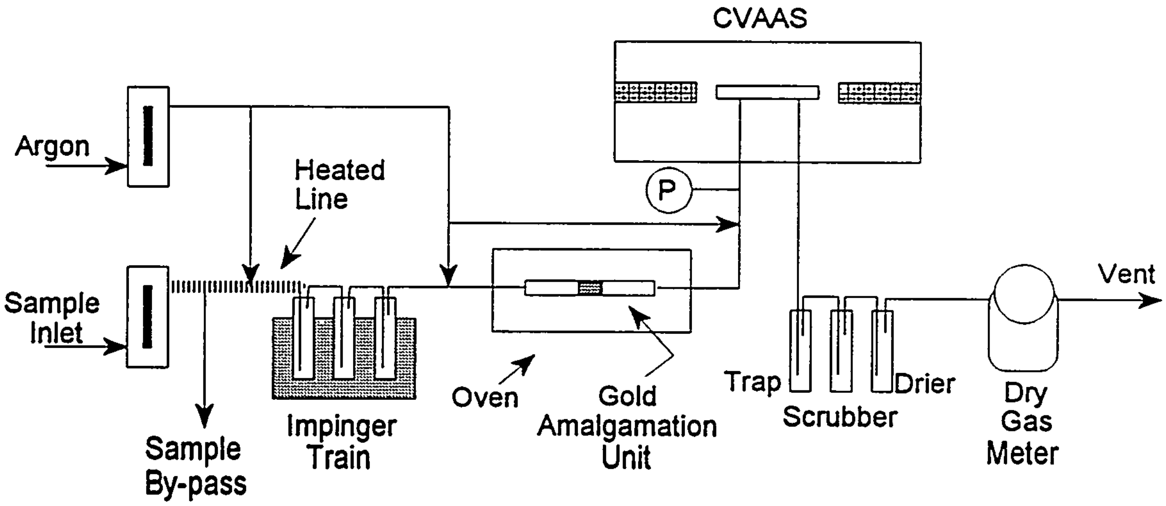

Figure 1. Schematic of CVAAS Sample Analysis System

The sample gas flowrate was 0.75 - 1.5 L/min through a series of ice-chilled impingers containing solutions designed to either pass or trap elemental and oxidized forms of mercury. The flow was controlled using calibrated flow meters and the volume was measured using a dry gas meter. The impingers consisted of 70 mL deep-well bottles with fritted tips. In most cases, solution volumes of 35 mL were used. The impinger solutions evaluated will be discussed below. Following the sample-gas purge, the impingers were flushed with argon to remove residual sample vapor.

Mercury from the gas stream was adsorbed onto the surface of cooled gold mesh, located in a half-inch quartz tube, to concentrate the mercury prior to analysis. The gold was then heated to 950°F, using a temperature-controlled tubular oven, to thermally desorb the mercury. A continuous flow of argon carried the desorbed mercury to the CVAAS cell for analysis. The CVAAS unit consisted of an ARL Model 93 atomic absorption spectrometer containing a 20 mL quartz analysis cell. The mercury absorbance at 253.3 nm was measured and results were recorded on a HP3390A integrator. The instrumental detection limit was determined to be 10 ng of mercury during this testing.

Impinger Solutions. The direct analysis in the field provided the opportunity to try several techniques for measuring total or speciated mercury. The impinger solutions used during this testing were chosen for their potential to either capture or pass different forms of mercury. Various combinations were used in attempts to overcome interferences associated with the syngas matrix. Various impingers, such as water, NaOH, and cold "knockouts," were evaluated for their ability to protect the mercury absorption and reduction solutions from these interferences.

Reductant solutions, such as 0.1M sodium borohydride ($NaBH_4$) and saturated stannous chloride ($SnCl_2$) in 10% H_2SO_4, were used to convert the mercury in the sample to the elemental form, Hg°. The Hg°, with a very low aqueous solubility, would be expected to remain in the gas stream and thus flow to the amalgamation unit where it would be adsorbed by the gold. These solutions were used exclusively to determine the total mercury in the gas stream. They were also used downstream of scrubbing impinger solutions designed to eliminate either the oxidized mercury or the matrix interferences.

Several solutions, including 4% hydrogen peroxide (H_2O_2), 80% isopropyl alcohol (IPA), and water, were tested for their abilities to capture oxidized mercury from the gas stream while enabling the Hg° to pass. These solutions were located either in the first impinger, or in the second behind a knockout impinger. The H_2O_2 solution was acidified with 5% HNO_3 to increase both the relative oxidation strength and metal solubility within the solution. Elemental mercury, with its low solubility, would be expected to pass through the H_2O_2 solution. The H_2S adsorption into the IPA should be low, thus reducing the possibility of reactions with the solubilized mercury. Such reactions may result in the reduction of the captured mercury and its subsequent release from the solution. Diethyldithiocarbamic acid (DEDTCA) was added to the IPA impingers to chelate the adsorbed mercury, thus preventing its release back to the gas stream.

The ability of 5% potassium permanganate ($KMnO_4$) (+10% H_2SO_4) to capture mercury from the gas stream was evaluated. The high oxidation potential of this solution enables it to absorb both elemental and oxidized forms of mercury. Initial tests verified previous results which showed that $KMnO_4$ is rapidly reduced by the H_2S present in the coal syngas. Therefore, these solutions were placed downstream of other impingers, such as NaOH, designed to remove the H_2S from the gas.

Gas Analysis. Gas samples were flowed through the impinger train as described above; sample volumes ranged from 20-60 L. The amount of mercury that passed through the impingers was determined by analyzing the quantity that adsorbed to the gold during sampling. Each impinger solution was analyzed individually by reducing it with $NaBH_4$ and purging the Hg^o with argon to the amalgamation unit for subsequent analysis. The pH of the H_2O_2 impingers was adjusted to 7 with NaOH prior to the reduction step. The $KMnO_4$ solutions were neutralized with hydroxylamine hydrochloride prior to the $NaBH_4$ addition. Each reagent solution was analyzed for mercury and blank subtraction was carried out for each analysis. The mercury captured in the H_2O_2 and IPA impingers was presumed to be oxidized. The total mercury was calculated as the sum of all the individual analyses for a given sample. Chemical spikes using Hg^o vapor and $HgCl_2$ standards were used to verify the recovery of elemental and oxidized mercury, respectively, from the impinger solutions.

RESULTS

The three mercury techniques were applied to the sour and sweet syngas. These two syngas streams are virtually identical in composition except for the H_2S and moisture content. Hydrogen sulfide in the sour syngas measured about 900 ppmv compared to about 30 ppmv in the sweet syngas. The sweet syngas is virtually dry while the sour syngas, although sampled downstream of a moisture knock-out, still contained a significant amount of water. Unfortunately, both H_2S and water can have an effect on some of the methods that were used. The results [and 95% confidence intervals (95% CI)] obtained from the charcoal and CVAAS methods are compared in Tables 1 and 2.

Table 1. Mercury Measured in Sour Syngas

Method	Impingers	Hg, µg/Nm³	95% CI
Charcoal	None	11	13
CVAAS	(1) 2N NaOH/$NaBH_4$	6.1	2.1
	(2) IPA/2N NaOH/$KMnO_4$	3.2	5.2

The following observations were made during this method comparison:

- Although highly variable, the charcoal tube method reported the higher total mercury value. These values are the average of three daily measurements and do not coincide with the test period using the CVAAS technique.

- The presence of H_2S appears to have an effect on the impinger capture (or measurement) of total mercury. Case 2 results by CVAAS is lower than Case 1. During sample collection in Case 2, there was H_2S breakthrough from the NaOH scrubbing solution, which may have biased the results low for Case 2.

Table 2. Mercury Measured in Sweet Syngas

Method	Impingers	Hg, µg/Nm³	95% CI
Charcoal	None	0.1	0.02
CVAAS	(1) 0.1N NaOH/$NaBH_4$	3.8	3.6
	(2) IPA/0.1N NaOH/$KMnO_4$	3.0	3.2
	(3) H_2O_2/0.1N NaOH/$KMnO_4$	3.6	2.3
	(4) IPA/0.1N NaOH/$NaBH_4$	3.1	1.5

The following observations were made regarding this data set for sweet syngas:

- Mercury collected on charcoal, with respect to the other collection/measurement methods, is significantly lower in the sweet syngas matrix. The reason for this is unknown.

- All of the impinger combinations used in the CVAAS study produced very similar results. Comparison with the charcoal or $NaBH_4$ results in Table 1 indicates 40-70% mercury removal across the Selectamine™ process.

- Results indicated the need for an H_2S scrubber upstream of the $KMnO_4$ or $NaBH_4$ impinger.

Mercury Speciation

Test results for oxidized mercury in the syngas are presented in Table 3. Due to schedule restraints, only a limited number of speciation runs were made at the sour syngas location. Hydrogen peroxide and isopropyl alcohol solutions were used to capture oxidized mercury in the CVAAS tests while 10% HNO_3/30% H_2O_2 was used in the M-29 testing.

Table 3. Mercury Speciation in Syngas

Absorbing Solution	Sweet Syngas		Sour Syngas	
	Oxidized Hg, µg/Nm³	95% CI	Oxidized Hg, µg/Nm³	95% CI
CVAAS: H_2O_2	1.01	1.04		
CVAAS: IPA	0.52	1.5	0.97	1.12
M-29: Nitric/Peroxide	0.23	0.22	0.81	0.93

The results in Table 3 show that measurable quantities of oxidized, or ionic mercury, species are present in the syngas.

- Despite relatively high variability, all three impingers measured the presence of oxidized mercury in the syngas streams.

- The numbers listed in Table 3 represent nominally 25% of the total mercury measured in the sweet syngas.

Elemental mercury spiked to these impingers was not retained. However, it is not known which forms of oxidized mercury are effectively retained or pass through these impinger solutions.

CONCLUSIONS AND RECOMMENDATIONS

Direct CVAAS analyses performed on-site identified promising alternatives or modifications to the Method 29 approach. Future efforts at quantifying mercury in synthesis gas should consider incorporating the following recommendations and assessing the results through a comprehensive quality control program.

- An H_2S scrubbing impinger (NaOH, etc) is required upstream of any reductant impingers to eliminate matrix effects with both the impinger solution and the gold amalgam trap. Sodium hydroxide appeared to work well for this purpose without absorbing any measurable quantities of mercury.

- The Method 29 HNO_3 /H_2O_2 impinger showed the ability to absorb mercury, presumably in the oxidized form, from the syngas. The results of this testing indicate that the addition of H_2S scrubbing impingers, upstream of the $KMnO_4$ impinger, may be a suitable modification to this method to enable the collection of mercury.

- Testing of charcoal sorbents in conjunction with the direct CVAAS system could a) determine breakthrough potential of charcoal; and b) indicate if charcoal adsorption of mercury is quantitative or species dependent.

- For measuring the effectiveness of sample collection methods and providing an alternate method for quantifying total mercury in syngas, the CVAAS experimental apparatus offers several advantages: 1) near real-time analysis of mercury for immediate feedback on the effectiveness of the measurement method; and 2) the ability to measure breakthrough of mercury through impingers by using the gold trap downstream of the impinger train.

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