

available oxygen to the fuel in the DTR, resulting in significantly higher PAH to fuel ratios than in pilot or demonstration scale combustors.

3.3 Trace Elements

Title III of the Clean Air Act Amendments of 1990 designated 189 hazardous air pollutants (HAPs) (later revised to 188 HAPs). Inorganic HAPs, herein referred to as IHAPs, include the following elements: arsenic (As), beryllium (Be), cadmium (Cd), cobalt (Co), manganese (Mn), nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), and total mercury (Hg). Mercury has been of primary concern given its significant negative health effects on humans and wildlife. The United States Environmental Protection Agency (EPA) initiated an information collection request (ICR) on January 1, 1999 for coal-fired electric utility steam generating units (> 25 MW) to document mercury levels in their fuels and emissions. The issuance of an ICR generally precedes the implementation of regulatory action by the EPA.

In December 2000, the U.S. EPA decided that regulation of mercury from coal-fired power plants was appropriate and necessary under Section 112 of the Clean Air Act due to the significant health hazards it presented to the public. EPA is scheduled to propose regulation of mercury emissions by December 2003 and promulgate them by December 2004. In order to come to this determination, the accurate measurements of mercury and its speciation are necessary.

Penn State conducted three activities in Phase III addressing issues EPA and DOE identified as requiring further study. These activities included evaluating ceramic filters for mercury removal as a control option, evaluating trace elements emissions from deeply-cleaned coals produced through DOE's Premium Clean Coal Program, and developing a sampling train and methodology capable of simultaneously sampling mercury species and all inorganic trace elements. As part of the ceramic filter evaluation, a long-term demonstration of the filters was performed, similar to the one in Phase II of the project, to assess the technical feasibility of using ceramic filters in lieu of fabric filters. The results of these activities are discussed in the following sections.

3.3.1 Fine Particulate Matter/Mercury

Additional efforts in Phase III, focusing on the control of fine particulate emissions when firing coal in an industrial boiler, were added to complement the trace element testing. In Phase II, approximately 900 hours of operation were obtained using ceramic membrane filters on the demonstration boiler (Miller et al., 1999). Although their performance was evaluated in Phase II, additional work was added (in conjunction with DOE) because it was determined near the end of the Phase II demonstration that there were design problems in the system, which resulted in the inability to regenerate the filters. If ceramic filters are to be considered as a control option for fine particulate matter (and mercury capture on the fine particles), it was decided to conduct a long-term demonstration of the filters along with mercury testing. Additional ceramic filter operation was conducted to assess Corning Incorporated worked closely with Penn State to redesign the venturis and chamber. Following modifications of the chamber, Corning Incorporated donated 80 new ceramic filters for a second demonstration testing. The results from the operability assessment and effect of particle control device on trace elements emissions are presented in this section.

3.3.1.1 Ceramic Filter Testing

A near-commercial ceramic filtering system was identified in Phase II of this project, in conjunction with DOE, for installation on the demonstration boiler. The demonstration boiler system is shown in Figures 3.2.2 and 3.2.2 and described in Section 3.2.3.2. The ceramic filtering system consisted of the ceramic membrane filters, chamber to house the filters, components to regenerate the filters, structural supports, walkways, steps and ladders, ducting valves, induced draft fan, and associated controls. The ceramic filtering system was described in detail in the Phase II final report (Miller et al., 2000). Brief descriptions of the major components, including the ceramic filters and filter chamber, as they relate to their continued evaluation in Phase III, are provided in this section.

Description of Ceramic Filter System

Ceramic Filters

The membrane filters, manufactured by Corning Incorporated (Corning), were formed by coating the walls of a cellular ceramic substrate with a patented inorganic membrane. The

membrane has a nominal pore size of 0.5 μm , which provides a barrier to particle penetration into the substrate while allowing for easy cleaning during the backpulse cycle.

The substrate is extruded and baked to form a cordierite composition. It has a multitude of parallel square passageways extending from one end face to the other. Ceramic plugs are applied to alternate ends of the substrate channel passageways, preventing the straight-through passage of combustion products. During operation, particle laden flue gas flows into the open passageways at the inlet end face. Particles are collected on the membrane surface and the filtered gas passes through the wall and exits the filter via the downstream end face open passageways. Figure 3.3.1 illustrates the details of the ceramic membrane gas filter.

The ceramic membrane filters are wrapped in a ceramic fiber mat to prevent by-pass of dirty gas and mounted in metal housings to support the filters within the filter chamber. The filters are 7 inches in diameter and 15 inches in length with a filter area of approximately 2,000 square feet.

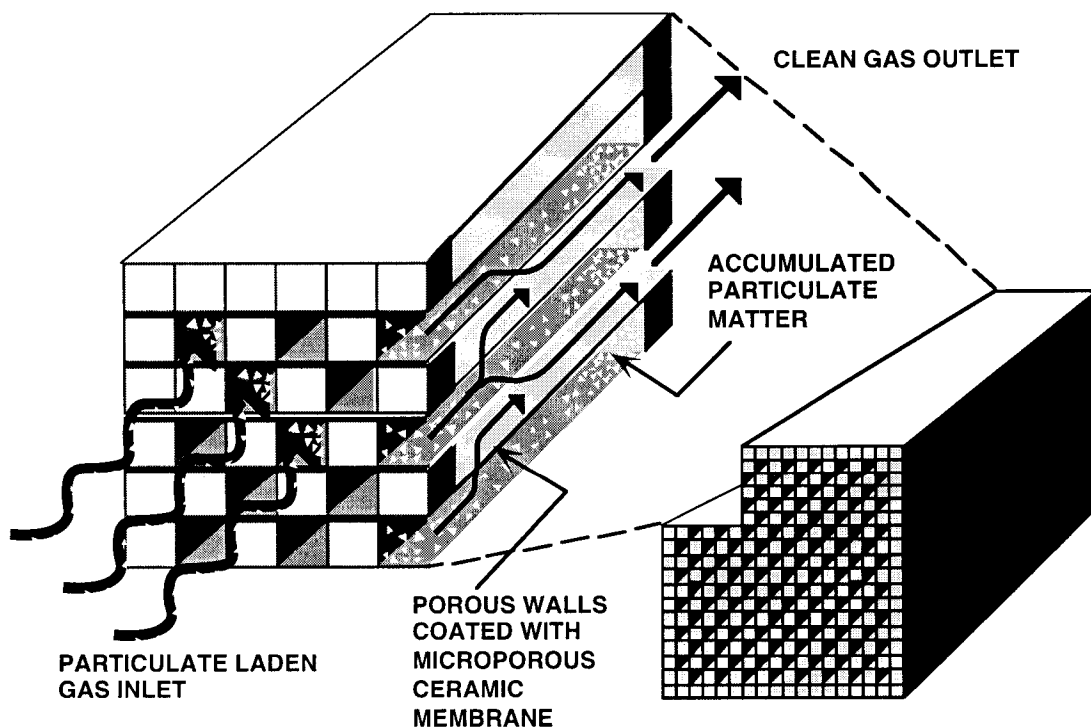


Figure 3.3.1 DETAILS OF CORNING INCORPORATED'S CERAMIC MEMBRANE GAS FILTER

Ceramic Filter Chamber

The original filter chamber was designed by Penn State with guidance from Corning, manufacturer of the ceramic filters. Installation of the main components of the system was conducted from mid-July through December 1996, with final installation, for such items as insulating the ceramic filter chamber, occurring in January and February 1997.

The chamber houses 80 filters, arranged in two groups of 40, with each group consisting of a common compressed air header for back pulsing. Figure 3.3.2 is a schematic diagram of the interior of the ceramic filter chamber showing the ceramic membrane filters with respect to the flue gas inlet and outlet. Backpulse hardware, similar to that used in pulse jet baghouses, is used to clean the filters. Each row of four filters is serviced by a single blowtube for backpulsing. The system is configured to backpulse two rows (one on each side of the chamber) of filters at a time.

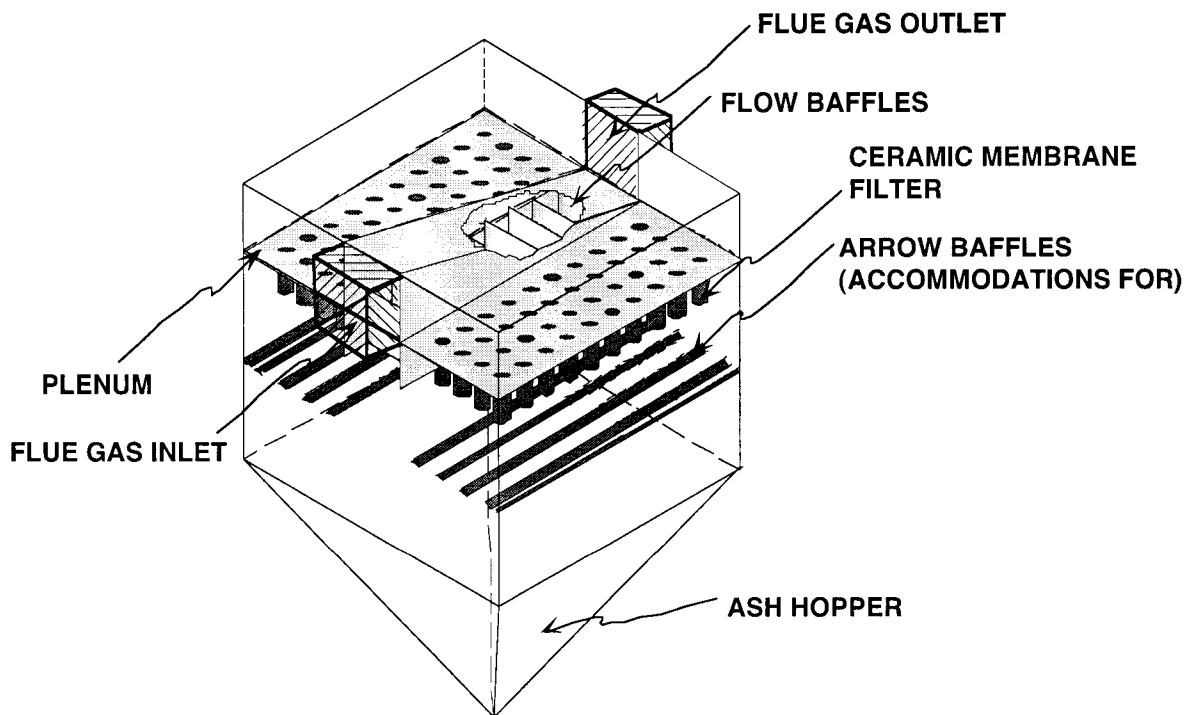


Figure 3.3.2 INTERIOR OF THE CERAMIC FILTER CHAMBER SHOWING Baffles AND CERAMIC MEMBRANE FILTERS

Modifications to the Ceramic Filter Chamber

Following the Phase II demonstration it was determined that design problems existed in the original system, which prevented regeneration of the filters. Therefore, modifications were

made to the chamber to correct these problems. The modifications included the following activities:

- Raised the roof to accommodate the new venturis, which are approximately 8 inches taller;
- Added a new roof that is rain and snow proof;
- Cleaned the tube sheet by sand blasting and then added a water-proof epoxy to the metal surfaces on the clean side of the tubesheet;
- Cleaned the compressed air headers and valve bodies;
- Replaced the venturis with new ones manufactured from 304 stainless steel;
- Replaced the blowtubes with ones constructed from 304 stainless steel;
- Replaced the filters and cans (cans are made from 304 stainless steel);
- Installed baffles in the bottom of the chamber;
- Determined, and subsequently used, an optimum regeneration protocol with the new design;
- Used an RTV seal on the roof doors, which will be used each time the chamber is closed;
- Added the capability to check face pressures on regeneration for two filters;
- Developed, and subsequently used, an optimum startup and shutdown protocol; and
- Installed sensors to measure actual flow rate into the chamber.

Ceramic Filter Operation – Second Demonstration

Following modification of the filtering system, preliminary testing of the ceramic filters was resumed in October 1999. Similar to Phase II, a number of operational parameters were monitored/ measured during the continued evaluation, including:

- Pressure drop history of the ceramic filter chamber. This included monitoring both the pressure drop across the chamber as a function of hours of firing coal as well as the pressure drop recovery (i.e., return to a baseline value). The pressure drop, when firing natural gas at 12 million (MM) Btu/h at 4% O₂ and 400 acfm of transfer air, was measured prior to firing coal at the beginning of a day of operation (normal operation consists of either one or two 8-hour shifts of operation) and after coal feed had been terminated and purged from the coal feed lines;
- Periodic checks on the filter face pressure and flow;
- Ceramic filter chamber fine particulate (i.e., PM₁₀ and PM_{2.5}) and condensable particulate matter (CPM) emissions measured by EPA Methods 201A (PM₁₀) modified to include PM_{2.5}, and 202 (CPM);
- Ceramic filter chamber fine particulate collection efficiency; and
- Comparison of particulate emissions and collection efficiency of the ceramic filter chamber and the fabric filter baghouse.

A summary of the burner settings and daily averages of the operating conditions, combustion performance, and boiler efficiencies is contained in Appendix 3A for all Phase III

demonstration boiler operation. This includes days when the fabric filter baghouse was used as well as the ceramic filter chamber.

As part of the second demonstration using the filters, Corning requested that filters be removed periodically (i.e., after 10, 70, 170 hours operation, etc.) and replaced with new ones. Corning was to perform a series of analyses on the filters, some of which were destructive. Likewise, Penn State periodically removed filters and analyzed them by nondestructive X-ray computerized tomography (CT) to: characterize the filters before and after use; evaluate the ability to map out filled channels in the filters; investigate the ability to detect erosion in the filters; and assess the topology of the end plugs.

The chamber was operated in October and November 1999 and approximately 80 hours of operation were obtained. During this time, two filters were removed for Corning at 10 and 80 hours of operation. When the chamber was opened to remove the filters, it was noted that the epoxy on the clean side of the tubesheet was discolored and a liquid residue was dripping onto the venturis and blowtubes. Samples of the material were collected and analyzed. It was found to be rich in zinc and chlorine. Further investigation found that the epoxy had a zinc base. Apparently the chlorine in the coal was reacting with the zinc-based epoxy. After discussions with Corning and the epoxy manufacturer, it was decided to remove the venturis and the filters, send the filters back to Corning for pressure drop determinations (to ensure that material was not trapped in the clean side of the filters which would negatively affect pressure drop), sandblast the upper plenum chamber to remove the remaining epoxy, add a different epoxy, and install a steam coil to keep the temperature of the upper plenum chamber above the dew point of the gases to ensure that moisture will not condense when the unit is shutdown at night. The boiler facility was being operated on a two-shift per day basis and the chamber cooled down at night.

During this investigation, another item was discovered that needed to be replaced. The boiler system has been engineered so that the entire flue gas stream leaving the boiler can be diverted to either the baghouse or ceramic filter. Isolation dampers are located at the inlet and outlet of each particulate removal device. When one particulate removal device is used, the dampers to the other device are closed. This is to ensure that all flue gas flow is being diverted to the device being tested. However, it was found upon close examination (by operating personnel crawling into the 24 inch diameter ducting), that the dampers were not zero-flow

dampers as requested during the design and construction phase of the filter chamber. Consequently, it was decided to replace the dampers with zero-flow valves.

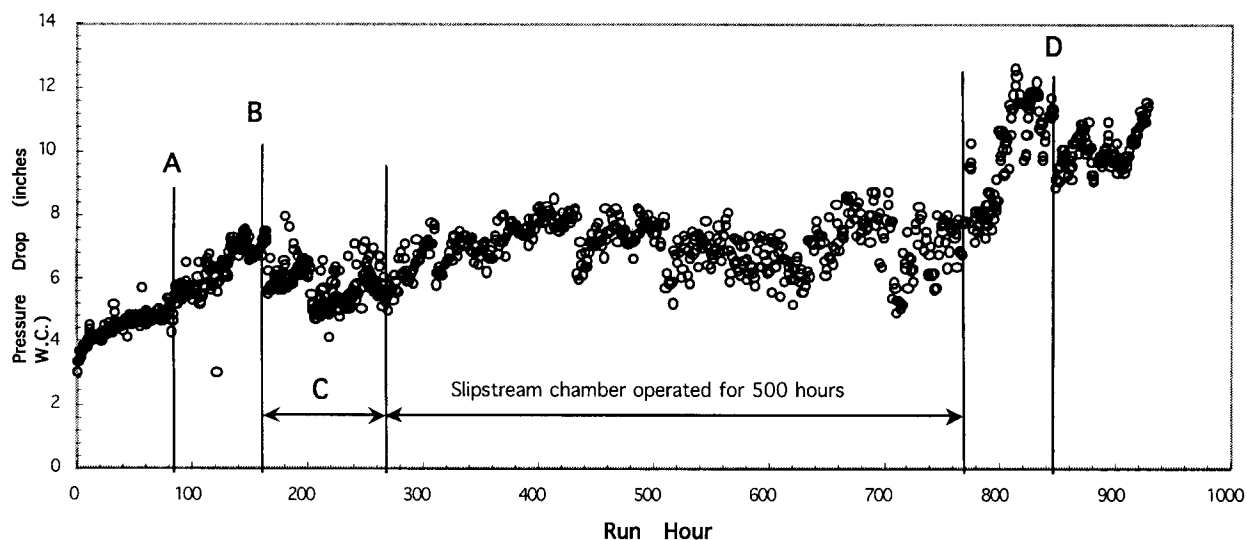
Ceramic Filter Operability

Approximately 930 hours of coal-fired operation were obtained using the ceramic filter chamber during Phase III. An important filtering system operating requirement is the ability to regenerate, i.e., clean the filters so that the pressure drop across them returns to the baseline value. During operation, the particulate matter accumulates on the membrane surface and the pressure drop increases. The ceramic membrane filter is then cleaned by backpulsing with compressed air in a manner similar to cleaning fabric filters in a pulse jet baghouse.

The pressure drop of the ceramic filter chamber was monitored as part of the system evaluation. It was recorded by both the taking of manual readings and using a computerized data acquisition system (DAS).

The typical operating procedure of the boiler begins by backpulsing each filter five times without the forced draft and induced draft fans operating. The boiler system is then preheated firing natural gas at a rate of 12 MM Btu/h until the ceramic filter chamber outlet temperature is ~300°F. The boiler is then transitioned from natural gas to firing micronized coal by reducing the quantity of natural gas in increments while simultaneously increasing the micronized coal feed. With the natural gas valve closed, the coal feed is adjusted to achieve a typical firing rate of 15 MM Btu/h. The system is allowed to stabilize then the DAS begins recording the filter pressure drop (data points are recorded every 30 seconds), while manual readings are taken every half hour. The boiler is typically operated 8 to 12 hours per day. Upon conclusion of testing, the coal feed is turned off, the coal line is purged of coal, and the natural gas rate increased until the firing rate is returned to 12 MM Btu/h. After the coal line has been purged, the natural gas is shut off and the ceramic filter chamber allowed to cool with the forced draft and induced fans running. When the chamber outlet temperature has decreased to 300°F, the fans are shut down and the backpulsing system allowed to cycle until each filter has been backpulsed at least five times.

Figure 3.3.3 is a plot of the ceramic filters' pressure drop as a function of time firing coal from October 25, 1999 through June 17, 2003. The data points are the manual readings taken



- A** Second period of modifications to chamber performed
- B** Stopped testing to re-evaluate increasing ΔP
- C** Slipstream chamber operated for 100 hours
- D** Period of 4 weeks of baghouse operation

Figure 3.3.3 CERAMIC FILTER PRESSURE DROP AS A FUNCTION OF TIME FIRING COAL (Second demonstration)

every half hour. Similar to the set of filters tested in Phase II, an initial increase in the pressure drop from ~ 3.0 to between 4.0 to 4.5 inches W.C., during the first 100 hours of operation, represents the conditioning of the filters (i.e., the approach to steady state, baseline fly ash loading on the membrane). Not all the fly ash is removed from the filters during backpulsing.

Following a second period of modifications to the ceramic filter chamber (Point A), the pressure drop continued to increase, approaching 7.5 to 8.0 inches W.C. This additional increase may be attributed to further conditioning of the filters. However, it is still below the design pressure drop of 8 to 10 inches W.C. predicted for a flow of 8,100 acfm @ 400°F. The system was designed based on a natural gas firing rate of ~ 19 MM Btu/h while the actual flue gas flow firing dry micronized coal (DMC) is approximately 5,600 acfm at 365°F. The DMC firing rate is maintained at approximately 15 MM Btu/h to reduce ash deposition in the convective pass. This lower flue gas flow rate would yield a lower pressure drop across the filters.

It should be noted that pressure drops that are significantly higher than the trend are due to operating the ceramic filters backpulse system. The backpulse system, used to remove ash from the filters' inlet surfaces, is operated at a selected frequency during boiler operation. The

frequency was varied from 15 to 45 seconds between backpulses during evaluation of this set of filters. The frequency and the duration, or length of backpulse, were occasionally varied in an attempt to improve cleaning efficiency and to lower the filters' pressure drop. When the backpulse system is operated, the additional air that is introduced into the filter chamber causes the measured pressure drop to increase several inches. Depending on when the pressure drop reading is recorded, higher than usual values can be obtained as the pressure drop is returning to its normal operating value. Greater detail of the pressure drop as a function of time firing coal is illustrated in Figures 3B-1 through 3B-19. These figures, contained in Appendix 3B, are plots of the pressure drop as a function of time firing coal for over 50 hours of operation. The use of the boiler's convective pass steam sootblower is also indicated in these figures.

A greater amount of scatter was observed in Figure 3.3.3 beginning at the 165 run hour (Point B). The primary difference between this demonstration and that performed in phase II, was that a slipstream system was installed on the demonstration boiler to evaluate ceramic filters for an industrial sponsor concurrent with the large ceramic filter chamber. Approximately 10% of the flue gas flow was removed from the boiler system at the boiler outlet, prior to entering the ceramic filter chamber, and routed to the slipstream system. At this time, 100 hours of shakedown operation were performed with 90% of the flue gas directed through the baghouse. A second 100-hour shakedown period was then conducted, Period C, but at this time the ceramic filter chamber was used to filter 90% of the flue gas. To ensure that the filter area (i.e., air-to-cloth ratio) of the ceramic filter chamber was consistent with the first demonstration and the first 165 hours of operation of the second demonstration, 10% of the ceramic filters (i.e., 8 filters) were removed. Testing that was conducted from Run Hour 165 to 770 was performed in this manner. The scatter in the data appear to be strongly influenced by the simultaneous operation of the slipstream system.

Another variable encountered during the second demonstration was varying coal ash content. Typically, the coal ash is maintained at 4.5 to 6 wt.% since this is a natural gas/ fuel oil-designed boiler retrofitted to fire coal-based fuels. However, the coal received during this testing contained ash contents ranging from approximately 3.5 to 10 wt.%. The coal company had laid out the coal in their coal yard to dry it (upon receiving it from the mine) and inadvertently picked up dirt prior to stockpiling the coal for Penn State. Consequently, the ash content fluctuated greatly from day-to-day during the latter part of this demonstration. The significant increase in

the pressure drop observed following testing of the slipstream system is believed to be a result of the higher coal ash contents. Changes in the backpulse frequency and duration were not able to maintain the pressure drop at the levels observed prior to the increase in the coal ash percent.

The loss of the filter's ceramic membrane coating on the inlet side, discussed in the following section, may also be a contributor to the filter's increased pressure drop. The loss of the membrane coating would allow the ash particles to penetrate the substrate pores, possibly preventing passage of the flue gas, thus increasing the overall pressure drop of the filters.

The pressure drops observed with the second set of filters from Corning were similar to those observed in the Phase II of the program (i.e., first demonstration). In Phase II, the pressure drop varied from 6-9 inches W.C., with much of the data between 7-8 inches W.C. for the first 700 hours of operation (excluding the filter conditioning during the first \approx 150 hours). The pressure drops then increased in two increments, 9-10 inches W.C. and 13-15 inches W.C., when problems arose with moisture infiltration. The pressure drops during the first 800 hours of the Phase III operation (Figure 3.3.3) varied between 6-9 inches W.C. and then increased to 10-12 inches W.C., which appears to be due to the loss of the membranes and capture of fine particles in the pore structure. This is a ceramic membrane design/manufacturing issue.

Filter Evaluation by Nondestructive X-Ray Computerized Tomography

Each new filter, following its manufacturing, was evaluated by Corning, Inc. using several measurement techniques. These measurements included the determination of pressure drop at relevant face velocities and testing for cracks using powdered graphite and alumina. A select sampling of the filters was removed during the first 770 hours of testing at time intervals chosen by Corning and returned to them for further examination. This examination included the physical cross-sectioning of filters, measurement of the depth of ash retained within the filter cells, and the examination of the cell walls by scanning electron microscope.

To support these diagnostic measurements and to gain a better understanding of factors affecting the filter's performance, an additional twelve filters were purchased from Corning. Five of these filters were scanned by a medical X-ray scanner in the Center for Quantitative Imaging at Penn State's Energy Institute. This nondestructive technique permits an internal examination of not only a filter's construction, but also how exposure to the flue gas affects a

filter's performance (i.e., map out the degree of channel filling and detect any erosion within the filter).

A Universal System's model HD250 computerized tomography scanner (CT scanner) was used to examine the filters. This is a fourth generation medical system that takes a single slice in one rotation. The filters were supported in a sample chuck mounted on the patient table for scanning. The CT scanner, with a filter centered within the scanning aperture, is shown in Figure 3.3.4.

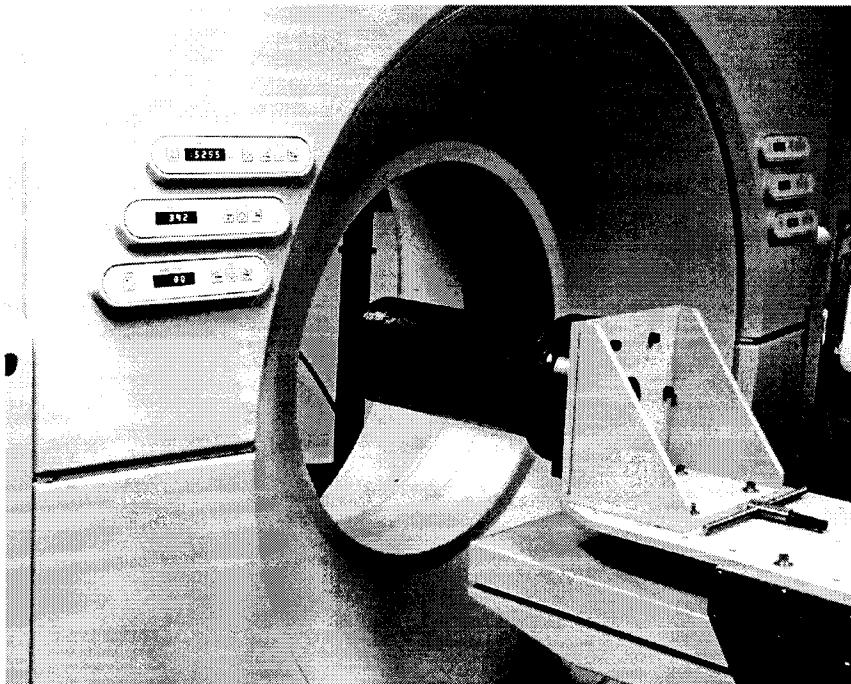


Figure 3.3.4 HD250 CT SCANNER WITH A FILTER SUPPORTED WITHIN THE SCANNING APERTURE

CT scanning passes X-rays through the filter. The X-rays are absorbed or attenuated (weakened) at differing levels by the filter creating a matrix or profile of X-ray beams of different strength. A set of detectors, mounted on the opposite side of the aperture from the X-ray tube or source, measures this profile. A computer then reconstructs the "raw CT data" into an image.

Each filter manufactured by Corning is canned in a shell made of 316 stainless steel. There was initial concern that this shell would interfere with the X-ray beam. However, the metal resulted in a sharpening of the beam producing a relatively clear image.

The HD250 CT scanner has a maximum energy level of 130kV at 125 mA. An energy level of 130 kV and 65 mA was used to scan the ceramic filters.

A baseline scanning was performed on each of the five new filters. This included a coarse scanning sequence performed over the filter's length using a 2 mm scan thickness and a 20 mm spacing between scans. This was followed with a more detailed scanning of the filter's inlet and outlet using a 2 mm scan thickness and spacing.

A digital radiograph was produced for each filter as part of the scanning sequences. The radiograph for filter #8122 is shown in Figure 3.3.5. The radiographs produced from the nondestructive technique of CT scanning provide details of the filter's internal structure. The extruded cell walls, inlet and outlet plugs, filter matting, and exterior metal shell are visible in the radiograph.

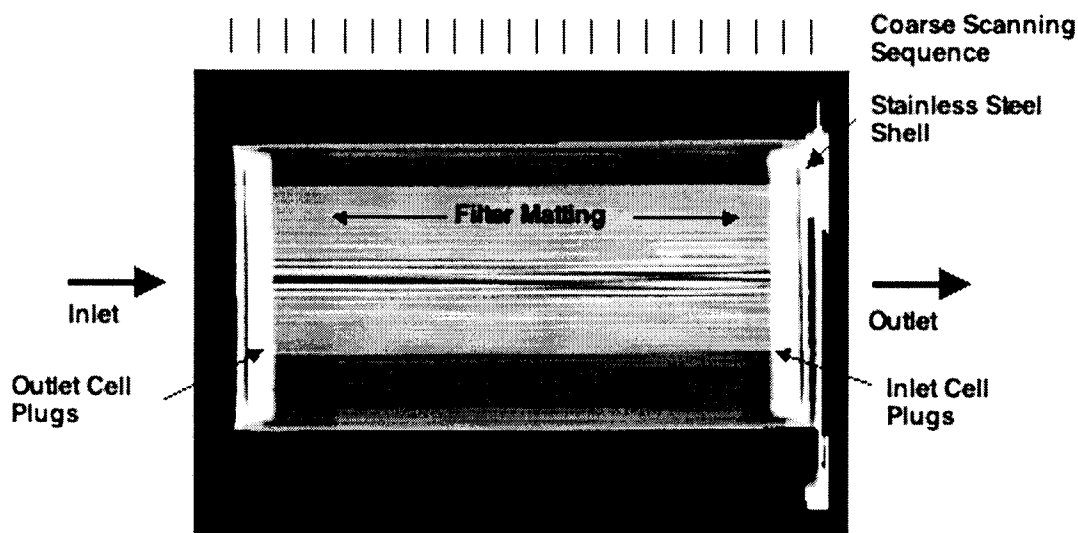


Figure 3.3.5 A DIGITAL RADIOGRAPH OF FILTER #8122

A series of CT slices (CT range: -1000 to 2000) produced for both the inlet and outlet of filter #8122 are shown in Figures 3.3.6 and 3.3.7, respectively. An examination of these series shows that the inlet and outlet plugs are approximately 12-14 mm in length. Cells that were found to leak during quality control testing were sealed on the inlet and outlet ends. These patches are visible as breaks in the alternating open and closed pattern within the cells.

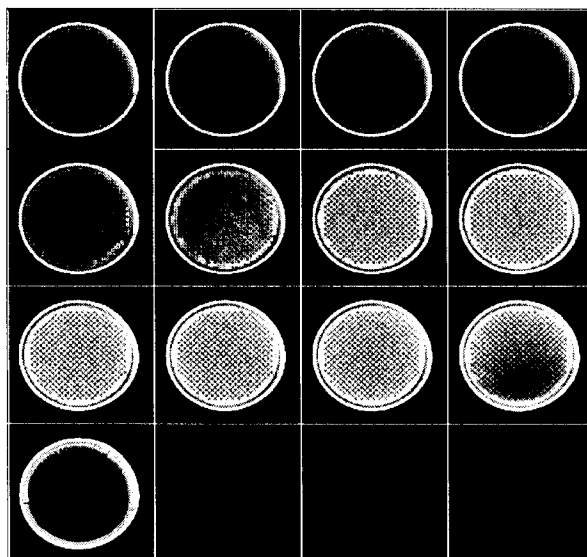


Figure 3.3.6 CT SCANS (2mm scan thickness and spacing) FOR THE INLET OF FILTER #8122 – CT Range: -1000 to 2000 (Scans progress from left to right starting at top left corner)

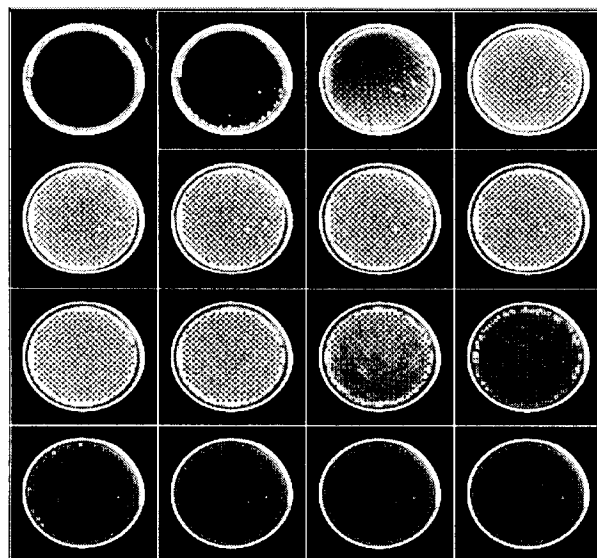


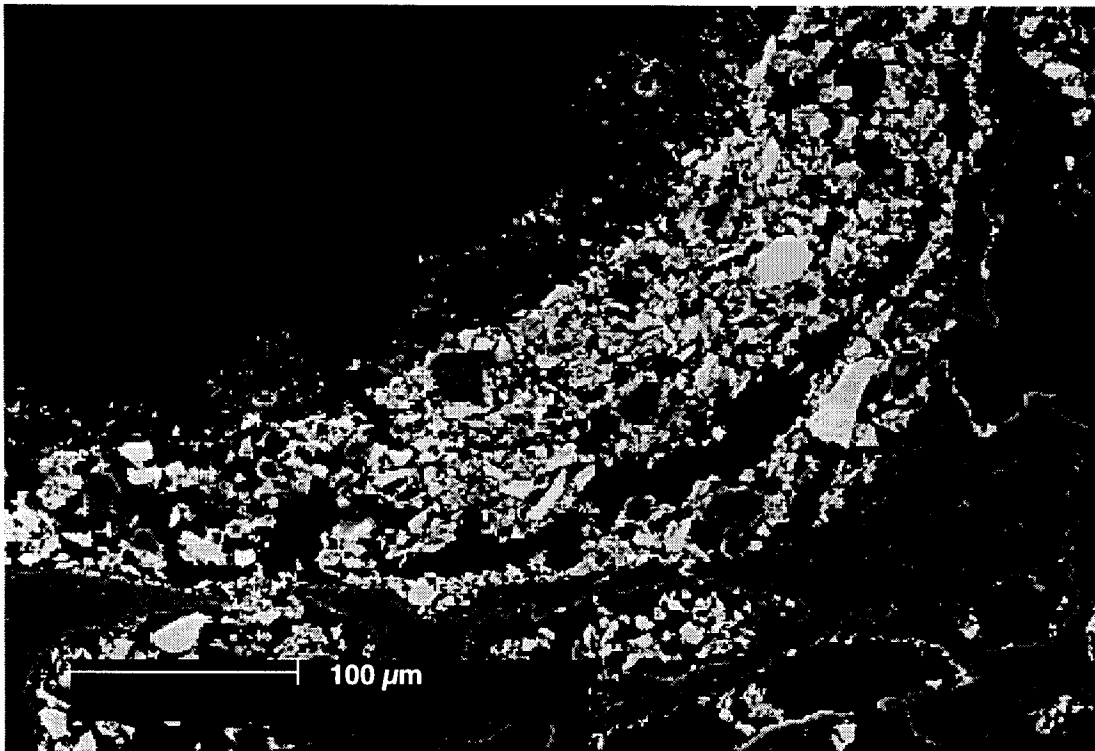
Figure 3.3.7 CT SCANS (2mm scan thickness and spacing) FOR THE OUTLET OF FILTER #8122 – CT Range: -1000 to 2000 (Scans progress from left to right starting at top left corner)

Following the baseline scanning, the five filters were installed on March 10, 2000 in the ceramic filter chamber and exposed to the ash laden flue gas produced from coal-fired operation of the boiler. The existing filters within the chamber had been exposed to approximately 80 hours of coal-fired operation prior to the installation of the five “CT” filters. The five filters were then removed following selected time intervals of operation. Corning had also chosen time intervals during which additional filters would be exchanged and those removed sent back to Corning for follow up diagnostic testing. To minimize the number of times the ceramic filter chamber would be opened, time intervals were chosen to correspond approximately to time intervals selected by Corning for the removal of filters. A summary of the filter exchange schedule including those exchanged or removed for Corning is given in Table 3.3.1.

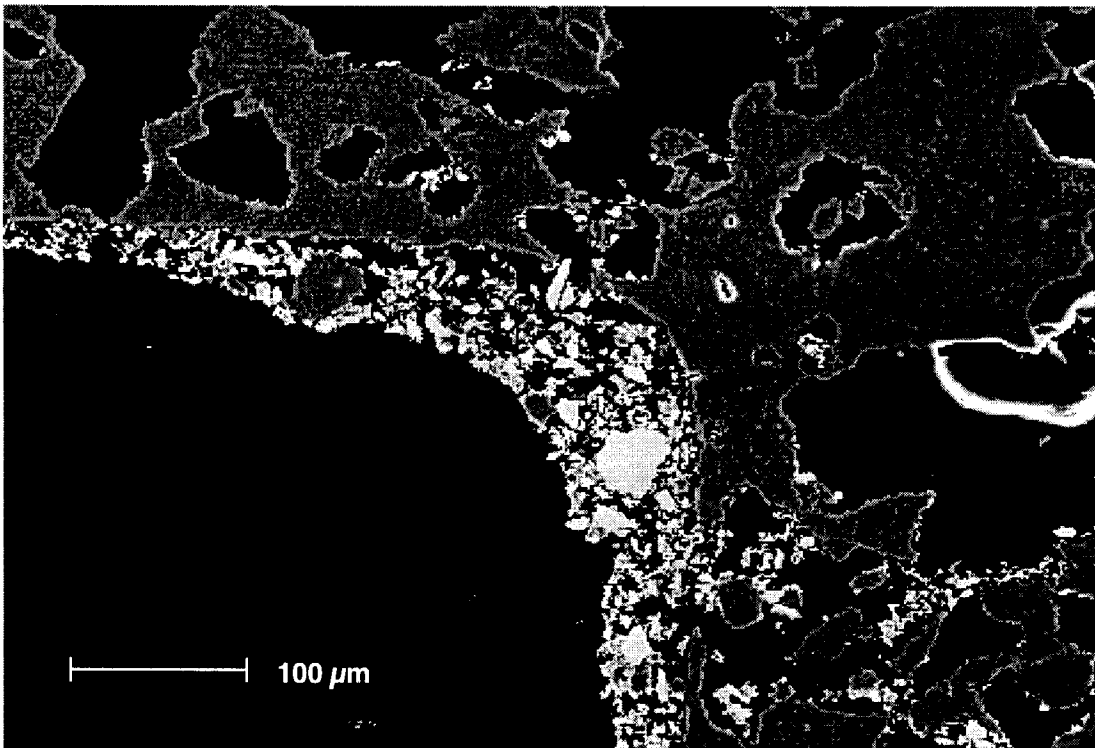
Table 3.3.1 Filter Exchange Schedule

Date	Total Hours of Operation	Filters Exchanged	
		For Corning	For PSU (Filter Number)
9/28/99	0	Initial set of 80 filters installed	
10/26/99	10	2	0
11/04/99	70	2	0
3/10/00	80	0	5 PSU filters installed
3/16/00	92	0	1 – (#8125)
4/20/00	165	8 filters blanked off for slip-stream testing	
6/13/00	165	5	1 – (#8122)
7/28/00	270	5	1 – (#8112)
9/11/00	510	0	1 – (#8114)
9/25/00	705	2	0
10/30/00	770	3	1 – (#8115)

The filters used in the chamber and evaluated by the CT scanner consist of a cordierite porous substrate with two membrane coatings on the inlet (dirty side) and one membrane coating on the outlet cell (clean side). Filter #8112 was sectioned, plugs were made from filter pieces from outlet end, middle, and inlet end of the filter, scanning electron microscope (SEM) photomicrographs were taken to compare to the CT scanner results. The one membrane coating on the clean side and the two membrane coatings on the dirty side, along with an ash layer on the membrane coatings in the inlet cell, can be seen in Figure 3.3.8.



(a)



(b)

Figure 3.3.8 SEM PHOTOGRAPH OF THE OUTLET END OF FILTER #8112 (a-Inlet Cell; b-Outlet Cell)

On April 20, 2000 eight filters were removed from the ceramic filter chamber and their openings blanked off. This was done in preparation for the beginning of testing using a slipstream system installed on the demonstration boiler system, which is part of a separately funded project and not reported herein. During operation of the slipstream system, approximately 10% of the total flue gas flow was diverted from the large ceramic filter chamber to a slipstream chamber that houses ceramic filters. To maintain an air/cloth ratio that was consistent with the previous testing on the large chamber, 10% of the filters (i.e., eight filters) were removed from the large chamber. This was done in order to accumulate relevant data on the large chamber while operating the slipstream system.

Following exposure to the flue gas, each removed filter was scanned in the same manner and orientation in the scanner as the baseline condition (i.e., virgin filter prior to installation in the chamber). All five of the Penn State filters were removed and rescanned. The comparison results are discussed here

A detailed comparison of the filter inlet CT scans before and after use indicated a loss of material within the inlet cells. This effect can be seen in the Figure 3.3.9 where slightly larger, darker areas represent larger openings within the inlet cells. Comparison of the filter outlet CT scans, however, showed an increase in the material detected within the inlet cells. This increase can be attributed to the retention of ash within the cells at the filter's outlet.

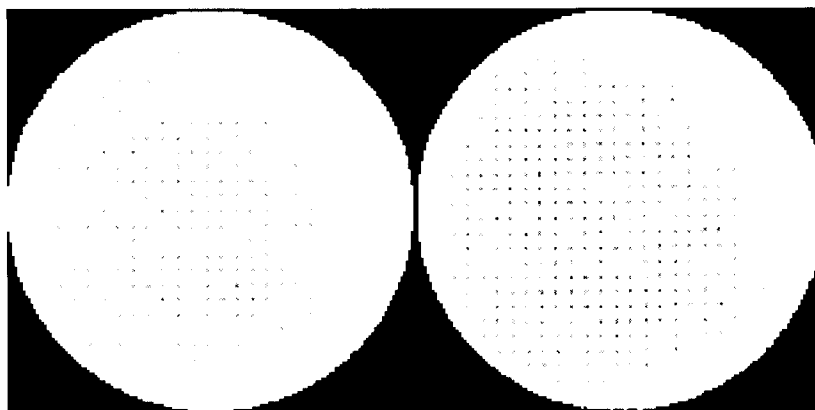


Figure 3.3.9 COMPARISON INLET CT SCANS OF FILTER #8122 BEFORE (Left Scan) AND AFTER USE (Right scan) (Note that scans were conducted at same location along filter length)

The loss of material at the filter's inlet is due to a loss of the membrane coatings on the dirty side of the inlet cells, which appears to be caused by erosion from the ash particles during backpulsing. The above observations are also evident in Figure 3.3.10 where an average CT number is plotted as a function of location in filter #8122 for the coarse CT scans. A greater CT number indicates an increase in filter material, while a drop in CT number indicates material loss. The ceramic plugs closing off inlet or outlet cells cause the large increases at either end of the plot.

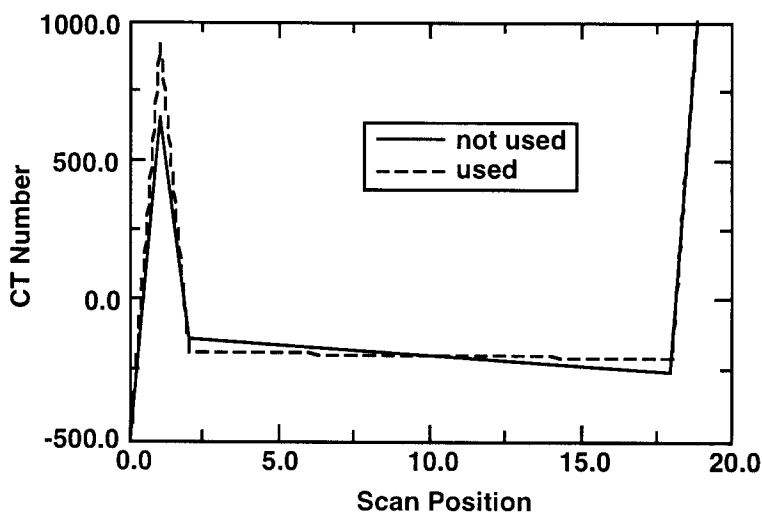


Figure 3.3.10 AVERAGE CT NUMBER AS A FUNCTION OF LOCATION IN THE FILTER (Zero represents filter inlet, scan spacing is 2 cm)

The above observations are also evident in Figures 3.3.11 and 3.3.12, which are SEM photomicrographs of the middle and inlet end of filter #8112, respectively. Figure 3.3.11 shows that the membrane coating in a dirty side (inlet) cell is still retained in the corners but has been eroded from the wall. Figure 3.3.12, on the other hand, shows that all of the membrane coating in the dirty side (inlet) cells has been removed. The sequence of photomicrographs shows that the membrane coating in the dirty side cells is progressively removed as one transits from the outlet end of the filter to the inlet end. As Figure 3.2.8 shows, there are no signs of erosion on the outlet end of the filter. One possible cause for the erosion is the high backpulse pressure utilized. This was done to maximize backpulse effectiveness.

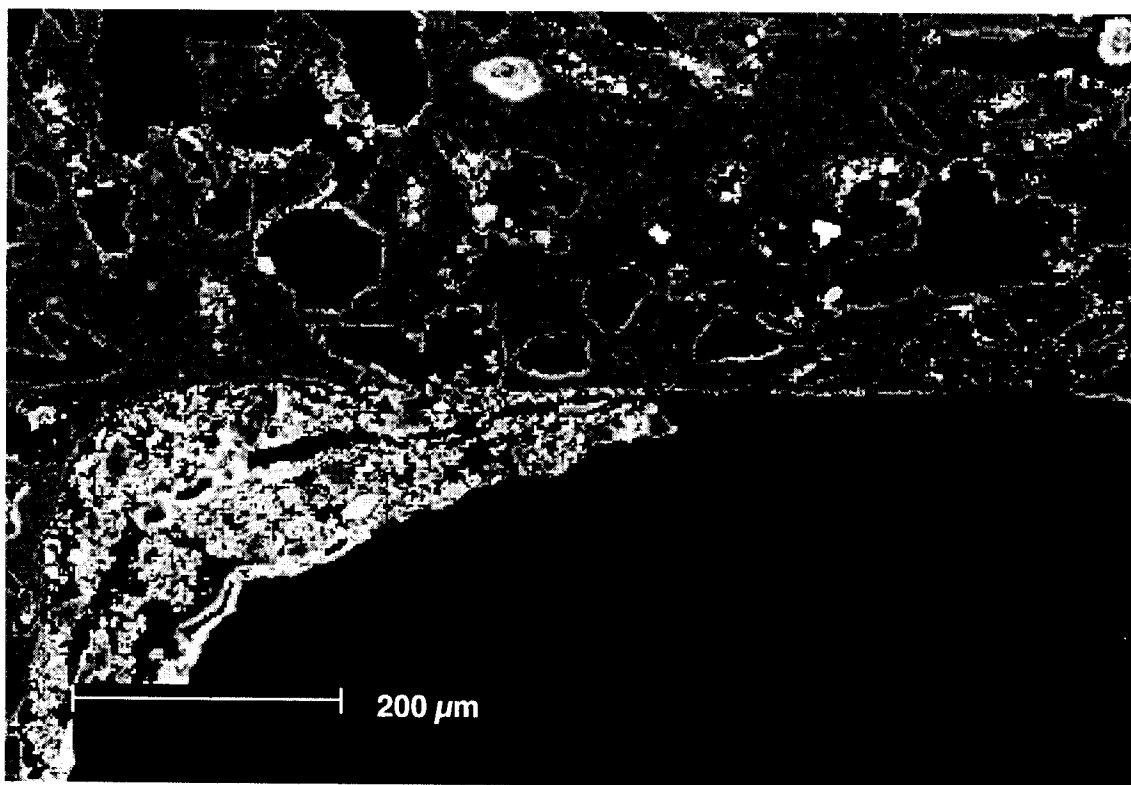


Figure 3.3.11 SEM PHOTOMICROGRAPH OF A DIRTY CELL (Inlet Cell) IN THE MIDDLE OF FILTER #8112

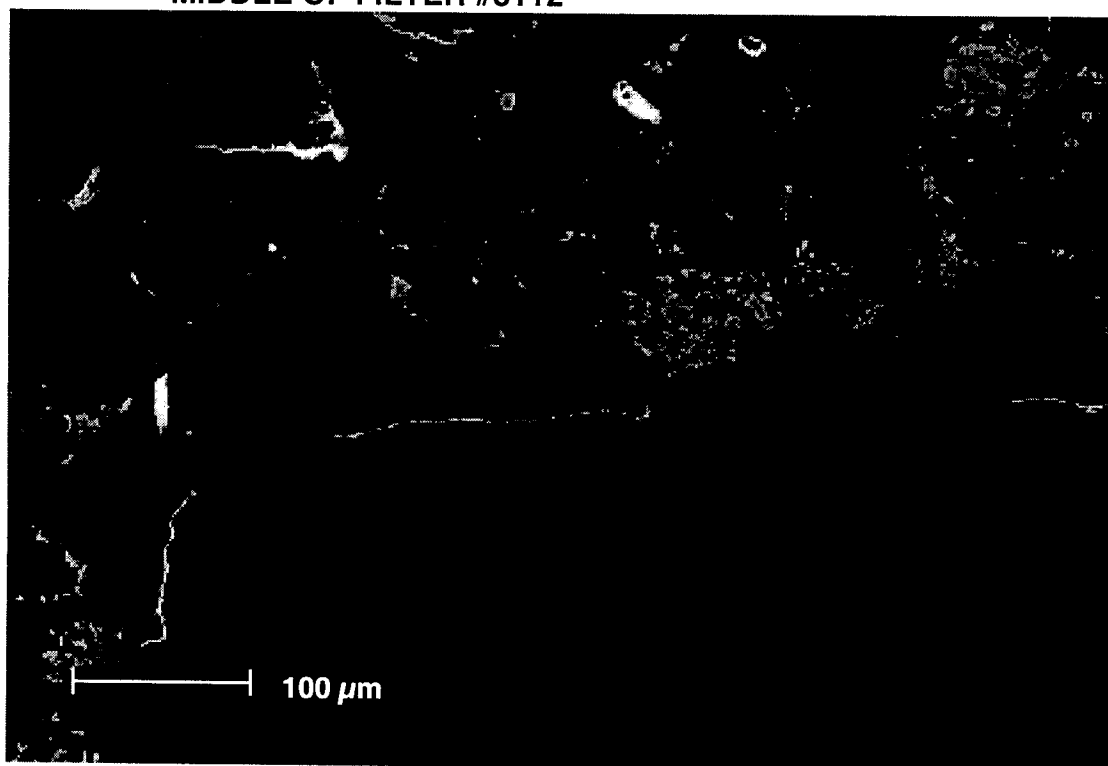


Figure 3.3.12 SEM PHOTOMICROGRAPH OF A DIRTY CELL (Inlet Cell) IN THE INLET END OF FILTER #8112

The loss of the filter's membrane coatings on the inlet cells allows the ash particles to penetrate into the substrate pores, resulting in an increased pressure drop across the filter. The average inlet CT number, as shown in Table 3.3.2, decreased dramatically for filter #8125 and then slowly for filters run for longer durations suggesting that the erosion occurred early on. It is not possible to quantify the amount of membrane lost throughout the filter's length because some ash is retained, especially at the outlet end. An increasing CT number with greater hours of operation suggests that additional ash is being retained at the outlet end of the filters. The phenomenon of ash filling the pores is verified in Figure 3.3.12 and also in Table 3.3.3.

Table 3.3.2 Change in the Average Inlet/Outlet CT Number as a Function of Hours of Operation

Filter Number	Hours of Operation	Change in Average CT Number	
		Inlet	Outlet
8125	12	-30	+19
8122	85	-36	+38
8112	190	-36	+51
8114	430	NM	NM
8115	690	NM	NM

Table 3.3.3 Bench-Top Filter Pressure Testing

Filter Number	Hours of Operation	Initial ΔP (in. W.C.)			Final ΔP (in. W.C.)		
		3 ft/min	4 ft/min	5 ft/min	3 ft/min	4 ft/min	5 ft/min
8125	12	2.1	2.9	3.6	5.1	7.0	8.9
8122	85	2.0	2.8	3.5	9.0	12.8	15.7
8112	190	2.1	3.0	3.8	7.1	9.9	12.4
8114	430	2.2	3.3	4.3	11.9	NA ^a	NA
8115	690	2.2	2.9	3.6	9.4	13.5	NA

^aNA-Not able to achieve set point for that flow.

In summary, through repeated scans, the CT scanning technique for examining filters has proven to be consistent and reproducible. It provides a nondestructive method to examine a filter's structure with a relatively high degree of accuracy. This technique also provides added information on factors affecting a ceramic filter's performance.

Stack Particulate Emissions and Ceramic Membrane Filter Collection Efficiency

Similar to the measurements performed in Phase II on the initial set of ceramic membrane filters, EPA Modified Method 201A (modified to include PM_{2.5}) particulate emissions tests were conducted to determine the dust loadings and collection efficiency for the second set of filters when firing micronized coal. The combined results for both sets of filters are shown in Table 3.3.4. The Modified Method 201A collection efficiency measured for the second set of filters ranged from 99.80 to 99.85%, indicating their performance in removing particulate matter from the flue gas was approximately that of the initial set of filters.

Also evident in Table 3.3.4 is that the particulate emissions from the ceramic membrane filters have met the Pennsylvania Department of Environmental Protection's permitted level of 0.1 lb/MM Btu, the New Source Performance Standards (NSPS) of 0.03 lb/MM Btu, and the LEBS target of 0.01 lb/MM Btu. The emissions, however, exceed the HIPPS target of 0.003 lb/MM Btu. An objective of the project was to meet the HIPPS target, however, the current design of the ceramic membrane filter evaluated has not been unable to accomplish this during the final phase of testing

Comparison of Particulate Emissions between the Ceramic Filter Chamber and Baghouse. The stack particulate emissions from the fabric filter baghouse were not measured in Phase III, however, a comparison with those measured on January 20, 1998 (Phase II) indicate a significantly lower collection efficiency was observed for the fabric filter baghouse while firing the Middle Kittanning Seam DMC. The combustion efficiency for the four tests Method 201A tests performed on the ceramic filter chamber (0502/2001, 06/12/2001, 05/15/2003, and 06/17/2003) ranged from 96.5 to 97.0%, with an average of 96.7%. Although the combustion efficiency for the baghouse test was slightly lower, 96.4%, the inlet particulate emissions were not higher than those measured for the ceramic filter chamber. Thus, an increased level of particulate within the inlet did not cause the lower collection efficiency for the fabric filter. The baghouse collection efficiency of 99.17% is the lowest efficiency obtained in all of the micronized coal testing.

Fine Particulate and Condensable Particulate Matter Emissions. The Modified EPA Method 201A provides information on the nature of the fine particulate emissions from the

Table 3.3.4. Particulate Emissions as Measured by EPA Methods 5 and Modified 201A (fly ash) when Firing Middle Kittanning Seam DMC. The Ceramic Filter Chamber was the Particulate Collection Device used Except where Noted

DATE	Inlet			Outlet			Collection Eff. (%)	Combustion Eff. (%)
	gr/dscf	lb/MM Btu	g/Nm ³	gr/dscf	lb/MM Btu	g/Nm ³		
Method 5 Sampling								
07/09/97	2.2791	4.0845	5.2148	0.0056	0.0101	0.0128	99.77 ^a	94.8
07/21/97	2.4609	4.2990	5.6308					92.4
07/24/97	1.6707	3.3096	3.8227					93.2
09/03/97	1.6654	3.3343	3.8106	0.0028	0.0060	0.0064	99.83	97.6
09/08/97	1.2621	2.7982	2.8878	0.0025	0.0053	0.0057	99.80	97.7
09/12/97	1.7068	3.3650	3.9053	0.0024	0.0053	0.0055	99.86 ^b	98.0
09/22/97	2.2223	4.3580	5.0848					96.0
09/23/97	1.9750	3.9139	4.5190	0.0045	0.0088	0.0103	99.80	97.6
11/05/97				0.0050	0.0105	0.0114	99.75	Not Measured
11/18/97								96.1
Method 201A Sampling								
11/25/97				0.0037	0.0071	0.0085		96.4
12/04/97				0.0037	0.0072	0.0085		96.5
12/09/97	1.6364	3.3442	3.7442	0.0038	0.0073	0.0087	99.77	97.1
12/11/97	1.2436	2.4624	2.8455					97.4
12/22/97	1.7584	3.4878	4.0234					97.0
01/15/98	3.8487	7.4084	8.8062	0.0048	0.0095	0.0110	99.88	92.2
02/17/98	1.6194	3.1838	3.7053	0.0053	0.0105	0.0121	99.67	97.0
02/19/98	2.3802	4.7504	5.4461	0.0044	0.0089	0.0101	99.82	97.1
05/02/01	2.3777	5.2713	5.4404	0.0042	0.0089	0.0096	99.80	97.0
06/12/01	2.2141	4.3277	5.0661	0.0045	0.0096	0.0103	99.80	96.6
05/15/03	2.8531	5.8943	6.5282	0.0041	0.0108	0.0096	99.86	96.6
06/17/03	2.0665	4.4428	4.7281	0.0039	0.0090	0.0096	99.81	96.5
01/20/98 (BH) ^c	1.5420	3.3491	3.5283	0.0126	0.0263	0.0288	99.17	96.4

^a Collection efficiency was determined using inlet results from 07/09/97.

^b Collection efficiency was determined using inlet results from 09/23/97.

^c This test was performed on the fabric filter baghouse when firing Brookville seam MCWM to obtain an operating permit from the Pennsylvania Department of Environmental Protection. The emissions cannot exceed 0.1 lb/MM Btu

↑
Phase II
Phase III
↓

ceramic membrane filters. The particulate is separated into three size fractions during sampling. These fractions are reported in Table 3.3.5 as $> 10 \mu\text{m}$ (initial cyclone), 2.5 to $10 \mu\text{m}$ (second cyclone), $<2.5 \mu\text{m}$ (filter paper). An EPA Method 202 (condensable particulate matter (CPM)) stack test was performed with each Modified Method 201A and the results are also given in Table 3.3.5. Similar levels of particulate emissions were measured for the ceramic membrane filter inlet. Similar to the Phase II testing, the largest portion of the fine particulate emissions was found in the $>10 \mu\text{m}$ and 2.5 to $10 \mu\text{m}$ fractions with the $>10 \mu\text{m}$ fraction being slightly greater than the 2.5 to $10 \mu\text{m}$ fraction. The smallest fraction was contained in the CPM with the $<2.5 \mu\text{m}$ fraction being slightly larger.

The outlet ash concentrations from the ceramic filter chamber measured prior to 2003 exhibited similar trends in that the $>10 \mu\text{m}$ and 2.5 to $10 \mu\text{m}$ fractions were nearly identical and were approximately twice that of the $<2.5 \mu\text{m}$ fraction. However, a significant decrease in the 2.5 to $10 \mu\text{m}$ fraction was measured during tests performed in 2003. The reason for this change in the particle size distribution at the outlet of the ceramic filter chamber is not known. However, the overall collection efficiency remained unchanged and was similar to that measured for the initial set of ceramic membrane filters evaluated in Phase II. There is continued variability within the CPM concentrations with this fraction being the largest measured at the outlet of the ceramic filter chamber. The Modified Method 201A and 202 results are provided in Figures 3.3.13 and 3.3.14 in increasing order of combustion efficiency. No trends in the results as a function of combustion efficiency were observed.

Fine Particulate Penetration of the Particulate Devices. The percent of each fraction that penetrated the ceramic membrane filters when burning DMC is shown in Figure 3.3.15. Similar to the results observed for the first demonstration, the CPM fraction had the greatest penetration. Also, the 2.5 to $10 \mu\text{m}$ fraction is the second largest fraction that is emitted from the collection device.

Concluding Remarks

In Phase III modifications were performed to the ceramic membrane filter chamber, a new set of ceramic membrane filters was installed, and their performance evaluated and

Table 3.3.5 Fine Particulate Emissions for the Ceramic Membrane Filter Chamber, as Determined by EPA Methods 201A (modified) and 202, when Firing Middle Kittanning Seam DMC

Date:	11/25/97	12/4/97	12/9/97	12/11/97	12/22/97	1/15/98	2/17/98	2/19/98	01/20/98 (BH) ^a	05/01/01	06/12/01	5/15/03	6/17/03
Inlet Part.													
Concen. (gr/dscf)													
> 10 µm	0.6784	0.6888	0.8863	2.3592	0.7132	0.9979	0.6282	1.1463	0.9445	1.7160	1.2005		
2.5-10 µm	0.6001	0.4459	0.7058	0.6668	0.7430	0.8676	0.4907	0.7930	0.9322	0.9629	0.7395		
< 2.5 µm	0.3579	0.1089	0.1663	0.8227	0.1632	0.5148	0.4051	0.4384	0.3374	0.1742	0.1265		
total ash	1.6364	1.2436	1.7584	3.8487	1.6194	2.3803	1.5240	2.3777	2.2141	2.8531	2.0665		
CPM ^b	0.0418	0.1635	0.0019	0.0600	0.0092	0.0050	0.0382	0.0348	0.0074 ^d	0.0201	0.1396		
total fine part.	1.6782	1.4071	1.7603	3.9087	1.6286	2.3853	1.5622	2.4125	2.2215	2.8732	2.2061		
Outlet Part.													
Concen. (gr/dscf)													
> 10 µm	0.0017	0.0016	0.0015	0.0019	0.0021	0.0018	0.0054	0.0015	0.0019	0.0020	0.0018		
2.5-10 µm	0.0014	0.0014	0.0016	0.0017	0.0024	0.0018	0.0043	0.0016	0.0018	0.0009	0.0003		
< 2.5 µm	0.0006	0.0007	0.0007	0.0012	0.0008	0.0008	0.0029	0.0011	0.0008	0.0012	0.0018		
total ash	0.0037	0.0037	0.0038	0.0048	0.0053	0.0044	0.0126	0.0042	0.0045	0.0041	0.0039		
CPM	0.0009	0.0019	0.0051	0.0044	0.0022	0.0011	0.0066	0.0076	0.0070	0.0022	0.0184		
total fine part.	0.0046	0.0056	0.0089	0.0092	0.0075	0.0055	0.0192	0.0118	0.0115	0.0063	0.0223		
Collection													
Eff. (%)	99.77	99.77	99.88	99.88	99.67	99.82	99.17	99.80	99.80	99.86	99.81		
Combustion													
Eff. (%)	96.4	96.5	97.1	97.4	97.0	97.1	96.4	97.0	96.6	96.6	96.5		
SO₂ (ppm)	502	451	517	508	494	483	497	417	442	465	476		
NO_x (ppm)	373	318	308	425	425	435	418	611	623	581	527		
O₂ (%)	3.2	3.2	3.2	3.0	3.0	3.5	3.6	3.8	3.4	3.3	3.5		

^a Baghouse

^b Condensable particulate matter

^c Collection efficiencies do not include CPM

^d This value is suspect

← Phase II Phase III →

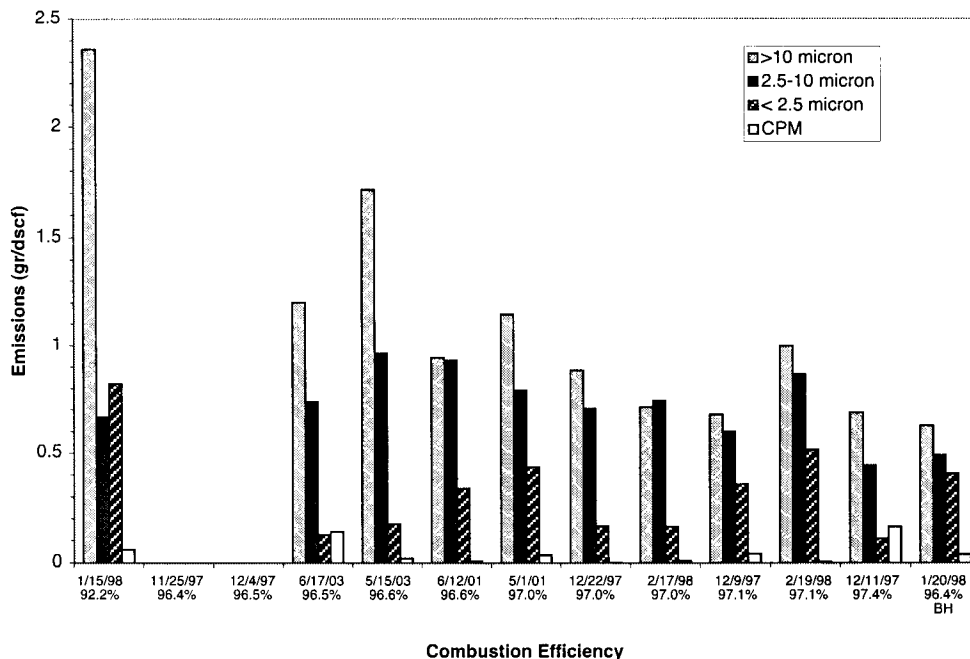


Figure 3.3.13 INLET FINE PARTICULATE EMISSIONS FROM THE CERAMIC MEMBRANE FILTER CHAMBER WHEN FIRING MIDDLE KITTANNING SEAM DMC COAL

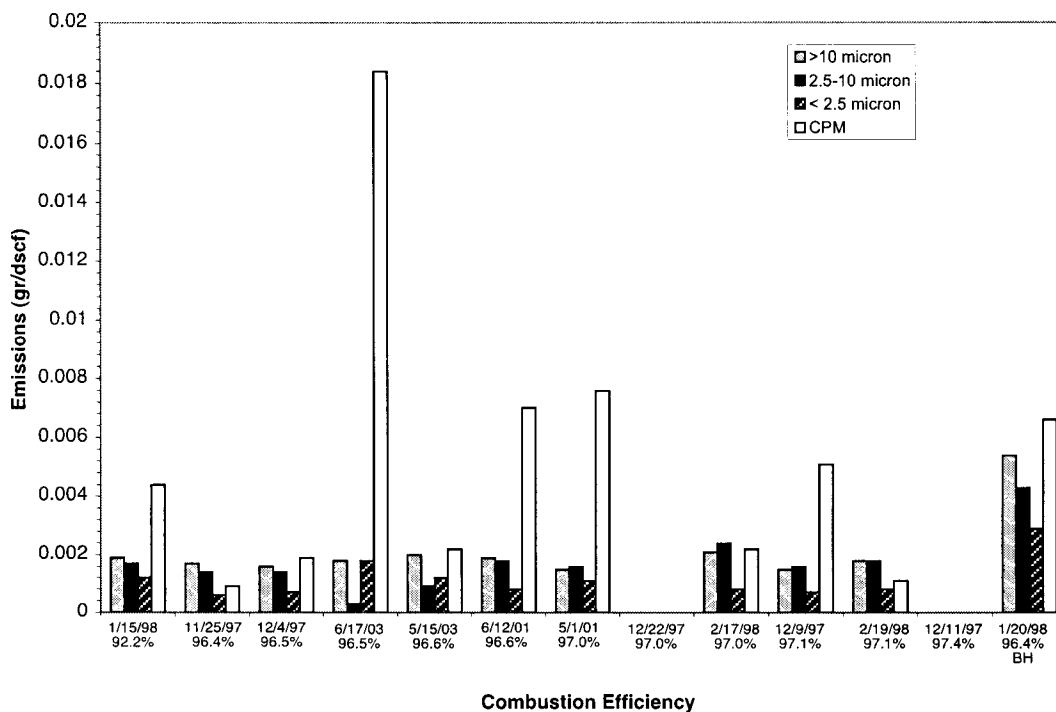


Figure 3.3.14 OUTLET FINE PARTICULATE EMISSIONS FROM THE CERAMIC MEMBRANE FILTER CHAMBER WHEN FIRING MIDDLE KITTANNING SEAM DMC COAL

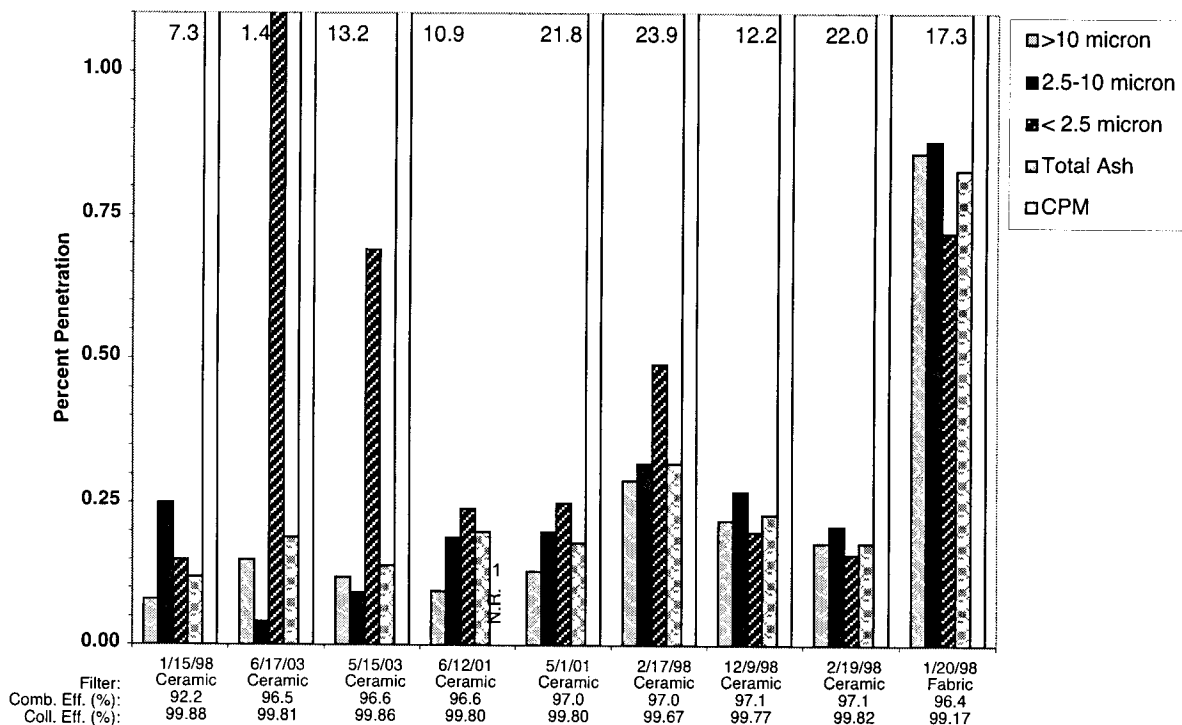


Figure 3.3.15 PERCENT OF EACH FINE PARTICULATE FRACTION THAT PENETRATES COLLECTION DEVICE

compared with DOE emissions targets and the performance of a fabric filter baghouse outfitted with high-performance bags. Specifically:

- The ceramic membrane filter system was operated for ~930 hours;
- The filters were regenerable through backpulsing with compressed air; however, the pressure drop continued to increase. The increase is believed to be due to higher ash percents in the feed coal and plugging of the substrate pores following loss of the membrane;
- The pressure drop data for Phase III were similar to those observed during Phase II, both of which were nearly 1,000 hours in length. The elevated pressure drop data for both demonstrations indicate that this is a ceramic membrane design/manufacturing issue and not operator induced. This is a concern for commercialization in a boiler setting and needs to be addressed by the manufacturer;

- The ceramic membrane filter particulate collection efficiencies ranged from 99.80 to 99.86% when firing Middle Kittanning seam DMC, which were higher than that observed when using the pulse-jet baghouse; and
- The stack particulate emissions are below Pennsylvania DEP's permit conditions (0.1 lb/MM Btu), the NSPS (0.03 lb/MM Btu), and DOE's LEBS target (0.01 lb/MM Btu), and approach DOE's HIPPS target (0.003 lb/MM Btu).

3.3.1.2 Effect of Particle Control Device on Trace Elements Emissions

The objective of this activity was to observe the effect of particulate control device (PCD), specifically baghouse and ceramic membrane filter, on trace element emissions. Trace element emission testing was performed in conjunction with DMC combustion tests conducted at the demonstration boiler, which are described in Section 5.4.1. These tests were performed as part of the study of the particulate capture characteristics and capacity of the ceramic membrane filters and fabric filters during combustion of a micronized Middle Kittanning seam coal.

As reported in the previous section (3.3.1.1), the fine particulate concentration to the baghouse was similar to that entering the ceramic filter chamber in previous tests. The emissions from the baghouse, however, were much greater than from the ceramic membrane filter. The collection efficiency of the baghouse was 99.2% compared to 99.67 to 99.88% for the ceramic filter chamber. The particulate emissions from the baghouse test were triple those from the ceramic filter chamber for similar combustion efficiencies. The combustion efficiency during the baghouse test was 96.4%, which is identical to the ceramic filter chamber tests.

The outlet ash concentrations from the ceramic filter chamber exhibited similar trends in that the >10 and 2.5 to 10 μm fractions were nearly identical and were approximately twice that of the <2.5 μm fraction. The condensable particulate material (CPM) concentrations were more variable and, in some cases, were the largest fractions. At the outlet of the baghouse the CPM fraction is by far the largest fraction that is emitted. With one exception, the 2.5 to 10 μm fraction is the next largest fraction that is emitted from the collection devices. Each size fraction emitted from the baghouse was greater than that emitted from the ceramic filter, with the exception of the CPM. In general, the ceramic membrane filter had greater capture efficiency and removed a greater percentage of fines than the fabric filter. The capture surface area of the two PCDs was approximately equal (2,000 sq. ft). A detailed discussion of the particulate

emissions and performance of the two PCDs is given in Section 3.3.1.1 and by Miller et al. (1998, 1999).

Duplicate inlet and outlet tests were performed on each particulate collection device, i.e., ceramic membrane filter chamber and baghouse. EPA Method 29 (Code of Federal Regulations 1996) was used to determine trace element concentrations. Method 29 was used since the evaluation of the unified sampling train/methodology (PSU Method), which is described in Section 3.3.3 was not yet completed. Extensive testing has shown that EPA Method 29 may not speciate mercury correctly; however, it may still be used to measure total mercury (EPRI 1996, 1997). Mercury is completely volatilized during coal combustion and forms elemental mercury (Hg^0) and may form mercury chloride (HgCl_2), mercuric oxide (HgO) and other mercury species as the flue gas cools. Due to their high vapor pressure, these species will remain in the gas phase unless they interact with a solid that traps the mercury through sorption. Currently numerous carbon- and noncarbon-based solid sorbents are being investigated as to their ability to react with gas phase mercury species. The potential of carbon-based sorbents for mercury capture is based on early observations that mercury species were removed from the gas phase via sorption onto the carbonaceous portion of char present in the gas stream and PCD. The effectiveness of different chars to remove mercury from the gas stream is not consistent even under similar combustion conditions and gas compositions. In general, the physical characteristics (e.g., surface area, porosity and permeability, particle size) of the char (carbonaceous and inorganic component) as well as the amount of residual carbon determine its effectiveness. Also important is the contact time between the sorbent, as a suspended particle in the gas stream or as a captured particle in the PCD.

The Energy and Environmental Research Center at The University of North Dakota investigated sorbent injection for mercury control in coal-fired boilers (Dunham et al. 1998). They investigated the effect of PCDs, i.e., pulse-jet baghouse, ESP and a compact hybrid particulate collector (COHPAC), on mercury emissions as determined by Method 29. They observed that for two subbituminous coals there was some inherent mercury capture even by fly ash having an LOI less than 1%. Some of this capture is due to the cooling of the stack gas to allow for some condensation of certain trace elements. They also note that total mercury and removal across a baghouse decreases as baghouse temperature increases. The percent removal of total mercury ranged from 81% at 250°F to approximately 10% at 400°F for an Absaloka coal

Interestingly a Blacksville coal showed only an 18% to 10% removal of mercury in the same temperature range. Dunham et al. (1998) showed that a lignite-based activated carbon removed over 80% of the total mercury at temperatures at or below 250°F. At 300°F, vapor-phase removal of mercury was reduced to 70, 50, and 0% for the Comanche, Absaloka, and Blacksville coals, respectively. Their results show that there is considerable variation in the effectiveness of a lignite-based activated carbon due to temperature and coal type. In addition, mercury speciation is affected by temperature.

It should be stated that temperature effects were not an issue in this study as the temperature in the ceramic and bag filters was approximately 400°F. Based on the work by Dunham et al. (1998), a PCD temperature of 400°F would represent a worst-case scenario with regards to the percent mercury removal across the PCDs. In addition, the capture surface areas of the two PCDs were approximately equal at 2,000 ft². Given that the particle size distribution of the captured fly ash and efficiency of removal of the two PCDs differ suggests the possibility that inherent capture of mercury and other trace elements might also differ.

Test Results

Trace Elements Excluding Mercury

The percent penetration for the more volatile elements through the two PCDs during the duplicate test is shown in Figure 3.3.16. The concentration of trace elements in the coal and emissions measured are given in Table 3.3.6. In general, the baghouse removed approximately 94.7 to 99.1% of all the trace elements excluding mercury. The ceramic membrane filter removed 97.3 to 99.7% of the trace elements excluding mercury. The ceramic filter accounted for an additional 45 to 61% reduction in emissions of the trace elements. This corresponds to removal levels observed by Dunham et al. (1998), in which greater efficiency of removal leads to a corresponding greater removal of trace elements associated with particulate capture. Variation in the percent penetration of selenium measured during the duplicate tests through the ceramic filter was greater than that measured through the baghouse but is not considered significant. There was good agreement between the duplicate tests based on the demonstrated reproducibility of Method 29.

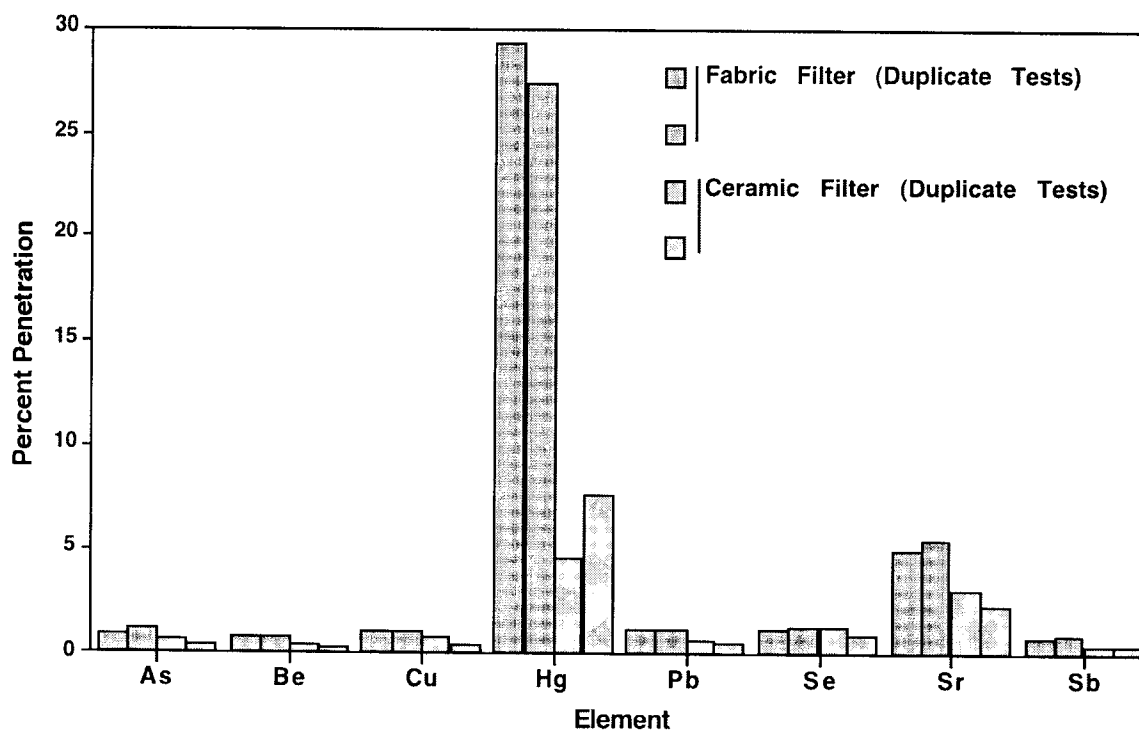


Figure 3.3.16 PERCENT FILTER PENETRATION OF SELECTED TRACE ELEMENTS FOR THE MIDDLE KITTANNING COAL (FABRIC FILTER VS. CERAMIC FILTER)

Table 3.3.6 Middle Kittanning Coal Analysis and Trace Element Emissions as a Function of PCD

Element	Coal mg/g	<i>Outlet Emissions</i> (10 ¹² Btu/lb)			
		Fabric Filter 1	Fabric Filter 2	Ceramic Filter 1	Ceramic Filter 2
As	2.43	1.51	2.12	0.94	1.08
Be	4.02	1.36	1.52	0.54	0.45
Cu	15.08	5.65	6.51	3.72	2.98
Hg	0.033	0.56	0.56	0.07	0.17
Pb	8.03	2.34	2.94	1.52	1.68
Se	1.33	0.70	0.99	0.74	0.82
Sr	27.16	10.83	9.89	3.63	4.09
Sb	4.59	1.39	1.91	0.64	0.82

Mercury Emissions

Duplicate inlet and outlet tests were performed on each particulate collection device, i.e., ceramic membrane filter chamber and baghouse, and the results for total mercury are shown in Figure 3.3.17. The inlet concentration of mercury, for the duplicate baghouse tests, was 1.90 and 2.06 lb/10¹² (trillion) Btu while the inlet concentration of mercury, for the duplicate ceramic filter tests, was 1.54 and 2.14 lb/10¹² Btu. The concentration of mercury in the outlet of the filters was 0.56 and 0.56 lb/10¹² Btu for the baghouse and 0.07 and 0.16 lb/10¹² Btu for the ceramic filter. A total of 2.38 lbs/10¹² Btu of mercury was present in the coal. The fabric filters retained 70.5 to 72.8% of the mercury that entered the baghouse. The ceramic membrane filters retained 92.3 to 95.3% of the mercury that entered the PCD. Overall, mercury emissions from the ceramic filter were 79% lower than those measured at the baghouse outlet.

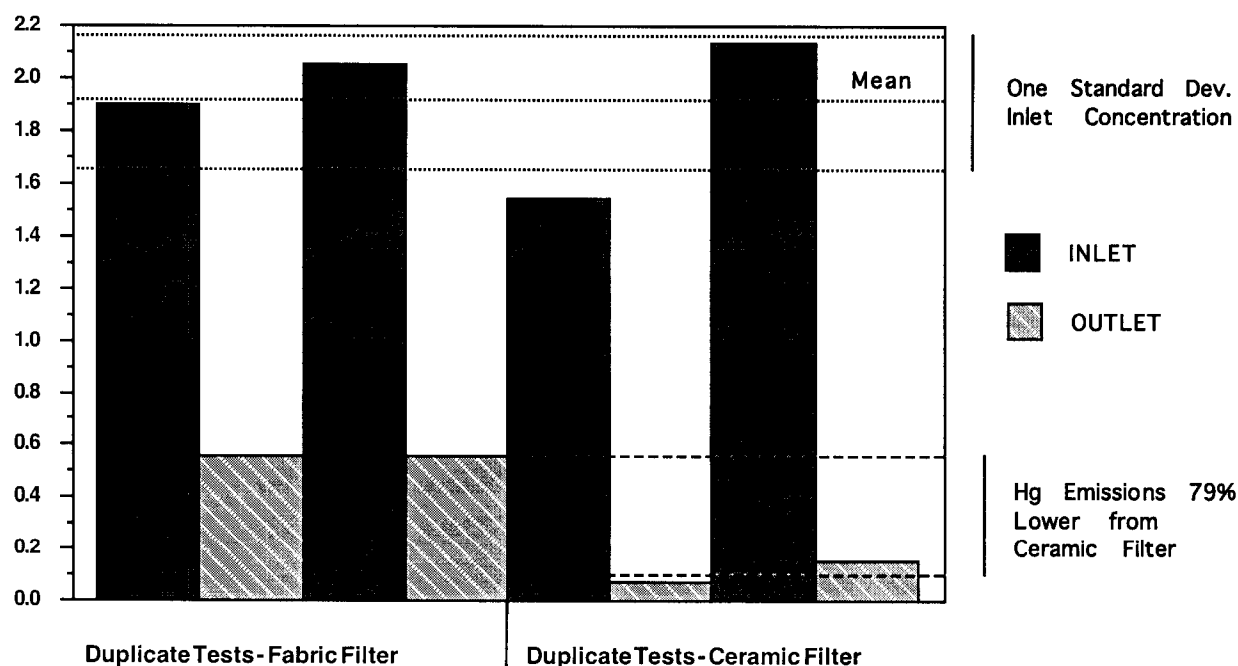


Figure 3.3.17 MERCURY EMISSIONS FROM THE DEMONSTRATION BOILER WHEN FIRING MIDDLE KITTANNING SEAM MICRONIZED COAL

Checks were done on the reproducibility of the sampling and analyses. In addition, closure on the material balances across the filters and system was calculated. Assuming that the inlet mercury concentrations are identical for the four tests, one standard deviation of the mean

was determined and is shown in Figure 3.3.17 along with the mean inlet mercury concentration (1.91 lb/10¹² Btu). This was done as a check on reproducibility and shows that it was good as three of the four inlets are within one standard deviation while one of the ceramic filter inlets is only slightly lower than one standard deviation. The material balances on mercury through the system and across the filters were also very good. Ash samples were collected every half hour from the ceramic filter chamber or baghouse during the testing. A composite was made for each test and analyzed for mercury (as well as the other inorganic trace elements). Filter balances, defined as

$$(Hg_i - Hg_o) / Hg_a$$

where Hg_i = flue gas inlet mercury

Hg_o = flue gas outlet mercury

Hg_a = mercury in the ash collected by the filtering devices

had closures of 1.05 and 1.10 for the baghouse and 0.95 and 0.98 for the ceramic filter. A value of 1.00 would be perfect closure. Similarly, the system balance, defined as

$$((Hg_{fuel} - Hg_i) + Hg_a + Hg_o) / Hg_{fuel}$$

where Hg_{fuel} = mercury in the fuel

had closures of 0.92 and 0.87 for the baghouse and 1.08 and 1.03 for the ceramic filter. This is quite good for total mercury using Method 29.

The percent of the mercury that penetrated the particulate collection devices is shown in Figure 3.3.18. Approximately 30% of the mercury that entered the baghouse was emitted to the atmosphere, whereas less than 10% of the mercury entering the ceramic filter was emitted. Since the ceramic filter captures more of the fine particulate, it is likely that the mercury is condensed on the fine particles.

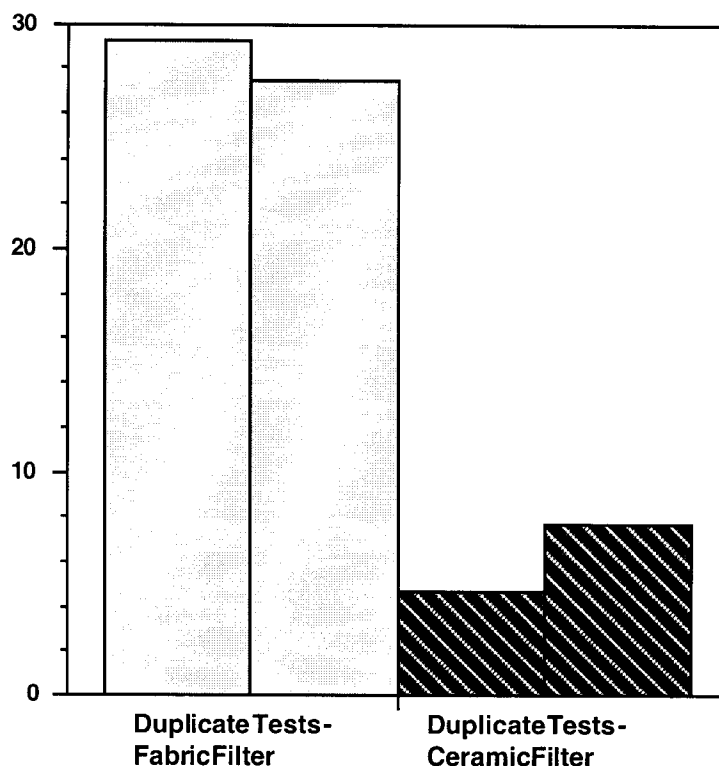


Figure 3.3.18 PERCENT MERCURY PENETRATION THROUGH THE FABRIC AND CERAMIC FILTERS WHEN FIRING MIDDLE KITTANNING SEAM MICRONIZED COAL

Conclusions

The ceramic membrane filters were not only more efficient in removing particulate matter but also in reducing trace elements in the stack gas. Total mercury emissions were reduced by 95%, as compared to 77.8% through the system via the ceramic filter and fabric filter, respectively. Refractory or less volatile trace elements are generally associated with particulate matter; therefore, their concentration would decrease in the stack gas as particulate removal increases. However, more volatile elements such as mercury and arsenic and selenium, to a lesser degree, are generally present in the gas phase. Their removal relies on the interaction of the gas phase species with other phases in the char. Given that measurements were made at the PCD inlet and outlet, the data represent reductions that occurred as a result of interactions between the gas and solid phases in the PCDs.

Both devices operated at approximately 400°F and had the approximately the same capture surface area (2,000 ft²). The average burnout for the duplicate tests for the fabric filter

and ceramic filter were essentially the same at 94.6%. This translates to the char having an ash content of $\approx 40\%$ or a carbon content of $\approx 60\%$ (which is a significant amount of carbon). Combustion efficiency is determined using the ash tracer technique discussed in Section 3.2.9.1. The only variable that differed between the tests that has been shown to impact the interaction of unburned carbon, acting as an activated carbon, with gas phase mercury is the reactive surface area of the char. The extent of sorption is a function of the amount of reactive surface area available. The fact that the ceramic membrane filter captures a greater percentage of fine particulate, as well as the fine particles being imbedded in the filters' pores, could result in a greater amount of reactive surface area than in the fabric filter. In addition, there has been speculation that gas phase species may react with the inorganic portion of the char (Dunham et al. 1998). Speciation measurements were not conducted at this time (due to lack of consensus of methodology in the literature at the time of testing).

The data are compelling and the duplicate runs show good agreement. The ceramic membrane filter effectively removed 79% more mercury from the gas phase than the fabric filter even at elevated temperature. The performance of the ceramic membrane filter is a promising environmental technology for both particulate and gas phase mercury emission control provided the high pressure drop issue can be resolved.

3.3.2 Effect of Coal Cleaning on Trace Element Emissions

The objective of this activity was to investigate the effect of coal cleaning on trace elements emissions using several coals provided by Cyprus-AMAX Research & Development Center and CQ Inc. The cleaned coals were produced via projects funded under the U.S. Department of Energy's Premium Fuel Program. For this work, filter cakes produced by AMAX from cleaned coal from the Taggart seam (Virginia) and Hiawatha seam (Utah) and Pittsburgh coal cleaned by CQ Inc. were used. The AMAX coals were cleaned using advanced column flotation and oil agglomeration to produce a filter cake. Elemental analysis of the parent coal and filter cake and the corresponding stack gas and fly ash was used to determine the percent penetration of various trace elements through the system. Of interest is whether extensive cleaning of the coals results in a benefit in reducing trace element emissions. The AMAX fuels were fired as MCWMs.

3.3.2.1 Background

AMAX Fuels

The AMAX cleaned fuels were produced as part of a Department of Energy funded study titled "Engineering Development of Advanced Physical Fine Coal Cleaning for Premium Fuel Application" (DOE Contract No. DE-AC22-92PC92208) conducted by AMAX Research and Development Center from October 1992 to September 1997 (Jha et al. 1997). The objective of the project was the engineering development of two advanced physical fine coal cleaning processes, column flotation and selective agglomeration, for premium fuel applications. The project included laboratory research and bench-scale testing on six coals and the design, construction and operation of a 2 t/h process development unit (PDU). The secondary objective of the project was to determine the removal of toxic trace elements during fine coal cleaning. Depending upon the coal, AMAX reported that advanced coal cleaning reduced the concentrations of toxic trace elements such as mercury and could be a part of a strategy to control hazardous air pollutants. A detail discussion of the cleaning technologies, flotation and agglomeration studies, and the physical characteristics of the filter cake produced are presented in the project final report by Jha et al. (1997).

According to Jha et al. (1997), the residual amounts of trace elements in the clean coals after cleaning were dependent upon the source coal. Generally, when prepared from the same coal, the advanced flotation and selective agglomeration clean coal contained about the same amounts of trace elements. The residual mercury and selenium analyses were interesting. Mercury was not detected (<0.01 ppm) in some clean coal samples and ranged up to 0.03 ppm in other samples.

There were substantial reductions (25-76%) in the concentration of ash, arsenic and manganese (lb/MM Btu) from the amount in the as-received test coals. There was little or no reduction (<25% or negative) in the amounts of antimony, beryllium, cobalt, nickel, and selenium in the as-received coal on the same basis. Little or no reduction in the concentration of an impurity means that the impurity is associated with the carbonaceous components of the coal. A substantial reduction signifies an association with the mineral matter in the coal. The reduction of other impurities, such as total sulfur, pyritic sulfur, cadmium, chromium, mercury, lead and chlorine varied from coal to coal.

According to Jha et al. (1997), the fine coal cleaning was effective for reducing the lb/MM Btu concentration of mercury in the Taggart coal by 39%. Since the Hiawatha coal contained less mercury to begin with, coal cleaning had less impact upon the final concentration of the mercury in the cleaned product.

The authors concluded that the two cleaning processes appeared to be equally effective for reducing the concentrations of impurities in the coal and were equally effective for cleaning coal to premium fuel specifications. However, for certain coals, cleaning resulted in substantially reducing the concentrations of some of the hazardous air pollutant trace elements, especially arsenic, chromium, cobalt, manganese, mercury, selenium and chlorine. Analysis of the filter cake at Penn State, reported on an lb/MM Btu basis, shows that the Taggart Oil Agglomeration fuel had approximately four times as much mercury as the Taggart Column Flotation fuel.

The AMAX project did not have a combustion test component to verify if the cleaned coals would produce reduced levels of trace element emissions as a function of the cleaning process. Significant quantities of cleaned coal were produced during the project, which could be used for pilot- or demonstration-scale testing. Penn State acquired several of the filter cakes produced during the AMAX project for this purpose. The filter cakes were used to formulate MCWMs, which were tested in Penn State's research and demonstration boilers.

CQ Inc. Fuels

CQ Inc. provided Penn State with coal from the Pittsburgh, Middle Kittanning, and Freeport (hvA bituminous coal) seams (Pennsylvania), which had been cleaned using a combination of heavy media cyclones, water spirals, and froth flotation. The Freeport and Kittanning coals were studied and reported on in the Phase II Final Report (Miller et al., 2000).

The Freeport seam parent and cleaned coals were fired as pulverized coal in the 500,000 Btu/h down-fired combustor described in Section 3.1.1. In general, coal cleaning was seen to have a beneficial effect on reducing the concentration of trace element emissions during combustion of the Freeport seam.

The Middle Kittanning seam coal was used to study the effect of fuel form on trace element emissions. Approximately 250 gallons of highly loaded MCWM were prepared from the Middle Kittanning seam parent coal. The Middle Kittanning DMC and MCWM were fired

in Penn State's research boiler. The boiler is a 1,000 lb saturated (@200 psig) steam/h watertube package boiler of A-frame construction, which was designed and built by Cleaver Brooks.

Coal cleaning was found to have a beneficial effect on reducing the concentration of trace element emissions during combustion of the Freeport coal. All of the trace elements in the flue gas from the clean coal were present at levels between 38 to 81% less than in the raw coal flue gas. The level of depletion of As, B, Cr, Hg, Mn, Pb, V, and Zn concentrations in the flue gas from the clean coal versus the raw coal was similar to that seen between the original fuels. The mercury concentration in the flue gas from the clean coal was 38% less than in that from the raw coal. This corresponds to the 32% depletion of mercury in the clean coal due to the cleaning process. Elements that were enriched in the clean coal, i.e., Ba, Be, Cd, and Se, were present in lower concentrations in the flue gas from the clean coal than in the flue gas from the raw coal.

Fuel form, i.e. DMC versus MCWM, was found to have little effect on emission levels during combustion of the Middle Kittanning seam coal. In general, the partitioning behavior of the elements during combustion of the Middle Kittanning seam coal was consistent with earlier tests conducted at Penn State and reported in the literature. All of the trace elements were depleted in the stack gas by 71.4 to 99.9% during DMC and MCWM combustion. There was no significant difference in the percent of penetration by most of the trace elements during combustion of the DMC and MCWM, however, the percent penetration by mercury and boron did vary between the two fuels. The partitioning of elements for both fuels was more of a function of their occurrence, i.e., mineral versus organic, in the fuel than the form in which they were fired. The formation of large agglomerates may have resulted in enhanced volatility of certain elements contributing to increased concentrations in submicron ash particles or the gas phase. Further details can be found in Miller et al. (1998, 2000).

In Phase III, the Pittsburgh seam coal was studied to determine the effects of coal cleaning on emissions using the PSU Method sample train during several replicate tests. The results are discussed in Section 3.3.3.

3.3.2.2 Analysis of AMAX Fuels

Four fuels were tested in this work. The Taggart seam (Virginia) and Hiawatha seam (Utah) filter cakes were produced using AMAX's PDU that was developed as part of the original DOE funded project. The PDU was an integrated 2 ton process that contained advanced flotation

and selective agglomeration modules for cleaning the test coals. Trace element analyses of the feed coal and cleaned products for the Taggart and Hiawatha seam coals are given in Tables 3.3.7 and 3.3.8. Unfortunately the feed coal used to produce the cleaned coals was unavailable to Penn State for complete elemental analysis or testing. AMAX Research and Development Center provided the feed coal trace element analysis.

Table 3.3.7 Fuel Analysis (ppm)

Element	Taggart			Hiawatha		
	^a Feed Coal	Oil Agglomeration	Column Flotation	^a Feed Coal	Oil Agglomeration	Column Flotation
As	3.69	1.64	1.54	0.71	0.76	1.00
Ba	na	16.61	20.37	na	10.62	18.77
Be	2.0	0.86	1.31	0.3	< 0.07	1.25
Cd	< 0.1	< 0.06	0.04	< 0.1	< 0.07	< 0.03
Co	8.7	12.3	5.26	0.8	5.31	6.47
Cr	6	8.24	8.54	4.8	7.04	4.69
Cu	na	6.89	8.67	na	3.19	8.34
Hg	0.02	0.027	< 0.01	0.01	0.011	0.014
Mn	7	5.17	7.23	8	3.85	6.05
Mo	na	5.78	1.97	na	4.25	3.02
Ni	11	9.23	8.02	1	4.38	8.34
Pb	4	1.32	2.35	< 2	1.14	2.15
Sb	0.8	0.68	0.60	0.09	0.50	0.67
Se	1.52	0.81	1.12	1.12	1.00	0.54
Sr	na	18.45	23.00	na	33.86	22.42
V	na	14.76	7.23	na	9.30	9.91
Zn	na	4.31	4.20	na	2.66	2.92

^a Data provided by AMAX (Jha et al. 1997)
na: data not available

The MCWM formulation is provided in detail in Section 5.2.3. The proximate and ultimate analyses and physical properties of the filter cakes and MCWMs are given in Table 3.3.9.

Figures 3.3.19 and 3.3.20 present the data in Tables 3.3.7 and 3.3.8 graphically. The Taggart Oil Agglomeration fuel had at least a four times greater level of mercury than measured in the Column Flotation fuel (3.03 versus <0.69 lbs/10¹²Btu). The Column Flotation fuel was lower in Co, Hg, Mo, Ni and V. The Oil Agglomeration had lower levels of Ba, Pb, Be and Sr. Both fuels had similar levels of As, Sb and Zn.

The Hiawatha fuels had similar levels of Hg, Zn, V and Sb. In general, the remaining elements were slightly elevated in the Column Flotation fuel compared to the Oil Agglomeration

Table 3.3.8 Fuel Analysis for Cleaned Coals (lb/MM Btu)

Element	Taggart		Hiawatha	
	Oil Agglomeration	Column Flotation	Oil Agglomeration	Column Flotation
As	184.15	176.00	97.93	129.14
Ba	1865.07	2328.00	1368.46	2424.01
Be	96.57	149.71	< 9.02	161.43
Cd	< 6.74	4.57	< 9.02	< 3.87
Co	1381.11	601.14	684.23	835.55
Cr	925.23	976.00	907.15	605.68
Cu	773.65	990.86	411.05	1077.05
Hg	3.03	< 0.69	1.42	1.81
Mn	580.52	826.29	496.10	781.31
Mo	649.01	225.14	547.64	390.01
Ni	1036.40	916.57	564.39	1077.05
Pb	148.22	268.57	146.90	277.66
Sb	76.35	68.57	64.43	86.53
Se	90.95	128.00	128.86	69.74
Sr	2071.67	2628.57	4363.10	2895.38
V	1657.34	826.29	1198.37	1279.81
Zn	483.95	480.00	342.76	377.10

fuel. The only exception was that the Oil Agglomeration fuel had a significantly higher concentration of Sr.

3.3.2.3 AMAX Combustion Tests and Results

Each of the cleaned coals from Cyprus-AMAX was tested in Penn State's demonstration boiler (15,000 lb saturated (@300 psig) steam/h watertube package boiler), which has been described elsewhere (Section 5.4 for MCWM firing). Each filter cake was formulated into a MCWM. The formulation procedure is described in detail in Section 5.2.3. General physical characteristics of the MCWMs are given in Table 3.3.9. All MCWMs were cofired with 30% (thermal input) natural gas support (Table 3.3.10). Pressures indicated under test variable refer to atomizing air pressure. Stack gas sampling was conducted according to Method 29 (described in detail in Section 3.3.3).

Two sequential tests were run during a test period in which Method 29 trains were run simultaneously at the particle control device inlet and outlet. The sampling protocol for EPA Method 29 was followed as outlined in the Code of Federal Register (1996). The emission levels of trace elements for the Taggart and Hiawatha seam fuels are shown in Figures 3.3.21 and 3.3.22.

Table 3.3.9 Filter Cake And MCWM Analysis

	Hiawatha Selective Agglomeration	Hiawatha Column Flotation	Taggart Selective Agglomeration	Taggart Column Flotation
Filter cake Properties				
Proximate Analysis (wt. %, dry basis)				
Volatile Matter	43.8	41.7	33.3	33.3
Ash	2.2	2.5	1.5	1.7
Fixed Carbon	54.0	55.8	65.2	65.0
Ultimate Analysis (wt. %, dry basis)				
Carbon	80.0	83.2	87.3	88.2
Hydrogen	5.8	6.1	6.4	5.7
Nitrogen	1.5	1.5	1.4	1.5
Sulfur	0.5	0.7	0.8	0.7
Oxygen	10.0	6.0	2.6	2.2
Higher Heating Value (Btu/lb, dry)	14,130	14,255	15,012	14,975
HGI	44 ^a	44 ^a	49 ^a	49 ^a
MCWM Properties				
Dispersant Conc.(wt.%)	0.35	0.35	0.30	0.30
Stabilizer Conc. (wt.%)	None	None	None	None
pH	7.2	7.1	5.7	6.2
Solids Loading (wt.%)	54.3	55.2	59.5	57.7
Apparent Viscosity (cp, @ 100 sec ⁻¹)	372	384	1,088	291
Particle Size Distribution (µm)				
Top Size	207	189	119	250
D(v,0.9)	70.7	73.2	57.7	101.0
D(v,0.5)	21.5	28.4	15.0	34.0
D(v,0.1)	5.5	6.1	4.6	6.1

^a From Jha *et al.*, 1997

Previous tests conducted in Phase II showed reductions in emissions similar to the reduction of trace elements seen in coal as a result of coal cleaning (Falcone Miller *et al.*, 1998a; Miller *et al.*, 2000). In Figures 3.3.23 and 3.3.24, the percent depletion/enrichment of various trace elements in the column flotation MCWM as compared to the oil agglomeration MCWM is plotted against their relative depletion/enrichment in the stack gas (e.g., $100 \times [AS_{\text{Oil Agglomeration}} - AS_{\text{Column Flotation}}] / [AS_{\text{Oil Agglomeration}}]$). The percent difference for each element in the fuel and

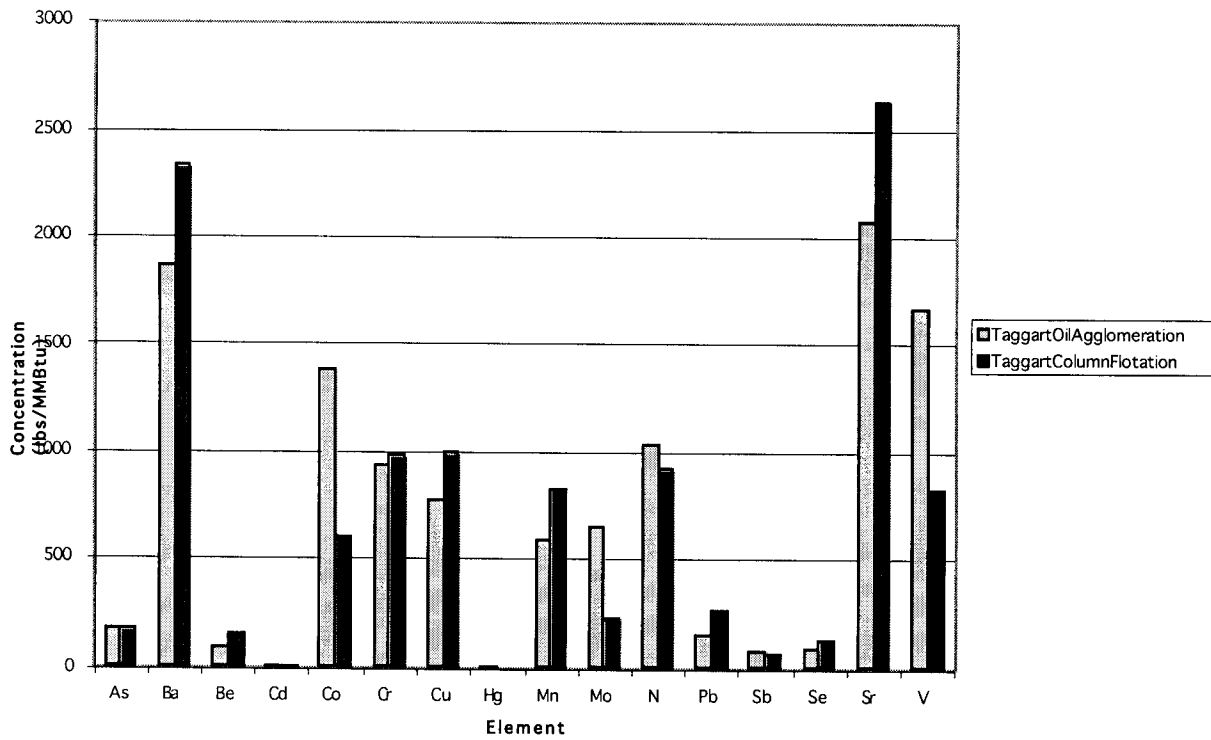


Figure 3.3.19 FUEL ANALYSIS OF CLEANED TAGGART FUELS

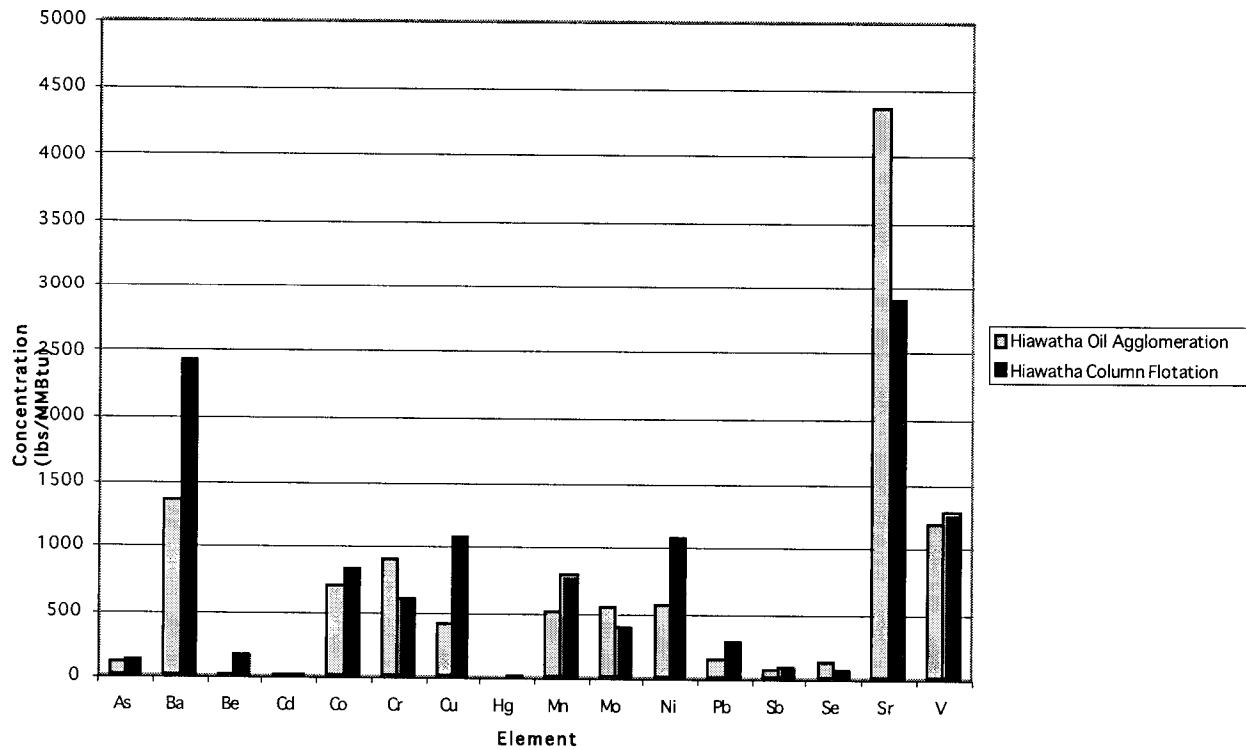


Figure 3.3.20 FUEL ANALYSIS OF CLEANED HIAWATHA FUELS

Table 3.3.10 Combustion Tests Completed on the Demonstration Boiler

Fuel	Cleaning Technique	Particulate Control Device	Test Variable
Taggart MCWM	Agglomeration	Baghouse	135 psig
			80 psig
Taggart MCWM	Flotation	Baghouse	135 psig
Hiawatha MCWM	Agglomeration	Baghouse	135 psig
Hiawatha MCWM	Agglomeration	Ceramic	
Hiawatha MCWM	Flotation	Baghouse	30 % Gas Support
Hiawatha MCWM	Flotation	Baghouse	26 % Gas Support

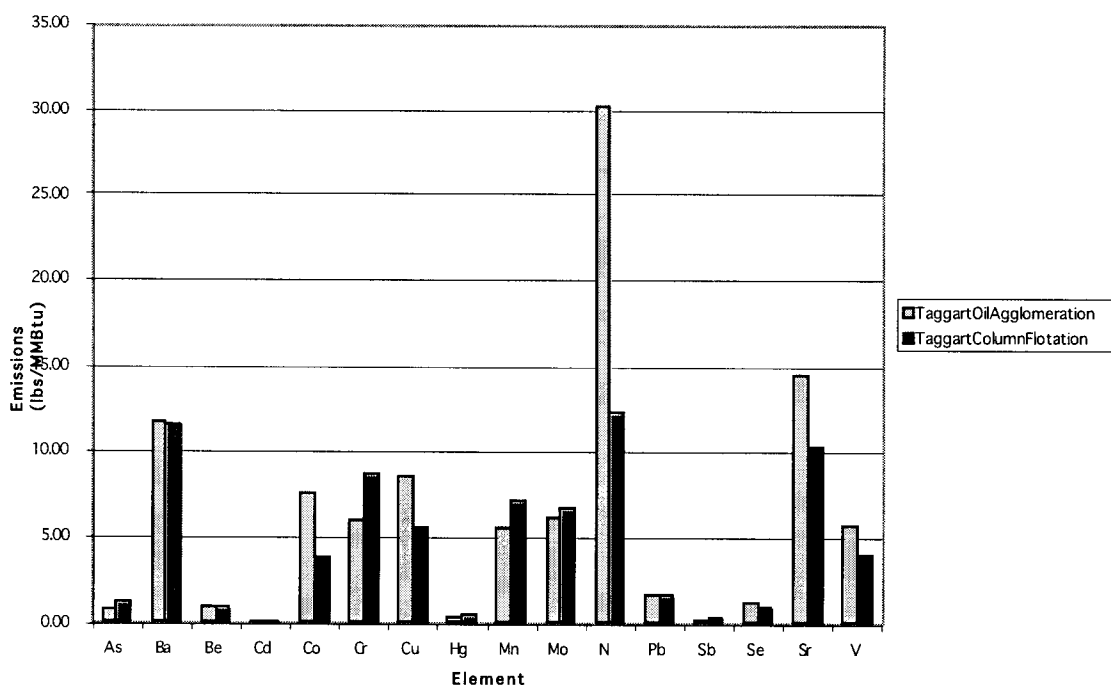


Figure 3.3.21 EMISSIONS MEASURED BY METHOD 29 AT PCD OUTLET DURING COMBUSTION OF TAGGART CLEAN COALS

emissions was calculated in this manner for each fuel. In theory, if there is a direct relationship between the depletion/enrichment of an element in a fuel and its depletion/enrichment in the flue gas then one would expect all of the elements to plot in the I and III quadrants. Ideally, the points should lie upon the solid line showing a 1:1 relationship between the extent of depletion/enrichment of an element in a fuel to its depletion/enrichment in the flue gas.

Those elements in Quadrant I are enhanced in the Oil Agglomeration Fuel and corresponding emissions. Those elements in Quadrants III are enhanced in the Column Flotation

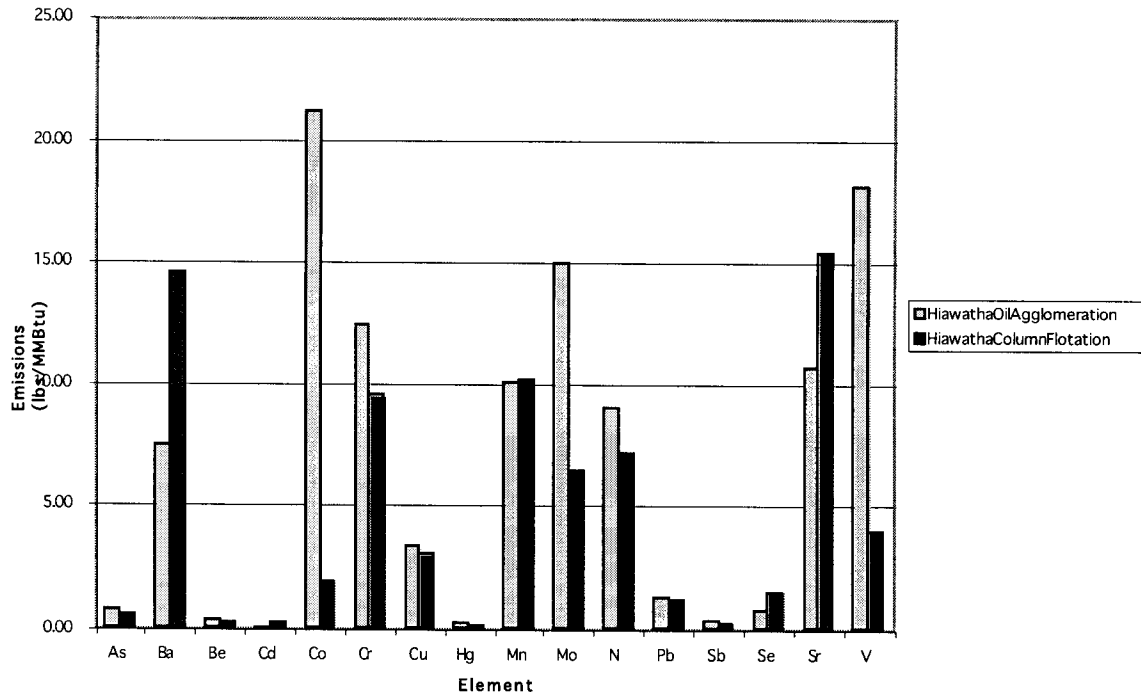


Figure 3.3.22 EMISSIONS MEASURED BY METHOD 29 AT PCD OUTLET DURING COMBUSTION OF HIAWATHA CLEAN COALS.

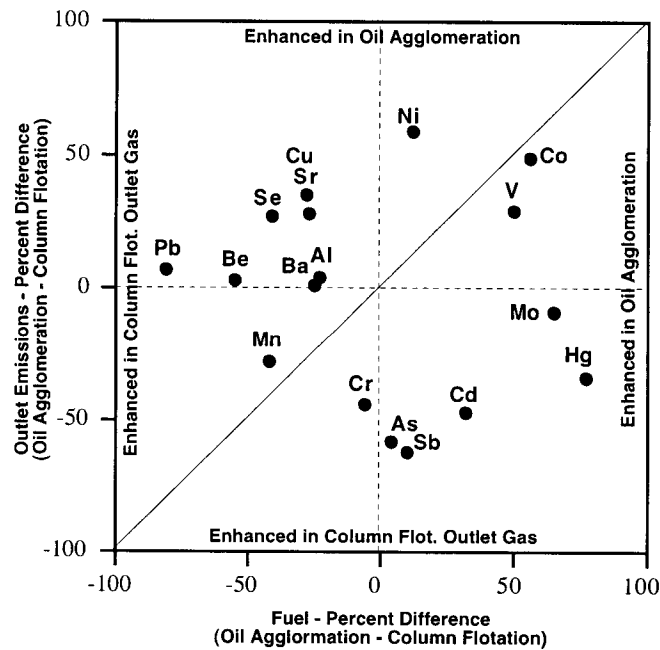


Figure 3.3.23 RELATIONSHIP OF ELEMENT CONCENTRATION IN FUEL AS A FUNCTION OF CLEANING AND CORRESPONDING ELEMENT EMISSIONS FOR THE TAGGART OIL AGGLOMERATION AND COLUMN FLOTATION FUELS

$$\% \text{ Difference} = (\text{Element}_{\text{Taggart Oil Agglomeration}} - \text{Element}_{\text{Taggart Column Flotation}}) / \text{Element}_{\text{Taggart Oil Agglomeration}}$$

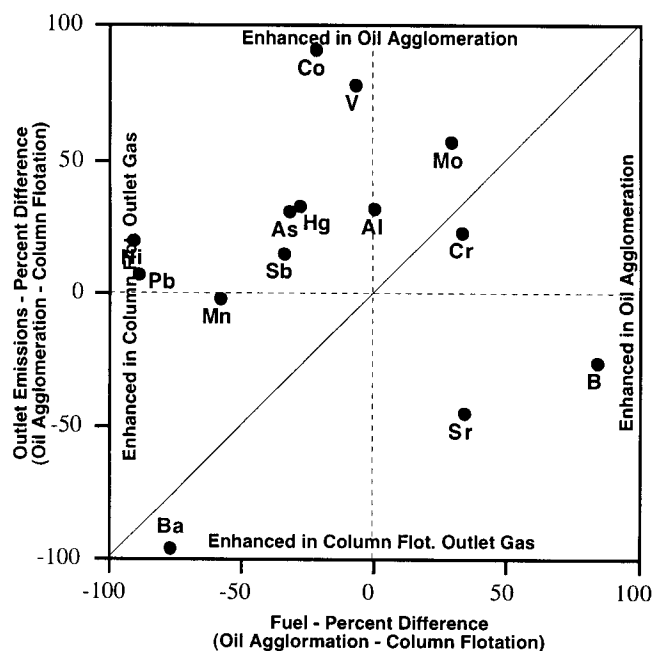


Figure 3.3.24 RELATIONSHIP OF ELEMENT CONCENTRATION IN FUEL AS A FUNCTION OF CLEANING AND CORRESPONDING ELEMENT EMISSIONS FOR THE HAIWATHA OIL AGGLOMERATION AND COLUMN FLOTATION FUELS

$$(\% \text{ Difference} = (\text{Element}_{\text{Hiawatha Oil Agglomeration}} - \text{Element}_{\text{Hiawatha Column Flotation}}) / \text{Element}_{\text{Hiawatha Oil Agglomeration}})$$

fuel and corresponding emissions. Elements that lie in these quadrants suggest a direct relationship with enhancement and reduction in the fuel to emissions. Elements in Quadrants II and IV do not demonstrate a direct relationship between enhancement or reduction of an element in the fuel to corresponding emissions.

In the case of the Taggart Fuels (Figure 3.3.23), Co, V, and Mn lie near the solid line in Quadrant I and Mn in Quadrant III suggesting that there is a direct relationship with enhancement and reduction in the fuel to emissions. However, many of the elements show inconsistent relationships. For example, Pb is significantly enhanced in the Column Flotation Fuel but present at roughly the same concentration in the emissions measured for the two fuels. Mercury is significantly higher in the Oil Agglomeration Fuel (77%) but the concentration of mercury measured in the Oil Agglomeration Fuel was less than in the Column Flotation Fuel (-33%).

In the case of the Hiawatha fuels (Figure 3.3.24), only Mo, Cr and Ba showed a proportional relationship with enhancement and reduction in the fuel to emissions. Most of the

elements are located in Quadrant IV. Elements are enhanced in the Column Flotation Fuel but are depleted in the corresponding emissions (or conversely enhanced in the Oil Agglomeration emissions. The variable or inconsistent nature of the data suggests that the amount of an element in a fuel is not the only variable that determines its concentration in the flue gas.

3.3.2.4 Combustion Tests and Results of the CQ, Inc. Coals

Pittsburgh seam raw and cleaned coals were fired in a 2 million Btu/hr A-frame watertube boiler. A schematic diagram of the 1,000 lb/h steam boiler is shown in Figure 3.3.25. The boiler is a 200 psig working pressure, A-Frame water-tube boiler, designed and built by Cleaver Brooks. The combustion chamber is a 3 ft x 3 ft x 7 ft chamber with a maximum heat release rate of 42,000 Btu/ft³-h. It contains 288 ft² of heating surface and the maximum fuel firing rate is two million Btu/h. It has been modified to fire any combination of natural gas, liquid fuels, or solid fuels.

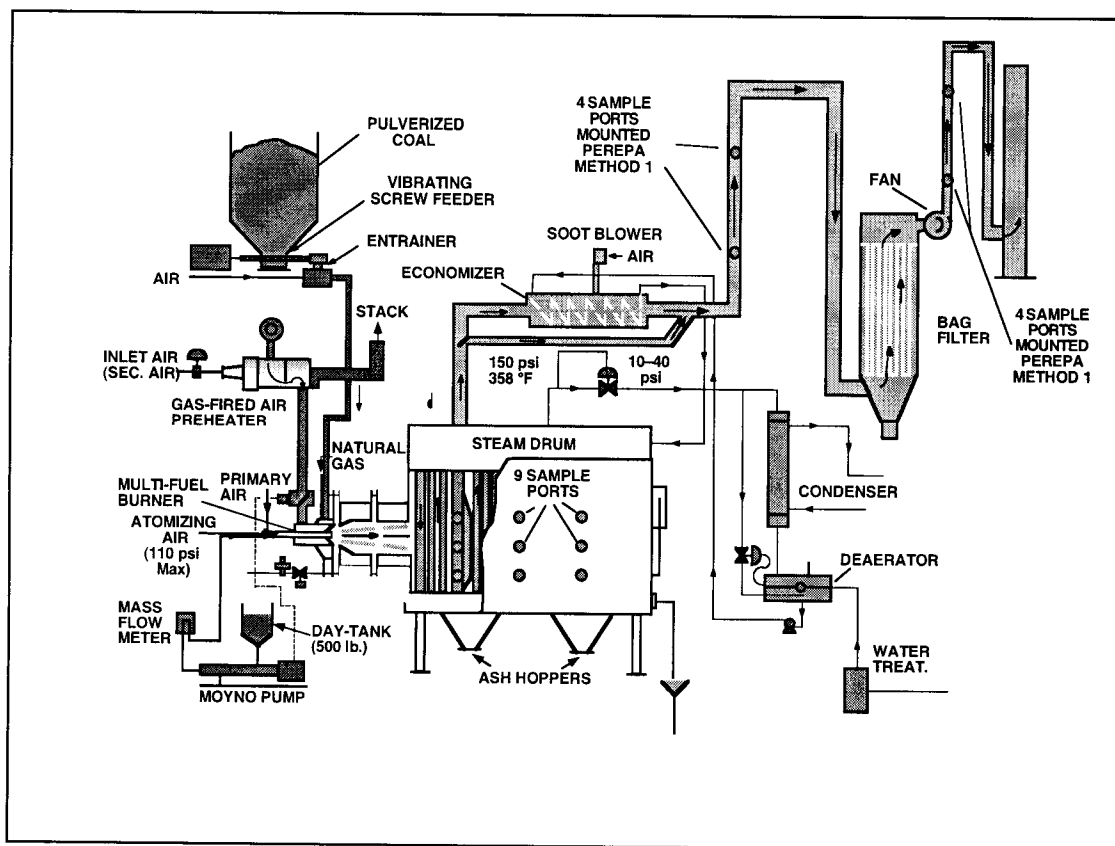


Figure 3.3.25 SCHEMATIC DIAGRAM OF THE RESEARCH BOILER

The boiler is equipped with eighteen side ports for gaseous and particulate sampling. Fourteen of the ports have diameters of 3 inches and four have diameters of 4 inches. The combustion gases split into two convective passes, one on each side of the radiant combustion chamber. There are access doors into each of the convective sections. There are also two ash hoppers under each convective section and there is a doorway into the radiant combustion chamber.

The steam pressure inside the boiler is maintained constant during tests by a back pressure regulator. The steam flow rate is measured by a steam flow meter before passing through a condenser. Condensed water flows through a deaerator before returning to the boiler.

To promote and enhance combustion, a ceramic burner throat extends the combustion chamber by two feet. This ceramic section, termed a quarl, is preheated by a natural gas flame prior to pulverized coal combustion. This section aids in the support of hard to ignite fuels by storing some of the radiant energy released by the flame. When firing DMC, it is screw fed from an 80 lbs capacity hopper to an eductor and transported by compressed air into the burner. When firing MCWM, it is gravity fed from a day tank into a progressive cavity pump.

Duplicate simultaneous sampling of the flue gas was conducted at the inlet and outlet of the baghouse using the PSU Method Train to sample combustion flue gas mercury species and inorganic trace elements. A description of the PSU Method can be found in Section 3.3.3. Analysis of the parent and cleaned coal is given in Table 3.3.11.

The process of cleaning the coal resulted in a reduction of all the trace elements on a lbs/10¹² Btu basis except for Sr which did not change appreciably. The percent reduction ranged from 15 (for Sb) to 82% for As. Mercury decreased by $\approx 37\%$.

The emission of trace elements measured at the baghouse outlet is given in Figure 3.3.26. The cleaned coal showed a reduction in all of the elements measured except for mercury. Interestingly mercury emission was $\approx 72\%$ higher in the cleaned coal stack gas.

A plot of the depletion/enrichment of an element in the fuel to its depletion/enrichment in the flue gas is given in Figure 3.3.27. In theory, all of the data points should fall in Quadrants I or III as close to the solid line (indicating a 1:1 relationship between reduction in the fuel and emissions). This assumes that there is a direct relationship between the depletion/enrichment of an element in the fuel to its depletion/enrichment in the flue gas. Most of the elements plot in Quadrant I. Therefore most of the elements are present in the cleaned fuel at lower levels than in

Table 3.3.11 Trace Element Analysis Of Parent And Cleaned Pittsburgh Coals

Element	Pittsburgh Parent Coal		Pittsburgh Cleaned Coal	
	ppm	Lbs/10 ¹² Btu	ppm	Lbs/10 ¹² Btu
As	9.88	813.0	2.09	145.7
Ba	59.70	4912.5	42.29	2948.2
Be	1.49	122.6	1	69.7
Cd	0.10	8.2	0.07	4.9
Co	15.17	1248.3	11.69	815.0
Cr	26.12	2149.3	14.68	1023.4
Cu	12.94	1064.8	6.47	451.1
Hg	0.120	9.9	0.089	6.2
Mn	16.17	1330.6	10.95	763.4
Mo	4.98	409.8	4.23	294.9
Ni	16.67	1371.7	8.96	624.6
Pb	7.39	608.1	1.62	112.9
Sb	0.75	61.7	0.75	52.3
Se	2.44	200.8	1.64	114.3
Sr	48.51	3991.7	58.46	4075.5
V	32.34	2661.1	19.9	1387.3
Zn	28.61	2354.2	15.92	1109.9

the parent raw coal and show a corresponding reduction in the flue gas. Several elements lie along or within $\pm 20\%$ of the solid line within Quadrant I suggesting that they follow approximately a direct relationship between reduction in the fuel and emissions, after accounting for sampling and analytical errors.

Elements, which significantly deviate from this relationship, are antimony and mercury. Mercury is singular in its behavior in that it is the only element that showed an increase in emission in the flue gas of the cleaned coal. One would expect to see a reduction in emissions if there was a corresponding reduction of trace elements in the fuel due to cleaning. In the case of mercury, there was a 38% reduction of mercury in the cleaned fuel yet there was 72%, i.e., 0.4 versus 0.69 lbs/10¹² Btu, more mercury emitted at the baghouse outlet. The material balance for mercury across the baghouse was 1.02 and 0.93 for the Pittsburgh raw and cleaned coal, respectively. This suggests that the measured levels of mercury in the flue gas are reliable.

One possible explanation may lie in the difference in the amount and/or nature of carbon present in the baghouse ash. Significant amounts of carbon in ash has resulted in increased retention of mercury in the particulate collected at the baghouse inlet during tests performed on the research and demonstration boilers at Penn State. The percent carbon measured in baghouse ash plotted against the percent of mercury measured in the particulate for a series of tests

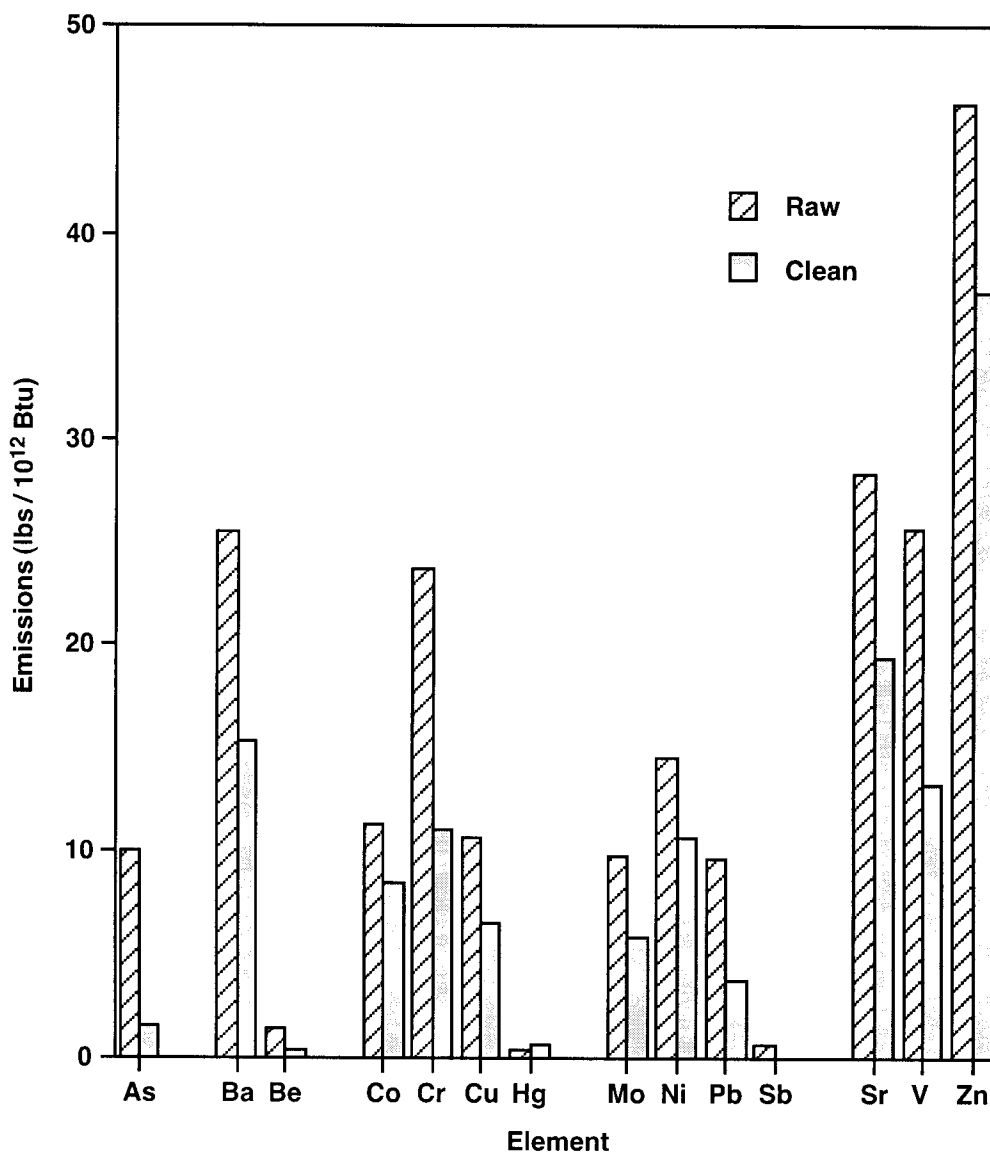


Figure 3.3.26 TRACE ELEMENTS EMISSIONS OF PITTSBURGH RAW AND CLEANED COAL

conducted using one fuel in the research and demonstration boilers is shown in Figure 3.3.28. In general, an increase in percent carbon results in an increase in the percent mercury in the particulate phase. The correlation (r) between percent carbon and percent particulate mercury for the research boiler tests was 0.628 and 0.996 for the demonstration boiler tests.

The percent carbon in the Pittsburgh raw coal and cleaned coal baghouse ash was quite similar, i.e., 13.9 and 16.4%, respectively. The percent burnout of the raw and cleaned Pittsburgh coal was 94.5 and 98.6%, respectively. The percent of particulate mercury measured

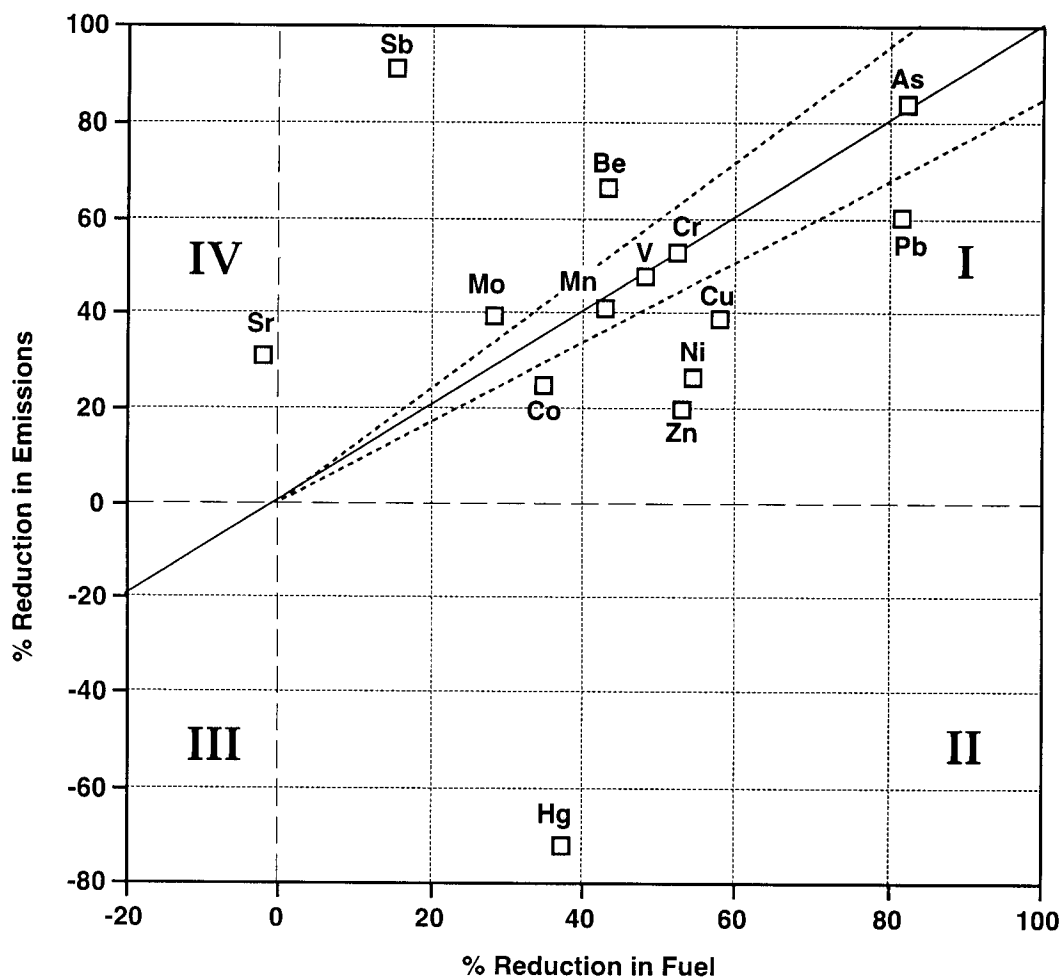


Figure 3.3.27 THE RELATIONSHIP BETWEEN REDUCTION IN TRACE ELEMENTS DUE TO COAL CLEANING AND THEIR REDUCTION IN STACK EMISSIONS FOR THE PITTSBURGH COAL
(Solid line represents theoretical 1:1, Dash lines represent $\pm 20\%$ of theoretical).

at the baghouse inlet was also similar for the raw and cleaned coal, i.e., 98.4 and 90%, respectively. However, the percent of particulate mercury measured at the baghouse outlet was quite different for the raw and cleaned coal, i.e., 85.6 and 36.8%, respectively. The data suggest that there was a significantly greater percentage of gas phase mercury exiting the baghouse during combustion of the cleaned coal than during combustion of the raw coal. During combustion of the raw coal 93.4% of the mercury that entered the baghouse was retained and presumably associated with ash and char particles. During combustion of the cleaned coal only 74.6% of the mercury that entered the baghouse was retained. The data support the work of

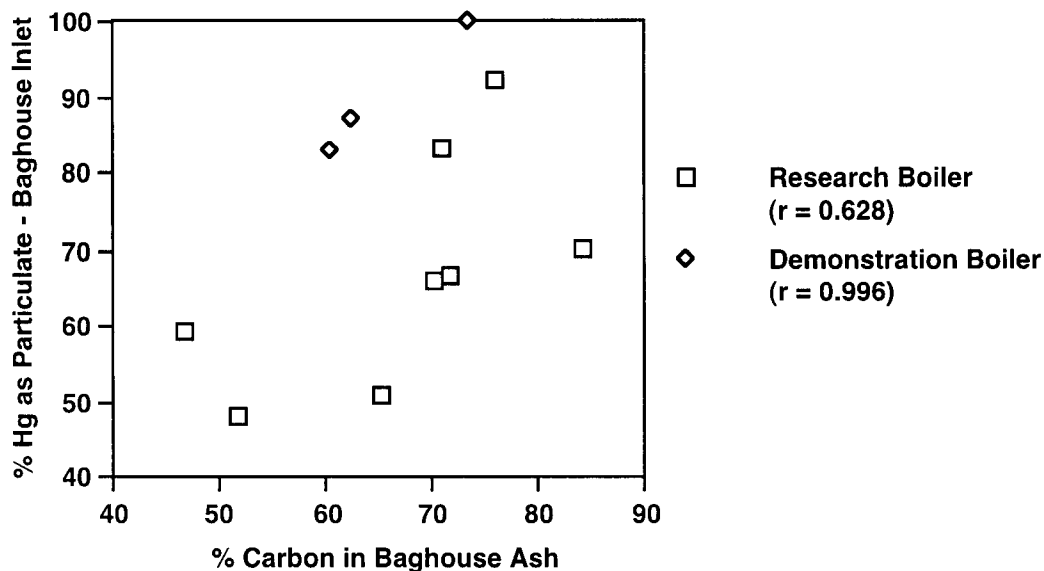


Figure 3.3.28 THE RELATIONSHIP BETWEEN CARBON IN ASH AND THE RETENTION OF MERCURY ON PARTICULATES

others showing the importance of the interaction of mercury in the gas phase with ash and char in particle control devices (Livengood et al., 1994; Senior et al., 1997). The percent carbon contained in the baghouse ash was essentially the same for the two fuels. It is possible that a difference in the inorganic chemistry of the ashes contributed to the difference in the retention of mercury in the baghouse.

3.3.2.5 Effect of Atomization Quality on Trace Element Emissions

The Taggart seam MCWM (oil agglomeration) was fired at two different atomizing pressures, i.e., 135 and 80 psig to determine what effect this had on trace element emissions. Numerous studies have suggested that the presence of carbon in char acts as a medium that absorbs mercury on active sites (Senior et al., 1997; Senior et al., 1998). Reducing the atomizing air pressure resulted in a decrease in the carbon burnout of the fuel from 97.8 to 94.8 %. In theory, the char character of the two fuels should be similar and only the amount of carbon present should differ by virtue of the reduced carbon burnout. This could enhance the retention of mercury in the baghouse.

The percent penetration of selected elements for the two tests is given in Figure 3.3.29. In general, there was a greater penetration of the highly volatile elements, i.e., Hg, in the test

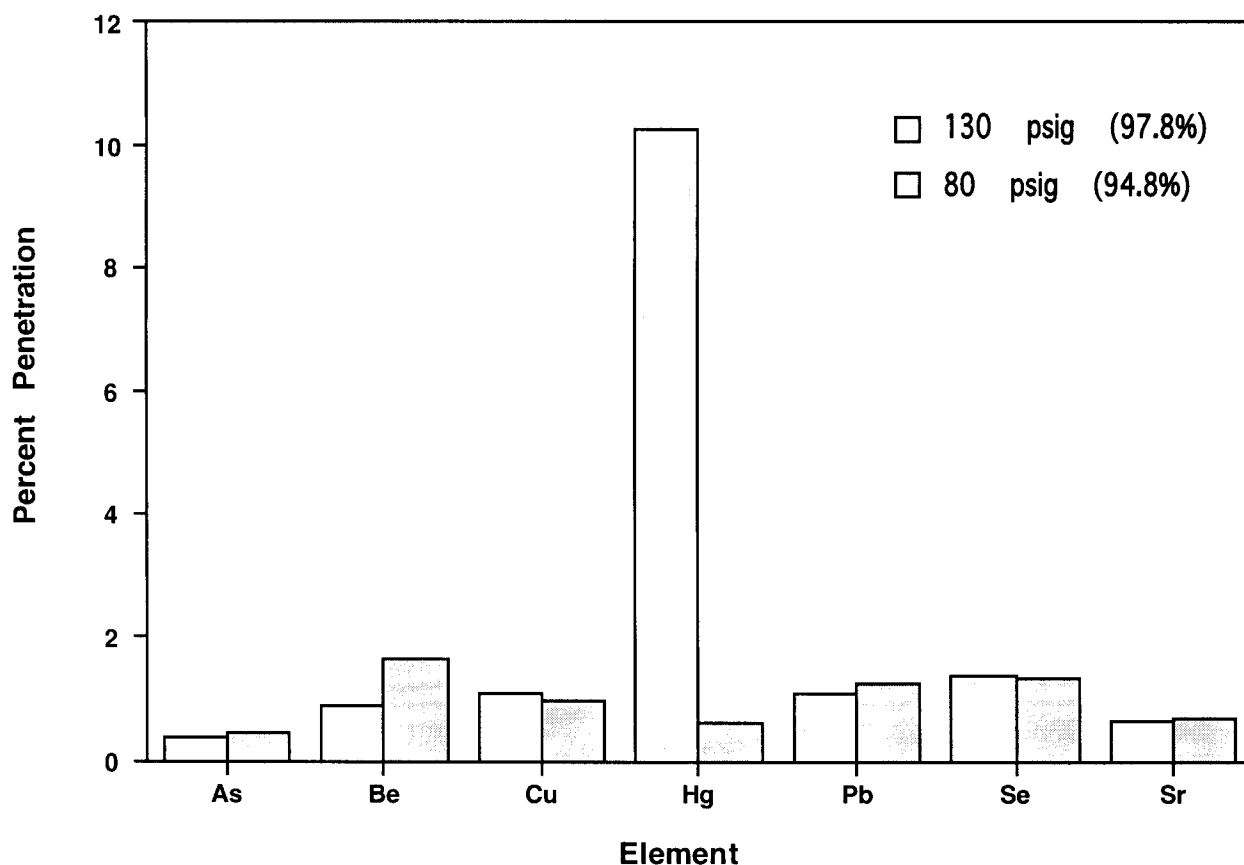


Figure 3.3.29 PERCENT SYSTEM PENETRATION OF SELECTED IHAPS FOR THE TAGGERT MCWM (Oil Agglomeration) AS A FUNCTION OF ATOMIZING AIR PRESSURE

conducted at 135 psig having the greater burnout. There was a 93% reduction in mercury penetration through the system at 80 psig and 94.8 % burnout as compared to the baseline test at 135 psig. The data suggest that the extent of burnout has less effect on the retention of elements that are less volatile than mercury.

3.3.2.6 Conclusions

The objective of this activity was to investigate the effect of coal cleaning on trace elements emissions. A basic assumption was made that there was a direct relationship between the depletion/enrichment of an element in the fuel to its depletion/enrichment in the flue gas. Earlier results reported in the Phase II final report using the Freeport seam coal cleaned by CQ Inc. suggested that there was a relationship between the extents to which trace elements were

removed during cleaning and their reduction in stack gas (Miller et al., 2000). Further studies were conducted to validate this assumption.

In the case of the AMAX fuels there was significant scatter in the data. In some cases, a percent reduction of elements due to cleaning made up a greater percentage of the trace elements analyzed for in the stack gas. The data indicate that there is not always a direct relationship between the reductions in trace elements in a fuel and a corresponding reduction in emissions. The atomization tests with the Taggart Oil Agglomeration Fuel were conducted to see if a decrease in burnout due to poorer atomization quality would affect trace element emissions. In general, there was a greater penetration of the highly volatile elements, i.e., Hg, in the test conducted at 135 psig having the greater burnout. There was a 93% reduction in mercury penetration through the system at 80 psig and 94.8 % burnout as compared to the baseline test at 135 psig. The data suggest that the extent of burnout had less effect on the retention of elements that are less volatile than mercury

By contrast, the data obtained during combustion of the Pittsburgh seam coal and cleaned coal (provided by CQ Inc.) suggested that there was a direct relationship between the depletion/enrichment of an element in the fuel to its depletion/enrichment in the flue gas. Most of the elements plotted in Quadrant I, therefore, most of the elements were present in the cleaned fuel at lower levels than in the parent raw coal and showed a corresponding reduction in the flue gas. One exception was mercury. Mercury concentration decreased by $\approx 37\%$ in the cleaned coal, however, mercury concentration was $\approx 72\%$ higher in the cleaned coal stack gas. Comparing the inlet and outlet data showed that there was a significantly greater percentage of gas phase mercury exiting the baghouse during combustion of the cleaned coal than during combustion of the raw coal. During combustion of the raw coal 93.4% of the mercury that entered the baghouse was retained and presumably associated with ash and char particles. During combustion of the cleaned coal only 74.6% of the mercury that entered the baghouse was retained. The data support the work of others showing the importance of the interaction of mercury in the gas phase with ash and char in particle control devices (Livengood et al., 1994; Senior et al., 1997). No specifics identifying the mechanism that caused this difference are given at this time.

The variation in the results obtained suggest that trace element emissions can not be predicted solely based on their concentration in the fuel. The interaction of the inorganics within

the system during combustion often affects the partitioning and concentration of trace elements in the gas and ash stream. Therefore, the effectiveness of extensive coal cleaning in the reduction of trace element emissions is dependent on coal composition and the system configuration.

3.3.3 Methodology Development

3.3.3.1 Introduction

In January 1999, the U.S. Environmental Protection Agency (EPA) initiated an Information Collection Request (ICR) for mercury emissions from electric utility steam generating units, which are 25 MW_e or greater in capacity (EPA ICR No. 1858.01). The ICR was conducted to assist the EPA in determining whether it is appropriate and necessary to regulate mercury emissions from electric utility steam generating units under Title III, Section 112 (n)(1)(A) of the Clean Air Act Amendments of 1990. The issuance of an ICR generally precedes the implementation of regulatory action by the EPA.

In December of 2000, the U.S. EPA decided that regulation of mercury from coal-fired power plants was appropriate and necessary under Section 112 of the Clean Air Act due to the significant health hazards it presented to the public health. The EPA is scheduled to propose regulation of mercury emissions by December 2003 and promulgate them by December 2004. In order to come to this determination, the accurate measurement of mercury and its speciation was necessary. These data could also be used to confirm measurements by online analyzers being developed for use in monitoring emissions and determining the effectiveness of new control technologies. It was stated by State and Local Stakeholders involved in the working group for the utility MACT formed under the Clean Air Act Advisory Committee that if multiple metals were to be regulated by the EPA, Method 29 should be the preferred method for measuring mercury until CEMs are commercially available.

Extensive testing has shown that EPA Method 29 may not speciate mercury correctly; however, it may still be used to measure total mercury (Electric Power Research Institute 1996, 1997). Early work by The University of North Dakota Energy and Environmental Center involved a self-validation test (EPA Method 301) to evaluate the precision and bias of Method 29 for the determination of mercury (Dunham et al. 1998; Heidt and Laudal, 1995). The overall pooled standard deviation for the inlet, outlet, and baghouse ash taken from nine pairs of

simultaneous tests (three tests on three coals) were 0.85, 0.97 and 0.60 mg/m³, respectively. The self-validation test included twelve pairs of simultaneous Method 29 samples, and resulted in a standard deviation of 0.58 mg/m³, which compares well with the 0.85 and 0.97 mg/m³. They concluded that about 60% of the variability is due to the sampling/analysis and 40% of the variability is due to the process.

Studies have shown that the speciation of mercury is extremely important in its environmental impact. Oxidized mercury (Hg⁺²) is highly reactive with surface water and is methylated and is incorporated into the food chain via ingestion by fish. The amount of oxidized mercury emitted from a particular power plant for a given coal can be variable.

The EPA had designated the Ontario Hydro Mercury Speciation Method for stack gas sampling to measure total, elemental and oxidized mercury. This recommendation is based on extensive work by the University of North Dakota Energy and Environmental Research Center (UNDEERC) in evaluating a series of methodologies for determining mercury speciation (Laudal et al. 1997). EPA had also designated the Method 29 sampling train for the sampling and measurement of IHAPs.

The Method 29 procedure is outlined in the Code of Federal Regulations, Protection of the Environment, 40, Part 60 (Code of Federal Regulations 1996). The Ontario Hydro Mercury Speciation Method used in this study is based on the draft procedure titled "Standard Test Method for Elemental, Oxidized, Particulate, and Total Mercury in Coal-Fired Stationary Sources (Ontario Hydro Mercury Speciation Method)" recommended by UNDEERC to the American Society for Testing and Materials (ASTM) and to EPA (U.S. EPA 1999). This is a version of the Ontario Hydro Method originally developed by Keith Curtis and others at Ontario Hydro Technologies.

Not all IHAPS elements are of equal environmental concern given their varied behavior in combustion systems. Elements that tend to volatilize during combustion, e.g., Hg, Se, As, and remain totally or partially in the gas phase and/or are readily re-emitted from the solid phase are of particular environmental importance. Currently there are no emission restrictions on these elements from power plants, however studies are being conducted as to their health risk and environmental impact as small particulate in the gas effluent and fly ash deposited in ash pits.

The objective of this study was to develop a sample train and methodology capable of simultaneously sampling mercury species and all inorganic trace elements listed as IHAPs. The

train and methodology, referred to as the PSU Method, consists of components of both the Ontario Hydro Mercury Speciation Method and Method 29 sampling trains. Of interest is whether the difference in the PSU Method train configuration compared to the Method 29 and Ontario Hydro trains compromises the measurement of either or both of the total trace elements or mercury species. Also at issue is whether the sample preparation and analytical methods outlined in Method 29 and the Ontario Hydro Mercury Speciation Method are appropriate for a multielemental train. The advantage of the PSU Method is that it will enable IHAPS and mercury species to be sampled simultaneously. This reduces the time required to change out sampling trains and obtain and recover samples, thereby allowing for a complete suite of data to be collected during one continuous run. The following discussion is taken from several conference papers by Falcone Miller et al. (1999a, 1999b, 1999c).

The trace element testing was performed on three test units at Penn State's Energy Institute – the 400,000 Btu/h DFC, the 1,000 lb saturated (@200 psig) steam/h research boiler, and the 15,000 lb saturated (@300 psig) steam/h demonstration boiler). These units have been described earlier in Section 3.0.

3.3.3.2 Early Development of the PSU Method

It was determined that the PSU Method would adapt features of the Method 29 (used for multielements) and the Ontario Hydro Mercury Speciation Method into a unified method and address any analytical limitations. A schematic of the Method 29, Ontario Hydro and PSU Method Trains is given in Figure 3.3.30. The sampling and recovery procedure used for the PSU Method is a combination of those used in the Method 29 and Ontario Hydro Mercury Speciation Methods (U.S. EPA 1999; Code of Federal Regulations 1996). Modification of the Ontario Hydro train included omission of one KCl impinger and one H₂SO₄/KMnO₄ impinger and the addition of a HNO₃/H₂O₂ impinger (Figure 3.3.30). The inclusion of an extra impinger (HNO₃/H₂O₂) in the PSU Method train should have no effect on the amount of mercury trapped compared to the Ontario Hydro train. The configuration was based on discussions with UNDEERC and earlier testing conducted at PSU. Tests conducted at PSU using one and two HNO₃/H₂O₂ impingers showed the presence of IHAPs in the second impinger. Therefore it was determined that two HNO₃/H₂O₂ impingers should be used to ensure the recovery of multielements. The recovery protocol for the filter, filter rinse, HNO₃/H₂O₂ and H₂SO₄/KMnO₄

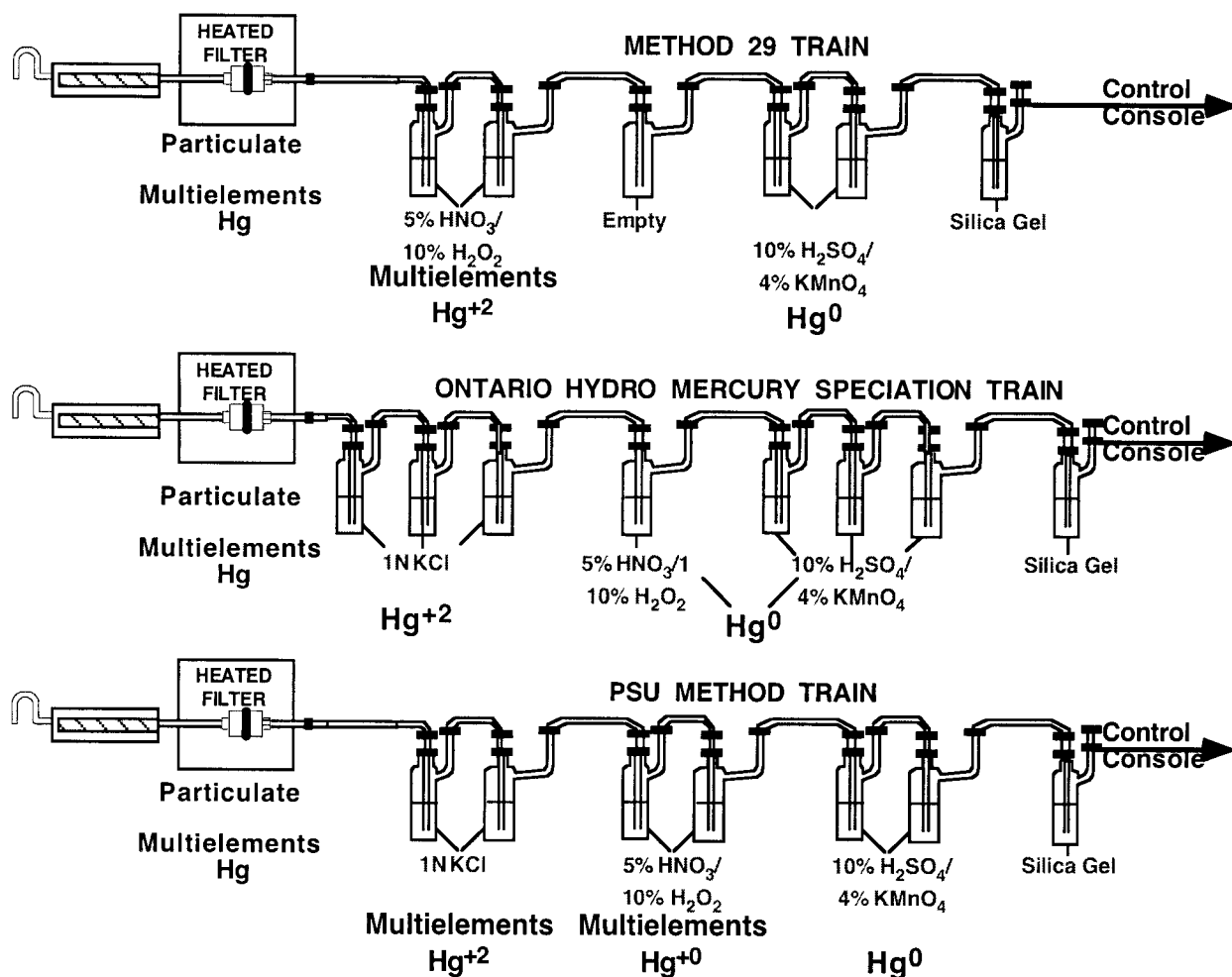


Figure 3.3.30 SAMPLE TRAIN CONFIGURATIONS FOR METHOD 29, ONTARIO HYDRO MERCURY SPECIATION METHOD AND PSU METHOD

samples are the same for Method 29 and the Ontario Hydro Mercury Speciation Method. The recovery and sample preservation of the KCl solution followed the Ontario Hydro Mercury Speciation Method. The sample preparation, *i.e.*, digestion techniques, and analytical techniques for the multielements and mercury for the current PSU Method are shown in Figure 3.3.31.

Early tests showed poor agreement between the data generated for samples following the digestion procedures in Method 29 and the Modified Ontario Hydro Method. Therefore, additional digestion techniques were evaluated including EPA Methods 7471, 3050 and 3051 (Mercury in Solid or Semisolid Waste – Manual Cold Vapor Technique; U.S. EPA 1988). Splits were made of each sample so that different sample preparations and analyses could be performed as appropriate. All of the analytical techniques used meet instrument detection levels outlined in

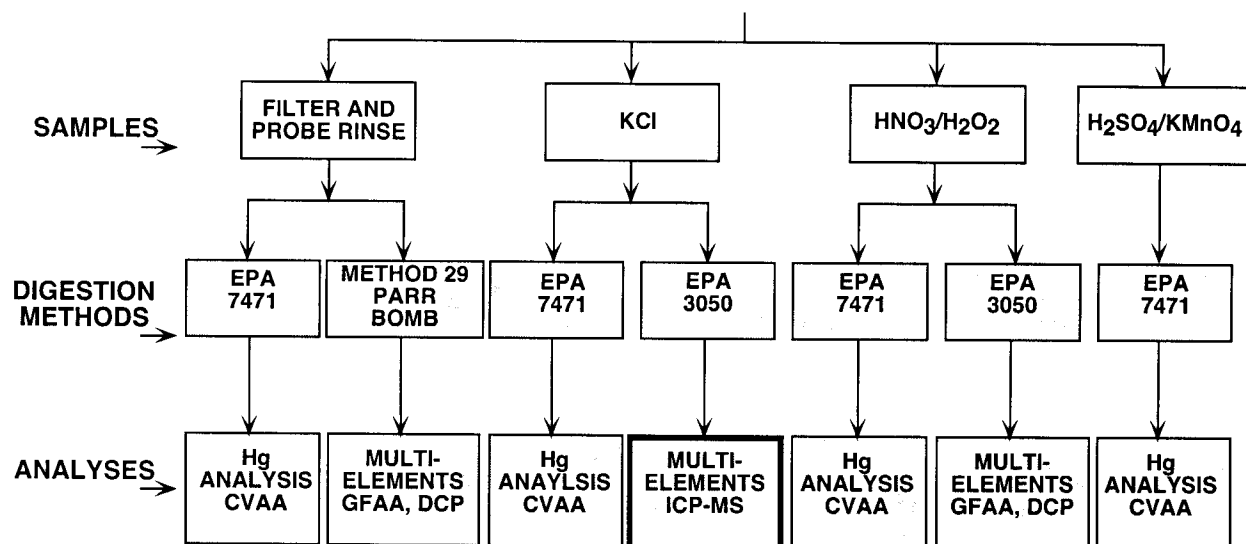


Figure 3.3.31 SAMPLING PREPARATION AND ANALYTICAL PROTOCOL FOR THE PSU METHOD (Falcone Miller, et al., 1999a)

both Method 29 and the Modified Ontario Hydro Method.

Solid samples consisted of the filter and rinse samples combined. One sample split was digested according to Method 7471 and the other by Method 29 Par Bomb digestion. The Method 7471 digested sample was analyzed for total mercury by CVAAS. GFAAS and DCP were used to analyze the sample digested by Method 29 for multielements.

The KCl solution (Impingers #1 and 2) was analyzed for multielements and mercury. Given that the KCl containing impinger precedes the H₂O₂ and the KMnO₄ solutions, it was a concern that multielements could be captured in the KCl solution. Therefore, analysis of only the H₂O₂ solution for multielements could result in under reporting the amount of gas phase multielements. There is no provision for analyzing multielements in the Modified Ontario Hydro Method in any of the impinger reagents. Therefore, the KCl solutions in Impingers #1 and 2 were combined and then split into two samples. One split was recovered according to the Modified Ontario Hydro Method using KMnO₄ as a stabilizer. The sample was then digested by Method 7471 and successfully analyzed for mercury (oxidized) by CVAAS. The second split was divided into two samples to be analyzed for multielements. One sample was digested by a modified Method 29 procedure using nitric acid and analyzed by DCP and GFAAS. Most of the multielements were present in concentrations below instrument detection limits. This was due to the fact that the high concentration of chlorine (contributed by the KCl reagent) in the samples

required excessive dilution to avoid interference effects in the DCP and GFAAS. The second sample was digested by Method 3050 and analyzed directly by an ICP-MS (quadrupole), DCP and GFAAS. DCP and GFAAS could not be used to analyze the second sample due to chlorine interference and dilution problems. However, analysis for multielements by ICP-MS was successful due to the increased resolution of the instrument and its ability to factor out interference due to chlorine present in the sample. One limitation of the quadrupole ICP-MS used is the high detection limit of mercury. The levels of mercury in the samples were at or near the detection limit of the ICP-MS (quadrupole) used.

The hydrogen peroxide ($\text{HNO}_3/\text{H}_2\text{O}_2$) solutions (Impingers #3 and 4) were combined and then split. One split was further divided into three samples: no digestion, digestion by the Modified Ontario Hydro Method, and digestion by Method 7470. Each sample was subsequently analyzed for elemental mercury by CVAAS. The samples digested by Method 7471 (indicated on Figure 3.3.31) gave the most reproducible results. The second split was digested according to Method 3050 and successfully analyzed for multielements by GFAAS and DCP. The potassium permanganate ($\text{H}_2\text{SO}_4/\text{KMNO}_4$) solutions (Impingers # 5 and 6) were combined and digested as outlined by Method 7470. The solution was then analyzed for mercury (elemental) by CVAAS.

3.3.3.3 Preliminary Test Results -- Multielements

A series of tests was conducted in the 20 million Btu/h demonstration boiler and the 2 million Btu/h research boiler using a deeply-cleaned Taggart seam hvA bituminous coal from Virginia. The coal was cleaned by AMAX using an advanced oil agglomeration process and then processed into a filter cake (Jha et al. 1997). A MCWM was prepared from the filter cake at Penn State. Details as to the preparation process, atomization character and combustion performance of this fuel are provided in Section 5.0. Samples were collected simultaneously at the baghouse inlet and outlet during each test.

Method 29 versus PSU Method

Emissions measured by Method 29 and the PSU Method at the inlet and outlet of the baghouse on the demonstration boiler and at the inlet of the baghouse on the research boiler are given in Figures 3.3.32 through 3.3.34. Emissions are reported in $\text{lb}/10^{12}$ Btu for each of the

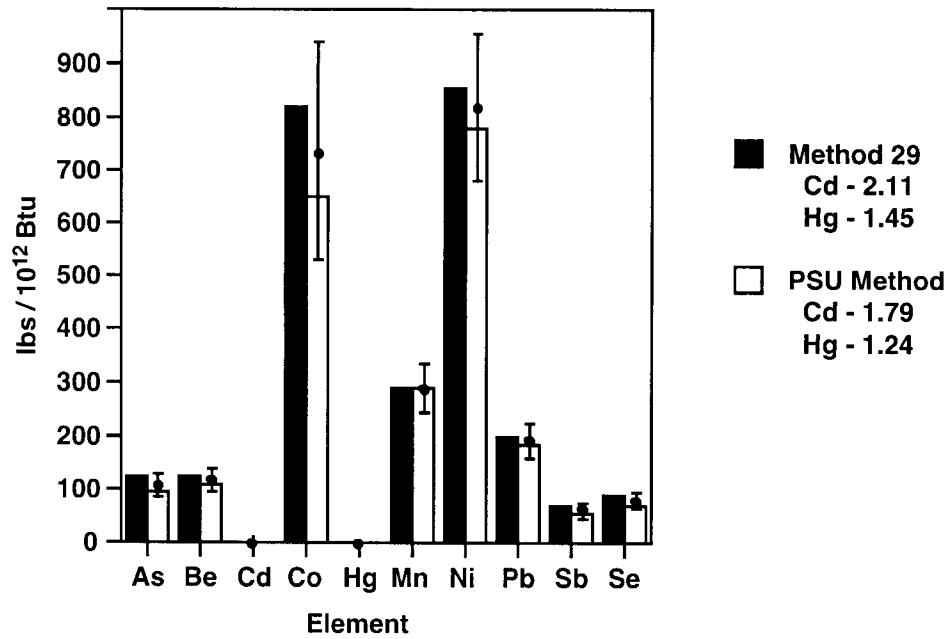


Figure 3.3.32 EMISSIONS MEASURED FOR THE TAGGART FUEL AT THE BAGHOUSE INLET OF THE DEMONSTRATION FACILITY

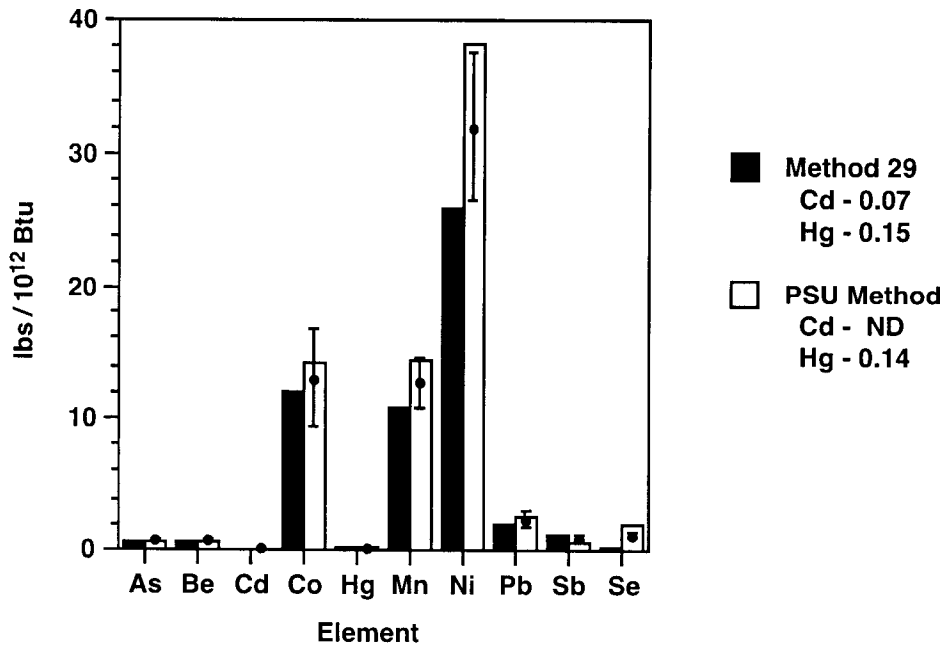


Figure 3.3.33 EMISSIONS MEASURED FOR THE TAGGART FUEL AT THE BAGHOUSE OUTLET OF THE DEMONSTRATION FACILITY

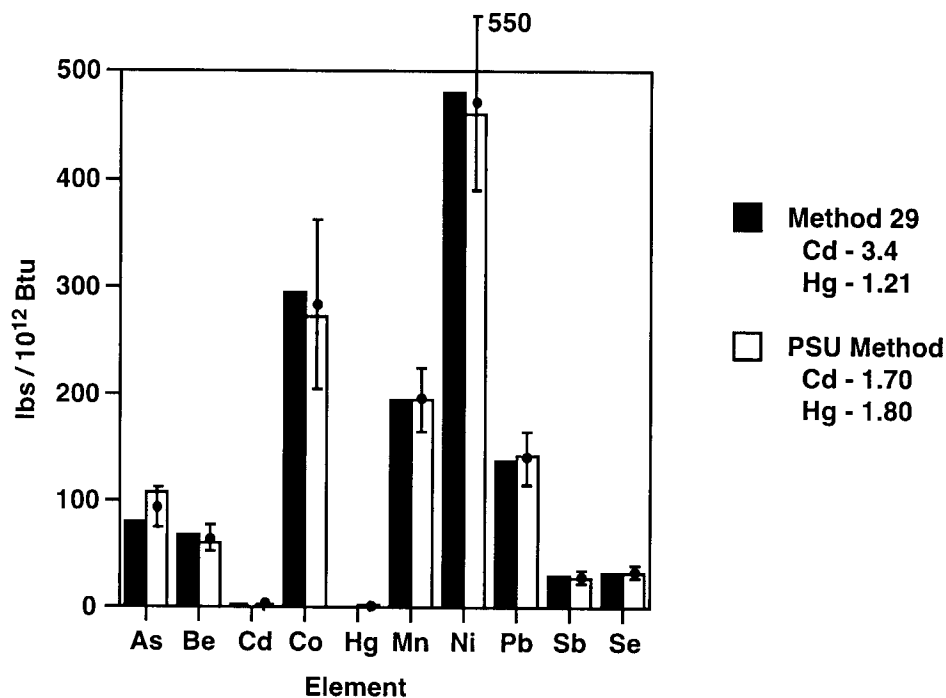


Figure 3.3.34 EMISSIONS MEASURED FOR THE TAGGART FUEL AT THE BAGHOUSE INLET OF THE RESEARCH BOILER

inorganic HAPs previously identified. In general there is good agreement between the Method 29 and PSU Method data for each test based on the reproducibility of Method 29.

Prior experience with Method 29 has shown that there is variability in the data due to sampling, recovery and sample preparation error (Dunham et al., 1998; Heidt and Laudal, 1995). In order to address this issue, a test series was conducted on the Middle Kittanning seam coal (hVA bituminous) from Jefferson County, Pennsylvania to determine the reproducibility of the data. Emission data were obtained for four identical runs conducted in the demonstration boiler. Samples at the baghouse inlet were analyzed and compared. A mean, standard deviation, margin of error and percent margin of error (based on a 95% confidence interval) for each element were calculated (Table 3.3.12).

The percent margin of error is taken to represent the range in values possible during a replicate run attributed to sampling, recovery, and instrument errors combined. The percent margin of error was then applied to the mean values obtained for each element measured by the Method 29 and PSU Method sampling trains. The mean emission of each element measured by the two sample techniques is indicated by a dot on the histogram. The bars represent the range

Table 3.3.12 Reproducibility of Replicate Tests using Method 29 in the Demonstration Test Facility

Element	Mean	Standard Deviation	*Margin of Error	*% Margin of Error
As	177.7	35.5	34.8	± 19.5
Be	164.9	31.8	31.2	± 18.9
Cd	2.6	0.8	0.8	± 30.0
Co	407.6	114.0	111.7	± 27.4
Hg	1.9	0.2	0.2	± 10.3
Mn	217.0	32.5	31.9	± 14.6
Ni	990.5	172.2	168.8	± 17.0
Pb	257.7	45.7	44.7	± 17.3
Sb	192.6	44.2	43.3	± 22.5
Se	68.3	13.3	13.0	± 19.1

* 95% Confidence Interval and n=4

of emission values calculated using the percent margin of error derived for each element. If the range in emission level for a particular element, measured by the two techniques for the Taggart seam fuel, is less than the margin of error obtained for the four Middle Kittanning seam runs, then there is no significant difference in the data measured by the two sampling techniques. The emission levels for cadmium and mercury in Figures 3.3.32 through 3.3.34 are given in the graph legends.

For all the elements measured at the demonstration boiler inlet (Figure 3.3.32) there is good agreement between the two techniques. At the outlet, the difference in the emission level of each element is within experimental error. The only exception is the range in cadmium and selenium, which exceeds the range of experimental error seen in the Middle Kittanning seam runs. The results at the research boiler inlet also show good agreement between the emissions measured by Method 29 and the PSU Method for the multielements, except for mercury. The percent margin of error for mercury was ±10.3% for the four samples at a 95% confidence interval. This compares well to Dunham et al. (1998) who reported ±13% for mercury for the same sample size (n = 4) and confidence interval (95%).

Ontario Hydro Method versus PSU Method

The Ontario Hydro train was run in conjunction with the Method 29 and PSU Method trains during emission tests of the Taggart fuel in the research boiler. Duplicate simultaneous samples were taken at the baghouse inlet and outlet during each test run. The results of the

preliminary tests for selected elements are shown in Figures 3.3.35 and 3.3.36. In general the Ontario Hydro train had consistently lower values, possibly due to the presence of only one H₂O₂ impinger in the sample train. Trace elements were present in the second H₂O₂ impinger in the PSU train. There was fair reproducibility for several elements:

As: 1s within $\pm 19\%$ of X (mean)

Be: 1s within $\pm 9\%$ of X (mean)

Pb: 1s within $\pm 9\%$ of X (mean)

Sb: 1s within $\pm 12\%$ of X (mean)

Se: 1s within $\pm 10\%$ of X (mean)

Method 29 values were within $\pm 1-10\%$ of the mean for the total sample set for each element.

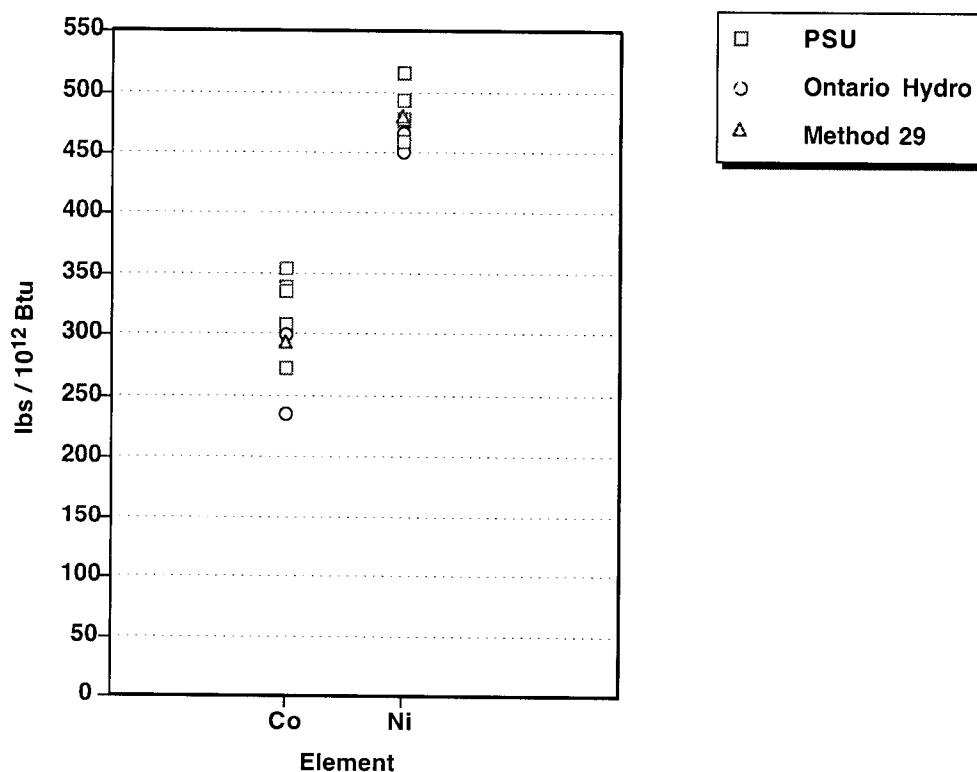


Figure 3.3.35 EMISSIONS DATA OF Co and Ni MEASURED BY MULTIPLE METHODS

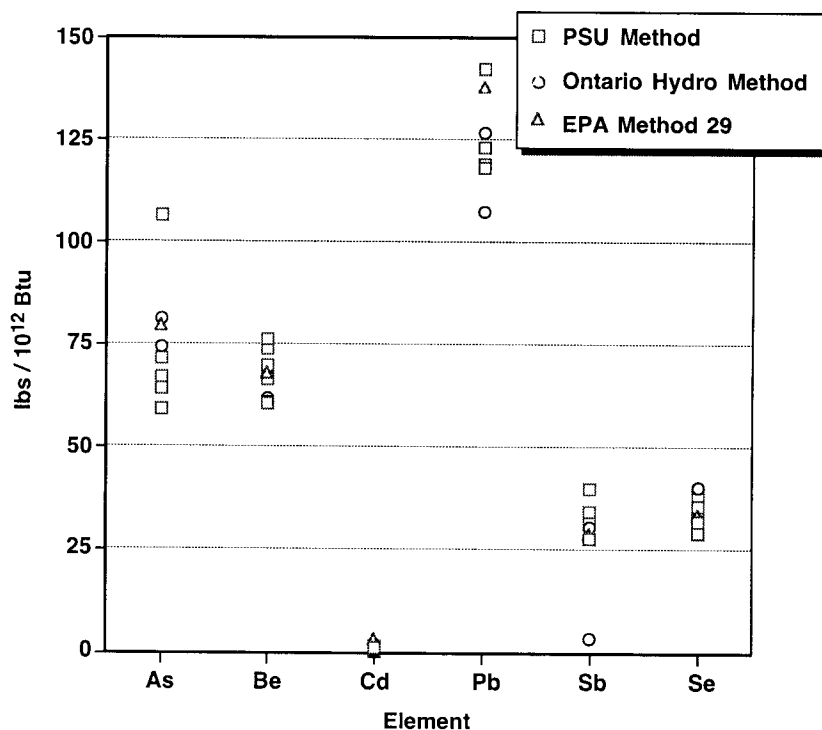


Figure 3.3.36 EMISSIONS DATA OF INORGANIC HAPS MEASURED BY MULTIPLE METHODS

3.3.3.4 Preliminary Test Results – Total Mercury

Method 29 versus PSU Method

The total, particulate (Hg), elemental (Hg^0) and oxidized (Hg^{+2}) mercury levels measured in the demonstration boiler test at the baghouse inlet and outlet are shown in Figure 3.3.37. The impinger solutions that were analyzed for mercury and mercury species for the two trains are indicated on Figure 3.3.30. It is acknowledged that Method 29 is not appropriate for detailed mercury speciation (Laudal et al., 1997). Therefore, the Modified Ontario Hydro method was adopted as the technique best suited to measuring the forms of mercury in the PSU Method.

Theoretically, the inclusion of an extra impinger containing $\text{HNO}_3/\text{H}_2\text{O}_2$ in the PSU train, as compared to the Modified Ontario Hydro train, should have no effect on the amount of mercury trapped. In addition, the interaction between mercury and the solid sample, i.e., ash and char, collected on the filter should be the same for both sample trains.

The total mercury measured by the two techniques in the demonstration boiler was within calculated experimental error. Both methods measured the amount of particulate mercury in

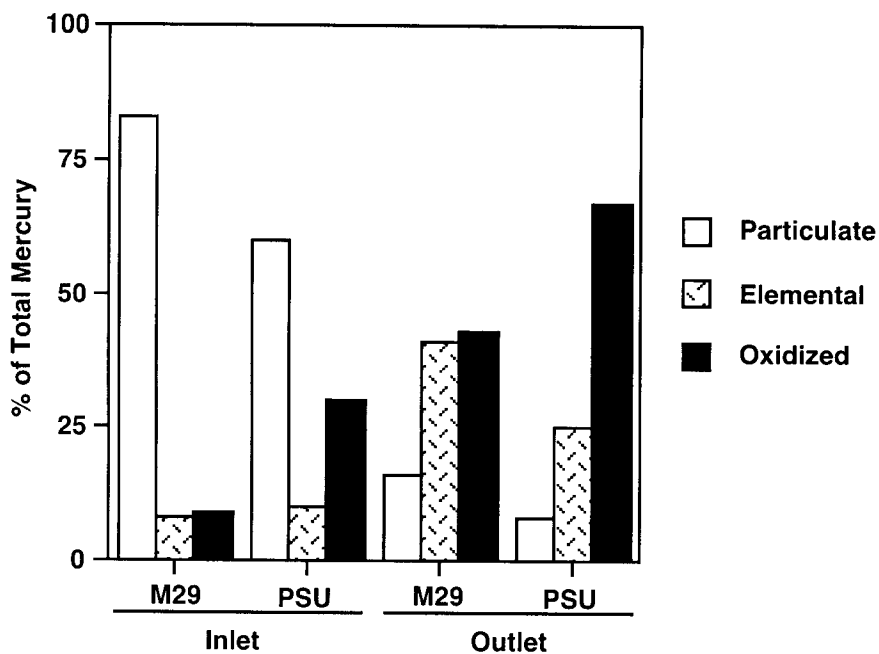


Figure 3.3.37 MERCURY SPECIES MEASURED BY METHOD 29 AND PSU METHOD AT THE DEMONSTRATION BOILER BAGHOUSE INLET AND OUTLET

both tests to within $\pm 10\%$ of an average emissions value. There was little agreement between the two techniques in the amount of Hg^{+2} present in the gas steam. Studies conducted at UNDEERC suggest that Method 29 tends to overestimate the mass percent of oxidized mercury by 10-30% (Zygarlicke and Pavlish, 1997). Interestingly the data presented in Figure 3.3.37 show the amount of Hg^{+2} measured by the PSU Method to be three times greater than that measured by Method 29. The percent of particulate Hg, Hg^0 and Hg^{+2} measured by the PSU Method at the demonstration boiler baghouse inlet was 60, 10, and 30, respectively, and was 8, 25 and 67, respectively, at the baghouse outlet. The reduction in particulate Hg was expected. The change, i.e., reduction in solid phase Hg and increase in Hg^{+2} , in the partitioning of mercury between the inlet and outlet, indicated by the two methods, was similar. There was no change in the level of Hg^0 emissions. It should be stressed that the mercury concentrations in the samples analyzed for Hg^{+2} were at or below instrument detection limits.

PSU Method versus Ontario Hydro Method

Tests were conducted to compare the total mercury measured by the Ontario Hydro Method and PSU Method with the new train configuration. Preliminary results with a small

sample size at the baghouse inlet (n=5, PSU Method; n=4, Ontario Hydro Method) and outlet (n=4, PSU Method; n=3, Ontario Hydro Method) are shown graphically in Figures 3.3.38 and 3.3.39.

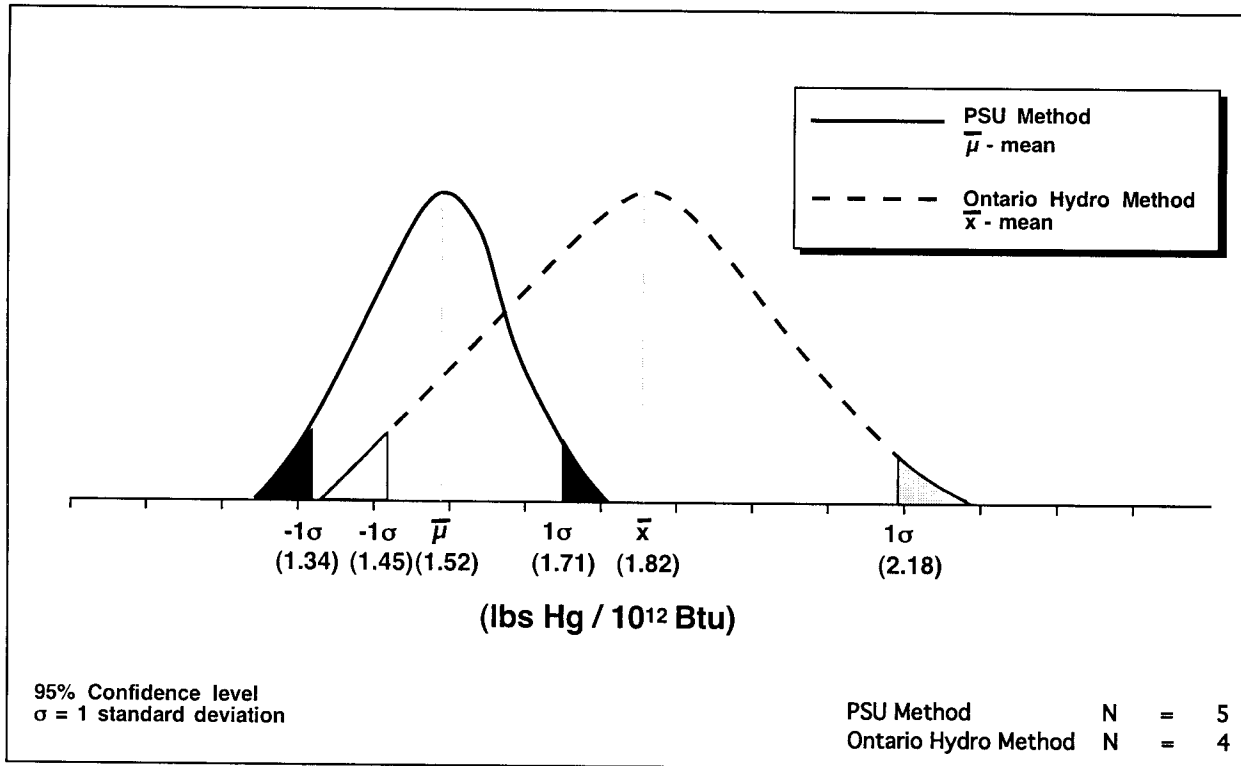


Figure 3.3.38 PRELIMINARY STATISTICAL REPRESENTATION OF TOTAL MERCURY DATA OBTAINED VIA THE PSU METHOD AND ONTARIO HYDRO METHOD AT THE BAGHOUSE INLET

Surprisingly, the means for the two sample sets were within one standard deviation of each other in spite of the small sample sizes. This implies that the two sample sets are from the same population. In theory, the statistical distribution of the two sample sets should approximate one another as the number of tests is increased. The data was assumed to be distributed normally.

3.3.3.5 Further Test Results

The preliminary test results suggested that the PSU Method performed as well as Method 29 for multielements and the Ontario Hydro Method for mercury speciation. Therefore, additional tests were conducted to expand the statistical database to confirm the preliminary test results. Duplicate simultaneous tests were performed at the inlet and outlet of a baghouse using

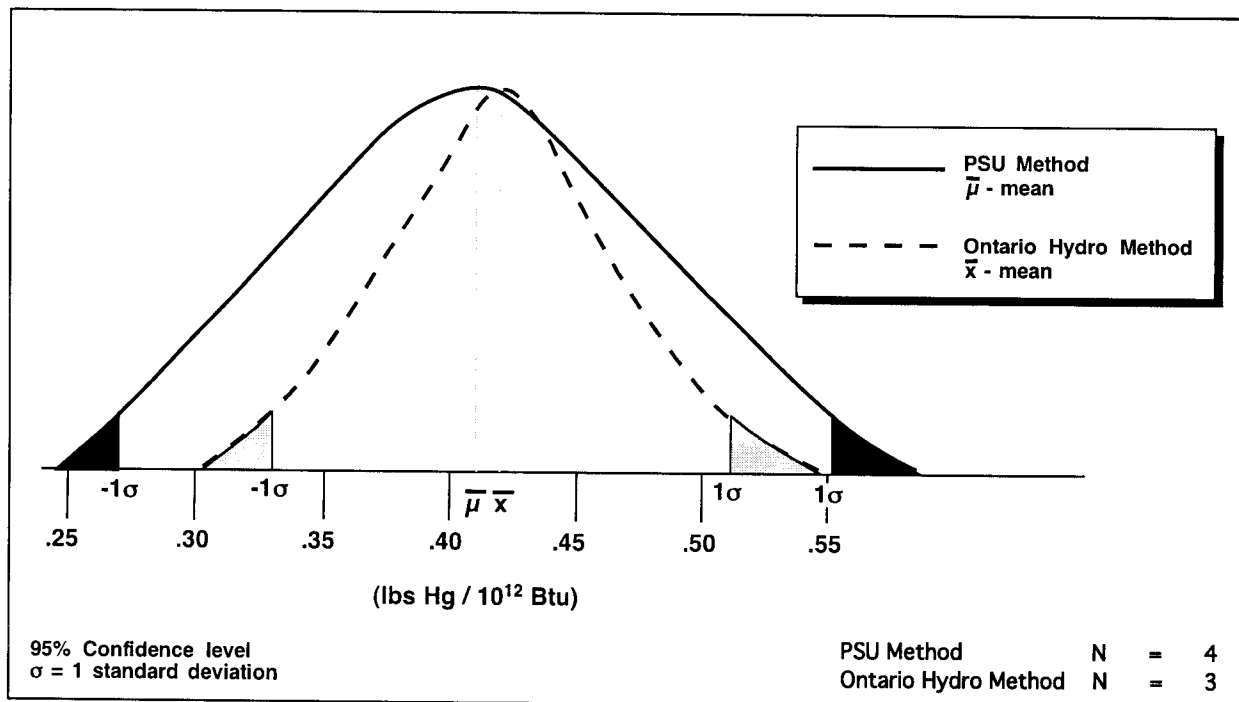


Figure 3.3.39 PRELIMINARY STATISTICAL REPRESENTATION OF TOTAL MERCURY DATA OBTAINED VIA THE PSU METHOD AND ONTARIO HYDRO METHOD AT THE BAGHOUSE OUTLET

the PSU Method, EPA Method 29 and Ontario Hydro Mercury Speciation Method sample trains. A total of fourteen tests were conducted on the 2 million Btu/h research boiler firing deeply-cleaned Taggart seam (Virginia), hvA bituminous coal as MCWM. Similar combustion conditions were maintained during all test runs. Coal analysis and average flue gas composition are given in Table 3.3.13.

Laudel et al. studied the effects of flue gas constituents on mercury speciation (Laudal, Brown and Nott, 1998). They evaluated the presence of SO₂, HCl, Cl₂, NO, NO₂, and fly ash individually and in different combinations at different concentrations on the oxidation of elemental mercury. The study concluded that Cl₂ present at 10ppm has a significant effect on mercury speciation as measured by the Ontario Hydro Mercury Speciation Method. However, it is not known if Cl₂ is present at such levels in coal flue gas. There is significant interaction, i.e., oxidation of elemental mercury, with fly ash, NO_x (NO/NO₂ at 600/30ppm), HCl (50ppm) and SO₂ (1,500ppm) when present in various combinations resulting in over estimation of oxidized mercury. HCl alone has little effect on mercury speciation at typical baghouse and stack temperatures. The concentration of SO₂ and HCl in the Taggart flue gas was significantly lower

Table 3.3.13 Average Coal, Fuel and Flue Gas Composition for Test Runs

<u>Coal Composition</u> <u>(Wt. %)</u>	<u>Coal</u> <u>(dry basis)</u>	<u>MCWM</u> <u>(as fired)</u>
C	85.1	51.9
H	5.6	3.4
O	5.5	3.3
N	1.5	0.9
S	0.7	0.4
Ash	1.7	1.0
H ₂ O	0	39.0
<u>Trace Elemental Analysis</u>		
<u>MCWM (as-fired)</u>	<u>µg/g</u>	<u>lbs/10¹²Btu</u>
As	1.32	144.2
Be	0.87	95.0
Cd	<0.04	<4.26
Co	5.22	570.2
Hg	0.031	3.4
Ni	6.97	761.3
Pb	2.77	302.6
Sb	0.9	98.3
Se	1.31	143.1
Sr	17.42	1,902
Cl*	85.4	9,100
<u>Flue Gas Composition</u>		
<u>(Vol %, dry basis)</u>		
CO ₂	13.6	
H ₂ O	(14.8)	
SO ₂	0.0296	
NO _x	0.0464	
O ₂	3.61	
HCl**	0.001069	

*Cl analysis provided by AMAX Research and Development Center

**Theoretical calculation assuming all Cl in the fuel is converted to HCl. This assumption is based on reports in which Cl₂ generally makes up only 5 to 7% of the total chloride (Cl₂ + HCl).

than the concentrations cited and therefore should not compromise the Ontario Hydro Mercury Speciation Method. The concentration of NO_x (464ppm) in the Taggart flue gas approached the concentration of 600ppm used by Laudal et al. (1998) suggesting that it may have some effect in oxidizing elemental mercury in the presence of fly ash.

The level of unburned carbon in the fly ash collected on the inlet filter was also high which may have compromised the speciation data. However, it should be noted that the PSU Method and Ontario Hydro Mercury Speciation Method train configurations, recovery and analysis are the same with regards to mercury speciation; therefore, any bias in speciation measurements would be reflected equally in both methods.

DeVito and Rosenhoover (1997) reported emissions measured by Method 29 from coal-fired power plants using coals having chlorine concentrations ranging from 300 to 1400 $\mu\text{g/g}$. The Taggart fuel contained only 85.4ppm chlorine. The study by DeVito and Rosenhoover showed good closure for coals containing 0.11 to 0.16% (db) chlorine as compared to the Taggart fuel that contained 0.014% (db) chlorine. This suggests that the data obtained by Method 29 from the Taggart fuel would not be compromised with regards to the content of chlorine in the fuel.

Statistical Analysis

The data were analyzed using a statistical software package via a two sample t -test with unpaired, i.e., unequal, variances (MINITAB Release 10Xtra 1995). A standard t -test assumes that the two samples come from populations with the same standard deviation/variance. If the standard deviations in the two groups are markedly different, the above assumption does not hold. An approximate test, i.e., the unpaired two sample t -test, allows for statistical comparison of unequal standard deviations/variances. The test determines whether both sample sets represent the same distinct population by determining the difference between the means of the two sets of observations and the sample variance. This test was also chosen due to the limited degrees of freedom of some of the elemental sample sets. The sample sets are assumed to be independent and quantitative and plausibly normal (Statistics at Square One 2000). A probability (P) is calculated for $\mu_1 - \mu_2$, where μ represents the mean for each population and tests $H_0: \mu_1 = \mu_2$ versus $H_1: \mu_1 \neq \mu_2$. H_0 represents the null hypothesis in which the two data sets are not distinct and represent the same statistical population. Rejecting the null hypothesis, i.e.,

accepting H_1 , means that the two data sets are distinct and could not have been sampled from the same population. The calculated P is the probability that the two sample sets would be obtained by sampling the same population for a given element.

The standard deviation of $\bar{x}_1 - \bar{x}_2$ is estimated by:

$$s = \sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}$$

where \bar{x} is the sample mean, s is the sample standard deviation and n is the sample size for each sample set. The test is based on the statistic that $t = (\bar{x}_1 - \bar{x}_2) / s$. This statistic has approximately a t-distribution with the degrees of freedom given by:

$$df = \frac{(VAR_1 + VAR_2)^2}{\left[\frac{(VAR_1)^2}{(n_1 - 1)} \right] + \left[\frac{(VAR_2)^2}{(n_2 - 1)} \right]}$$

where VAR is the sample variance for each sample set. The confidence interval is given by $(\bar{x}_1 - \bar{x}_2) - ts$ and $(\bar{x}_1 - \bar{x}_2) + ts$ where t is the value from the t -table corresponding to a specific confidence interval. In this case a 95% confidence interval was used. The probability (P) that a value exceeds the confidence interval is 0.05 at 1.96 standard deviations, marking the points within which 95% of the observations lie. This means that the null hypothesis ($H_0: \mu_1 = \mu_2$) is accepted if the calculated probability (P) is > 0.05 and rejected if P is ≤ 0.05 .

It was necessary to determine if the PSU Method produced data that were statistically similar or different than data produced by Method 29 and the Ontario Hydro Mercury Speciation Method for HAPs and mercury species. Before accepting the PSU Method, it is necessary to accept the null hypothesis ($H_0: \mu_1 = \mu_2$), when comparing the data sets obtained by Method 29 and the PSU Method for multielements and when comparing the sample sets obtained by the Ontario Hydro and PSU Methods for mercury species. Descriptive statistics were also performed to determine the reproducibility of each of the methodologies. Statistical analysis was performed on the inlet and outlet samples for all trace elements and mercury species.

Results and Discussion – Multielements and Total Mercury

Quality of Methodology

Average percent closure across the baghouse for the two methodologies is given in Table 3.3.14. The baghouse ash and fuel were analyzed in the same manner as the particulate samples collected by the sample trains. Average burnout values were calculated from a series of ash samples collected during a test and ranged from 96 to 99 wt%. UNDEERC reported excellent mercury mass balances at $\pm 15\%$ for measurements made at a series of power plants. DeVito et al. (1993) reported that total mercury measurements obtained by Method 29 from a pilot-scale combustor had an accuracy of 20-40%. DeVito and Rosenhoover (1997) later reported on the fate of mercury in coal-fired power plants equipped with wet scrubbers. They sampled flue gas using a Method 29 and an Ontario Hydro sampling train. The Method 29 train was modified to include two deionized water impingers prior to the nitric acid/peroxide impingers. The percent closure reported for mercury for three plants (eleven material balances total) ranged from 72 to 131% with an average of 100%. For each plant the average closure was 103%, 85% and 115%, respectively. The percent closures were within the QA project objective of $\pm 20\%$ closure for the average material balance and no test closure being greater than $\pm 30\%$. The material balances obtained by the PSU Method and Method 29 for mercury are within those obtained by DeVito et al. (1993), DeVito and Rosenhoover (1997) and UNDEER (University of North Dakota Energy and Environmental Research Center 1999).

Table 3.3.14 Average Percent Closure across the Baghouse

Element	PSU Method	Method 29
As	73	110
Be	113	110
Cd	73	120
Co	118	136
Hg	81	110
Ni	110	116
Pb	101	93
Sb	111	113
Se	96	113
Sr	134	52

The material balances of the other elements are within acceptable sampling and analytical error. Miller et al. (1996) reported intralaboratory repeatability for coal analysis averaged 14.6% for trace elements and the percent difference for individual elements ranged from 7.8% for Cr to 33% for Cd.

PSU Method Compared to EPA Method 29

Preliminary tests comparing the sampling and measurement of trace elements by Method 29 and the PSU Method Train were conducted on the Middle Kittanning seam coal (dry micronized coal) fired in Penn State's demonstration boiler. Figure 3.3.40 shows the system capture (lbs/10¹² Btu) measured for a series of elements as a function of method. There was good agreement between the methods. Method 29 tended to overestimate the total mercury as compared to the PSU Method. These preliminary results suggested that a more detailed investigation of the use of the modified Ontario-Hydro Method train as a multielement and mercury speciation method was appropriate.

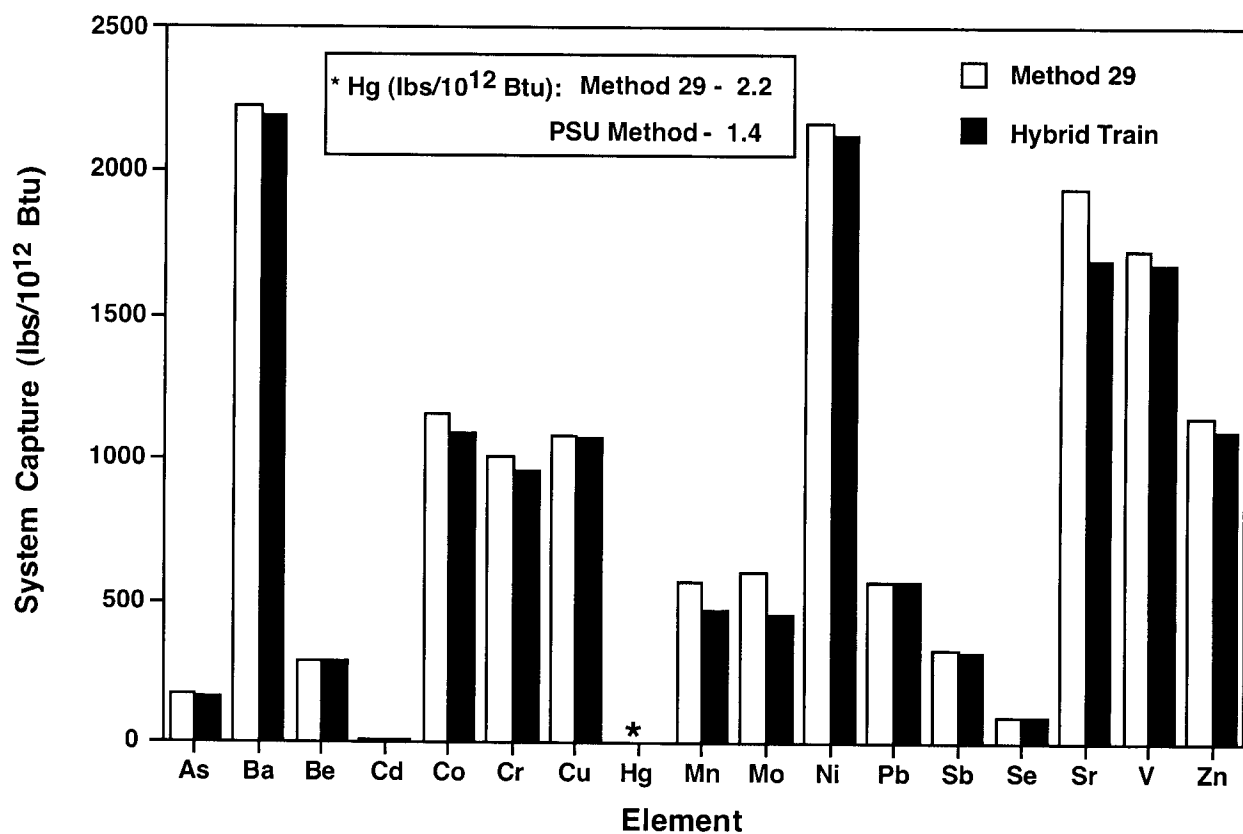


Figure 3.3.40 SYSTEM CAPTURE MEASURED BY METHOD 29 AND PSU METHOD

Statistical analysis of the data collected at the inlet and outlet of the baghouse showed acceptance of the null hypothesis ($H_0: \mu_1 = \mu_2$) for all trace elements. The statistical analysis demonstrated that the two sample sets generated for each element, by the two methods at the inlet, were from the same population at a 95% confidence interval ($P > 0.05$). This was also true of the data sets generated at the baghouse outlet. A plot of P for each element measured at the baghouse inlet and outlet is shown in Figure 3.3.41. The PSU Method produced data for the multielements that were statistically indistinguishable from data produced by Method 29.

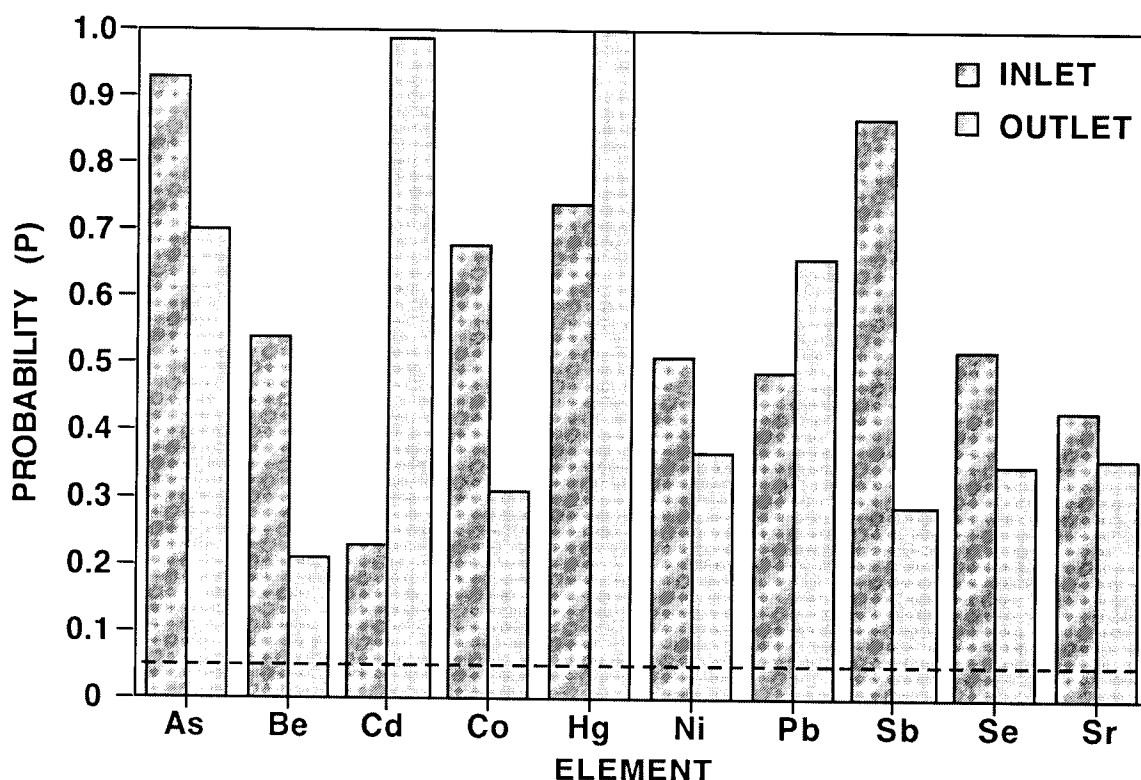


Figure 3.3.41 PROBABILITY DISTRIBUTION OF MULTIELEMENTS MEASURED AT THE BAGHOUSE INLET AND OUTLET AS CALCULATED BY THE TWO SAMPLE T-TEST. (DASHED LINE REPRESENTS $P=0.05$ ACCEPTANCE OF $H_0: \mu_1 = \mu_2$ AT THE 95% CONFIDENCE INTERVAL)

The P calculated at the inlet for all elements ranged from 0.23 for cadmium to 0.93 for arsenic. The P calculated at the outlet for all elements ranged from 0.21 for barium to 1.0 for mercury. Total mercury data had a $P=0.74$ and 1.0 at the inlet and outlet, respectively. Arsenic had a $P=0.93$ and 0.70 in the inlet and outlet sample sets, respectively.

In theory, all else being equal, the P values should be similar at the inlet and outlet, given that the same sampling and analytical methodologies were followed at both sites. However, studies have shown that there are issues of reproducibility for Method 29 (Falcone Miller et al., 1999a, 1999b; Zygarlicke and Pavlish, 1997). These variations are to be expected in the PSU Methodology as well. Therefore the calculated P values will vary reflecting the inherent error in the methodologies. It is noteworthy that the calculated P values for the cadmium data sets measured at the inlet and outlet by the two methods were significantly different, i.e., 0.23 and 0.99, respectively. The only difference between the sampling conducted at the inlet and outlet of the baghouse was the total mass collected of each element. In addition, two more data points for cadmium were available at the baghouse outlet than at the inlet due to operational problems during sampling. This resulted in a difference in the degrees of freedom for the statistical calculations performed on the inlet and outlet data, thereby affecting the t -value for rejecting the H_0 . In addition, the smaller sample size of the Method 29 cadmium data set makes the assumption that the data are representative of the total population less reliable. The mean (\bar{x}), standard deviation (s) and standard error of the mean (s_M) for the two sample sets at the baghouse inlet and outlet are given in Tables 3.3.15 and 3.3.16, respectively. The standard error of the mean is the standard deviation of the sampling distribution of the mean and is defined as:

$$s_M = \frac{s}{\sqrt{n}}$$

Ontario Hydro Mercury Speciation Method Compared to EPA Method 29

Statistical analysis of the data collected at the inlet of the baghouse by the Ontario Hydro Mercury Speciation Method was not possible for all the trace elements, as not all the Ontario Hydro test runs were analyzed for all elements. Therefore, there was an insufficient sample size to run a t -test. Statistical analysis of the mercury data generated by Method 29 and the Ontario Hydro Mercury Speciation Method was possible. The result was acceptance of the null hypothesis ($H_0: \mu_1 + \mu_2$) for total mercury at the inlet ($P=0.97$) and the outlet ($P=0.57$).

Table 3.3.15 Descriptive Statistics for Emissions Measured at the Inlet (Units in lb/10¹²Btu)

Element	METHODOLOGY					
	PSU Method			EPA Method 29		
	(\bar{x})	(s)	(s_M)	(\bar{x})	(s)	(s_M)
As	74.0	18.74	8.38	73.01	9.36	6.61
Be	69.6	6.22	2.78	81.7	19.00	13.5
Cd	1.23	0.54	0.24	2.86	0.79	0.56
Co	322.8	32.6	14.6	358.3	89.8	63.5
Hg	1.36	0.28	0.12	1.31	0.13	0.09
Ni	485.1	20.99	9.38	586.0	148.0	105.0
Pb	124.4	10.44	4.67	131.27	9.44	6.67
Sb	33.2	4.44	1.99	34.35	7.57	5.35
Se	33.6	3.37	1.51	35.58	2.86	2.02
Sr	660.7	163.9	73.3	755.2	106.4	75.2

Table 3.3.16 Descriptive Statistics for Emissions Measured at the Outlet (Units in lb/10¹²Btu)

Element	METHODOLOGY					
	PSU Method			EPA Method 29		
	(\bar{x})	(s)	(s_M)	(\bar{x})	(s)	(s_M)
As	3.51	3.51	1.75	2.58	2.82	1.75
Be	0.60	.013	0.06	2.66	2.62	1.31
Cd	0.22	0.28	0.14	0.23	0.22	0.11
Co	3.82	2.94	1.47	14.8	17.99	9.00
Hg	0.26*	0.07	0.03	0.26*	0.24	0.12
Ni	7.06	1.89	0.95	17.08	19.01	9.51
Pb	3.86	0.37	0.19	5.17	5.42	2.71
Sb	0.40	0.13	0.07	1.34	1.46	0.73
Se	2.38	1.86	0.93	1.15	1.49	0.74
Sr	9.88	4.77	2.39	38.2	52.1	26.1

*Equivalent to 0.28 μ g/m³

Results and Discussion – Mercury Speciation

PSU Method Compared to Ontario Hydro Mercury Speciation Method

The PSU and Ontario Hydro Mercury Speciation Methods measured the oxidized (Hg^+), elemental (Hg^0) and particulate mercury (Hg_p) at the baghouse inlet and outlet. Method 29 samples were analyzed only for total mercury as it has been shown that the method does not accurately measure mercury species (Zygarlicke and Pavlish, 1997; Laudal and Schultz, 1997). Actual measured emissions at the baghouse inlet are shown in Figure 3.3.42.

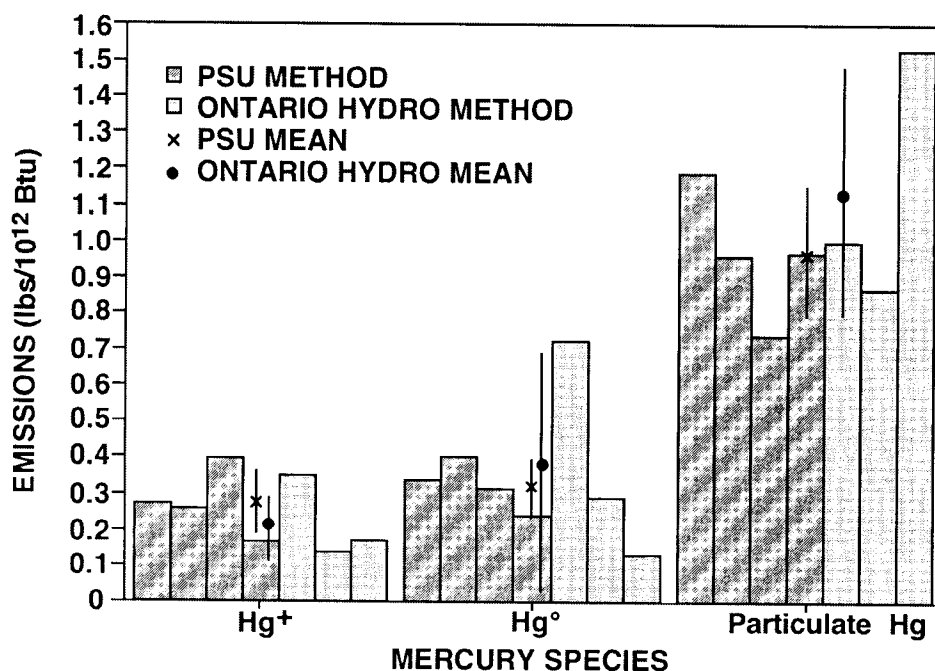


FIGURE 3.3.42 MERCURY SPECIES EMISSIONS MEASURED BY PSU METHOD ($n=4$) AND ONTARIO HYDRO MERCURY SPECIATION METHOD ($n=3$) AT THE BAGHOUSE INLET.

(Bars represent one standard deviation from the mean.)

Statistical analysis of the sample sets showed acceptance of the null hypothesis that the sample sets were equal and derived from the same population. The calculated P values for the different mercury species are shown in Figure 3.3.43. The mercury species data sets generated by the PSU Method and Ontario Hydro Mercury Speciation Method are not distinguishable at a 95% confidence interval and $n=4$. P values for elemental mercury were greatest at 0.77 and 0.73

at the inlet and outlet, respectively. Descriptive statistics for the PSU and Ontario Hydro Mercury Speciation Methods sample sets are given in Tables 3.3.17 and 3.3.18.

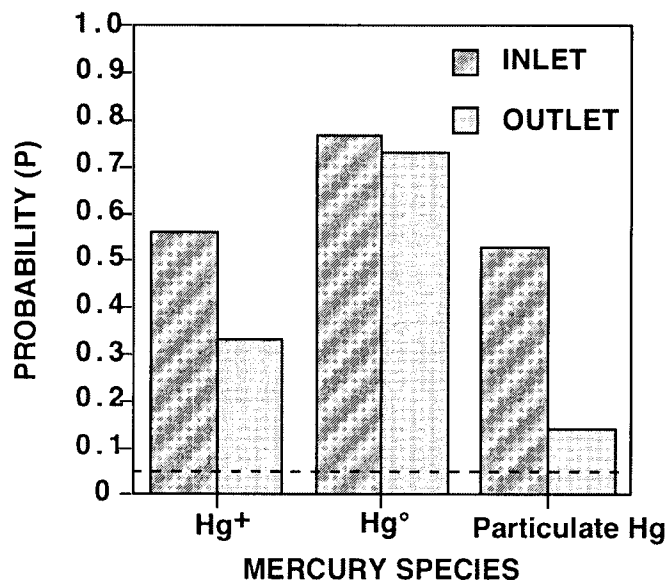


Figure 3.3.43 PROBABILITY (P) CALCULATED BY TWO SAMPLE T -TEST FOR MERCURY SPECIES MEASURED BY THE PSU METHOD AND ONTARIO HYDRO MERCURY SPECIATION METHOD.

(Dashed line represents $P=0.05$ acceptance of $H_0:\mu_1=\mu_2$ at the 95% confidence interval.)

Table 3.3.17 Descriptive Statistics for Mercury Emissions Measured at the Baghouse Inlet (Units in lb/10¹²Btu)

Mercury Species	PSU Method			Ontario Hydro Mercury Speciation Method		
	(\bar{x})	(s)	(s_M)	(\bar{x})	(s)	(s_M)
Hg ⁺	0.27	0.09	0.05	0.22	0.11	0.07
Hg [°]	0.32	0.07	0.03	0.38	0.31	0.18
Hg _P	0.97	0.18	0.09	1.13	0.35	0.20

A significant percentage of the total mercury measured at the inlet is present within the particulate portion, i.e., 48 to 83%. This is not typical of power plant ash. The elevated level of particulate mercury is attributed to the significant amount of carbon present in the char, i.e., 47 to 84%, due to the low level of burnout attained in the test facility and the low ash content of the fuel ($\approx 1.4\%$). The calculated burnout in the baghouse ash averaged 96.1% for the PSU Method

Table 3.3.18 Descriptive Statistics for Mercury Emissions Measured at the Baghouse Outlet (Units in lb/10¹²Btu)

Mercury Species	PSU Method			Ontario Hydro Mercury Speciation Method		
	(\bar{x})	(s)	(s_M)	(\bar{x})	(s)	(s_M)
Hg ⁺	0.17	0.07	0.03	0.13	0.04	0.02
Hg ^o	0.21	0.08	0.04	0.23	0.08	0.04
Hg _p	0.03	0.01	0.00	0.05	0.02	0.01

tests and 96.7% for the Ontario Hydro Mercury Speciation Method tests. Interestingly, there is a correlation of 0.61 between the percent of carbon present in the char and the percent of particulate mercury measured at the inlet and outlet. This supports the work of others showing the interaction of mercury in the gas phase with char (Livengood et al., 1994; Senior et al., 1997).

The concentration of mercury in the fuel was quite low (0.031 μg/g or 3.31 lbs Hg/10¹² Btu). The coal was cleaned by oil agglomeration making it less than ideal from the standpoint that the total mass of mercury in the system during testing was quite low. The test results represent a worst-case scenario for the methodologies given the high percentage of carbon in the char and low mercury levels.

3.3.3.6 Comparison of PSU Method to ATS Unified Method

ATS conducted comparative sampling of air toxic emissions from DOE's 500 lb/h combustor at the National Energy Technology Laboratory located in Pittsburgh, Pennsylvania. ATS evaluated two sampling methodologies (ATS Methods 1 and 2) in conjunction with the Method 29 and Ontario-Hydro Method (Advanced Technology Systems, Inc 1996a, 1996b). Four tests were conducted during which two different methodologies were run simultaneously. The ATS Methods 1 and 2 are quite different from the PSU Method proposed here (Figure 3.3.44). ATS Method 1 combines the first four impingers (1 M KCl and acidified H₂O₂) of the Ontario-Hydro Method. ATS Method 2 replaces the KCl reagent with 0.5% BaCl₂ combined with acidified H₂O₂.

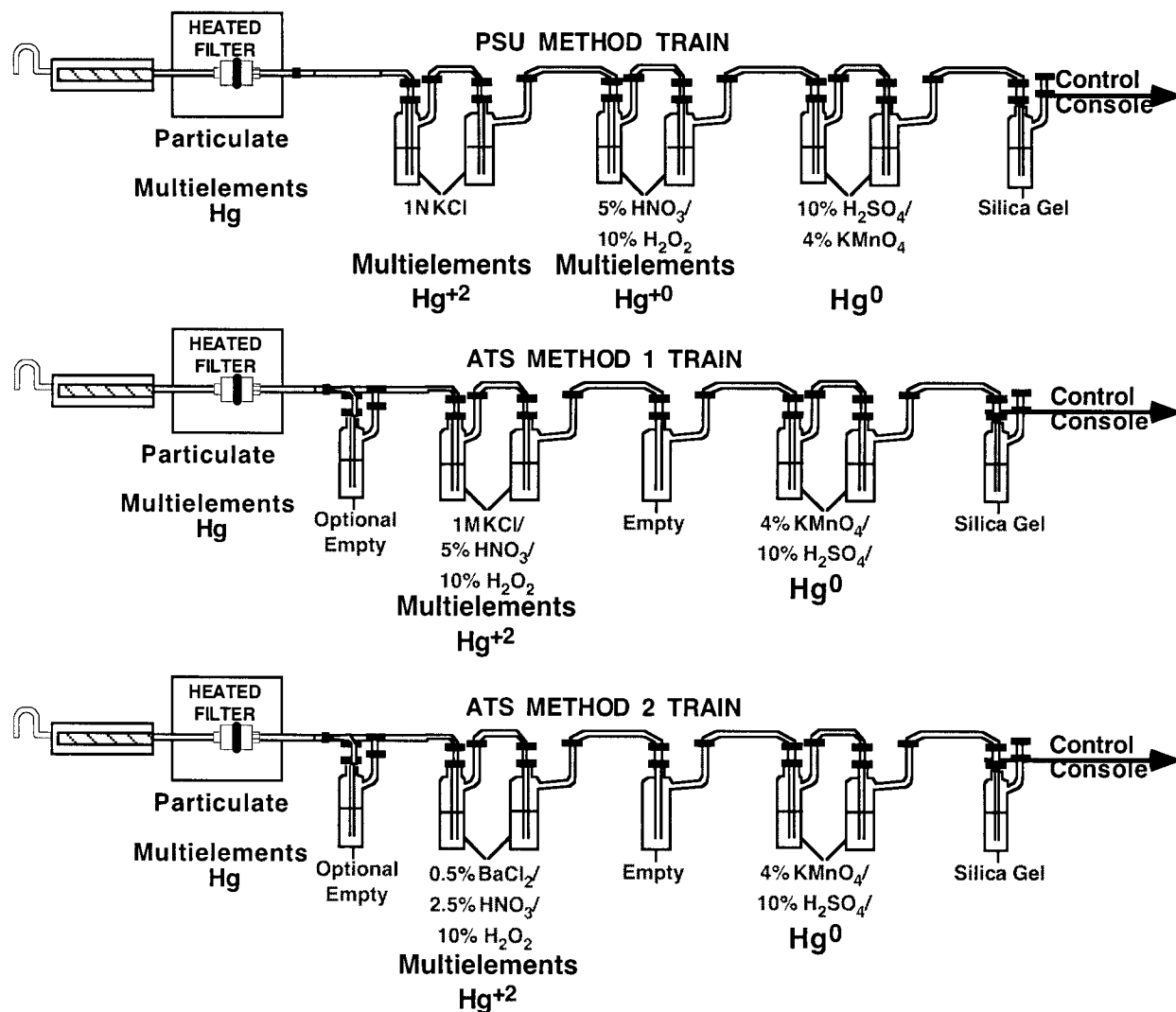


Figure 3.3.44 PSU AND ATS METHOD TRAINS

In both methodologies, multielements were analyzed in the KCl and BaCl₂ reagents by Inductively Coupled Argon Plasma Atomic Emission Spectroscopy (ICPAES). This analytical technique is appropriate for analysis for multielements in the H₂O₂ impinger solution in Method 29 as recommended by EPA SW 846 Method 6010 (U.S. EPA, 1988). The use of ICP and GFAAS for analysis of the combined KCl and H₂O₂ impinger solutions is not appropriate due to the effect of chlorine on sample viscosity and reduced detection levels. ATS has acknowledged that the use of an ICP and GFAAS for analyzing multielements is not appropriate for the combined KCl and H₂O₂ impinger (ATS Method 1) and the BaCl₂ impinger (ATS Method 2) (McManus, 1999). A significant percentage of the concentrations measured by the ICP and

GFAAS were below instrument detection level. This is not to say that the sample train set up is flawed but rather the analytical protocol used is inappropriate. Therefore, the multielemental data presented by ATS in their reports on “Comparative Method Evaluation for the Assessment of Mercury and Other Metal Air Toxic Emissions from a Pilot-Scale Combustion Unit” dated August and November 1996 is suspect (Advanced Technology Systems, Inc 1996a, 1996b). The ATS Method 1 may be appropriate if another analytical protocol is developed, however, it is our understanding that there is no future plans for additional testing by ATS of their proposed methodologies.

3.3.3.7 Conclusions

Statistical analysis of the data verified the use of the PSU Method for measuring trace elements and mercury species in combustion flue gas. Two sample sets generated for each element by the PSU Method and Method 29 at the inlet were from the same population at a 95% confidence interval ($P > 0.05$). This was also true of the data sets generated at the baghouse outlet. The PSU Method produced data for the multielements that were statistically indistinguishable from data produced by Method 29. The P calculated at the inlet for all elements ranged from 0.23 for cadmium to 0.93 for arsenic. The P calculated at the outlet for all the elements ranged from 0.21 for barium to 1.0 for mercury. Total mercury data had a $P=0.74$ and 1.0 at the inlet and outlet, respectively. Arsenic had a $P=0.93$ and 0.70 in the inlet and outlet sample sets, respectively. Statistical analysis of the sample sets also showed acceptance of the null hypothesis that the sample sets generated by the PSU Method and Ontario Hydro Mercury Speciation Method were equal and derived from the same population with regard to the measurement of mercury species in the flue gas.

The statistics reflect the sometimes high variance in the data obtained by both methodologies for particular elements. This variance is attributed to the issue of reproducibility due to procedural and analytical error. However, both methods produced similar means and levels of variance so as to be statistically indistinguishable. This new method represents a time and cost savings for the complete characterization of trace elements in combustion flue gas.

The study suggests that the PSU Method is capable of simultaneously sampling all inorganic trace elements listed as HAPs and mercury species, and produces data which are