

FINAL TECHNICAL REPORT  
September 1, 2006, through December 31, 2007

Project Title: **LIFE CYCLE ASSESSMENT OF MERCURY IN ILLINOIS COALS**

ICCI Project Number: 06-1/10.1A-7  
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ABSTRACT

Mercury is associated mostly with pyrite in Illinois coals. Conventional and advanced physical coal cleaning processes remove part of the mercury from in-ground Illinois coals. During combustion in utility boilers, mercury in coal transforms into three species: ionic mercury ( $\text{Hg}^{2+}$ ), particulate mercury ( $\text{Hg}_p$ ), and elemental mercury ( $\text{Hg}^0$ ). Unlike  $\text{Hg}^0$ ,  $\text{Hg}^{2+}$  is highly soluble in water and can be captured in wet flue gas desulfurization (WFGD) processes.  $\text{Hg}_p$  is mostly associated with unburned carbon in fly ash and bottom ash. It can also be present in the WFGD gypsum byproduct. Fly ash  $\text{Hg}_p$  is captured in particulate control devices such as an electrostatic precipitator (ESP).

The objective of this study was to quantify the fate of mercury in Illinois coal during physical cleaning, combustion in a utility boiler, flue gas cleaning in a WFGD, and byproducts disposal. Around six hundred samples of an as-mined Illinois coal, clean coal, rejects, and liquid effluents at a coal preparation plant, and representative samples of coal, bottom ash, fly ash, limestone, make-up water, WFGD sludge, and liquid effluents at a power plant were collected. The power plant samples were collected while gas-phase mercury concentrations were measured at various locations. The solid samples were characterized for Hg content, proximate analysis, heating value and sulfur content, and liquid samples were characterized for Hg content. Data were analyzed and interpreted using statistical models. Detailed mass balance calculations were conducted to quantify the fate of mercury in various stages of processing and combustion.

The results of this study revealed that the coal cleaning process removed 40 to 50% (lbs/trillion BTU basis) of mercury from the as-mined raw coal. The average mercury reduction at the power plant was around 63% in non-ozone season (when selective catalytic reduction unit was not in operation) and around 40% in ozone season. During the ozone season, the concentration of mercury was lower in the FGD gypsum cake and higher in the FGD waste water than their counterparts during the non-ozone season. The fly ash had comparable mercury content in ozone and non-ozone seasons. The results from a cost study revealed that a mercury compliance coal would provide an economic alternative to installation of activated carbon injection (ACI) to meet Illinois mercury rule if it costs less than \$4/ton above the cost of the coal currently burnt at the power plant.

## EXECUTIVE SUMMARY

In March 2005, the US EPA issued the Clean Air Mercury Ruling (CAMR) to permanently cap and reduce mercury emissions from coal-fired power plants in the United States (47% by 2010 and 79% by 2018). The state of Illinois has a more stringent mercury emission control (90% reduction) for coal fired power plants by mid-2009.

Mercury is associated mostly with pyrite in Illinois coals. During conventional and advanced physical coal cleaning processes, part of the mercury in the in-ground coal is removed. Mercury remaining in cleaned coal transforms into three forms during combustion in a utility boiler: particulate mercury ( $Hg_p$ ), ionic mercury ( $Hg^{2+}$ ), and elemental mercury ( $Hg^0$ ).  $Hg_p$  is mostly associated with unburned carbon in fly ash and to a lesser extent with the bottom ash. Fly ash  $Hg_p$  is captured in particulate control devices such as an electrostatic precipitator (ESP) or a fabric filter (FF). It can also be present in the wet flue gas desulfurization (WFGD) gypsum byproduct.  $Hg^{2+}$  is highly soluble in water and can be easily captured in a limestone-based WFGD.  $Hg^0$  is generally more difficult to capture and in the absence of a mercury control process, such as carbon injection, is mostly released to the atmosphere.

The objective of this study was to quantify the fate of mercury in Illinois coal during physical cleaning, combustion in a utility boiler, flue gas cleaning in a WFGD, and byproducts disposal. The main goal was to gain more insight than currently available on the fate of mercury from mining to combustion and byproducts disposal and provide an assessment of the effectiveness of various mercury control options for Illinois coals.

To accomplish the objectives of this study, about six hundred samples from a coal preparation plant (CP-1) and a power plant (PP-1) located in Illinois were collected. The coal preparation plant (CP-1) employed gravity and cyclone separation for coal cleaning. Representative samples of the as-mined coal, magnetite, clean coal, rejects, and liquid effluents at several locations of the preparation plant were collected. The sampling at CP-1 was conducted for two days in April 2007 (non-ozone season) and for two days in May 2007 (ozone season).

The power plant had two cyclone boilers, two selective catalytic reduction units (SCR), two electrostatic precipitators (ESP), one wet flue gas desulfurization (WFGD) unit and one stack to treat the combined flue gases of the two units. Representative samples of feed coal, bottom ash, fly ash, limestone, make-up water, WFGD sludge (gypsum) and liquid effluents were collected at the power plant. The samples were collected while gas-phase mercury concentrations were measured at SCR inlet, SCR outlet, FGD inlet, and at the stack. The Western Kentucky University performed the gas-phase mercury measurements. The sampling at the PP-1 was conducted for three days in April 2007 (non-ozone season) and for three days in May 2007 (ozone season).

Four sets of samples, two sets collected in non-ozone season and two sets collected in ozone season, each from CP-1 and PP-1 (total eight sets of samples) were selected for processing and characterization using ASTM standards and methods. Analysis performed

included total moisture in the solid and coal samples, Hg content, proximate analysis, heating value and sulfur content. The liquid samples were characterized for Hg content.

Data generated were analyzed and interpreted using statistical models (Excel 2003 data analysis software) to establish consistency of the results. Detailed mass balance calculations were performed on Excel spread sheets to quantify the amount of mercury in various stages of processing and combustion.

The mass balance of mercury for CP-1 for four sets of samples (collected at an interval of more than one month) was between -10 to 13%. Coal cleaning reduced the mercury content by an average of around 57 wt% or about 40% to 50% on lbs/trillion BTU basis.

There was no significant variation in mercury content in the feed coal at the power plant. The average variation between the mercury input and output for the each of two sets of sample collected in the non-ozone and ozone seasons was 4% and 10%, respectively. Overall, the mass balance of mercury for four sets of samples collected at an interval of more than one month ranged between -5 and 23 %. The average mercury reduction at the power plant was around 63% in non-ozone season (when the selective catalytic reduction unit was not in operation) and around 40% in ozone season. During the ozone season, the concentration of mercury was lower in the FGD gypsum cake and higher in the FGD waste water than their counterparts during the non-ozone season. During the non-ozone season, more than 50% of mercury removed was contained in the FGD cake. There were no significant differences in mercury content of the fly ash samples during the ozone or non-ozone season.

A preliminary cost study was performed to assess the relative cost benefit from additional coal cleaning (40%) to achieve the same level of mercury control (85%) with activated carbon injection (ACI). For the PP-1 power plant, about 85% Hg removal was required to achieve the mercury emissions within the Illinois regulation limit of 0.008 lb/GWh. The Integrated Environmental Control Model (IECM, May, 2007) developed by Carnegie Mellon University was used in the analysis. The results showed that a mercury-compliance coal would provide an economic alternative to installation of ACI to meet Illinois mercury rule if it costs less than \$4/ton above the cost of the coal (\$35/ton) currently burnt at the power plant. Further studies are required to determine if sufficient mercury removal through coal cleaning could be achieved to meet emission standards.

## OBJECTIVES

The objective of this study was to quantify the fate of mercury in Illinois coal during physical cleaning, combustion in a utility boiler, flue gas cleaning in a wet flue gas desulfurization (WFGD), and byproducts disposal. The goal was to gain more insight on the fate of mercury from mining to combustion and byproducts disposal.

## INTRODUCTION AND BACKGROUND

Over 81 percent of Illinois coal produced is purchased by the electric utility industry. According to the Toxic Release Inventory (TRI) report of the US EPA, electric utilities reported the largest air emissions of any industry sector of the US, with 68% (96,663 pounds) of all air emissions of mercury and mercury compounds in the year 2005. While overall air emissions of mercury and mercury compounds decreased, air emissions from electric utilities increased by almost 2,100 pounds (2%), from 94,571 pounds in 2004 to 96,663 pounds in 2005<sup>(1)</sup>. As per the TRI Explorer Report, a total of 6,019 lbs of mercury and mercury compounds in the solid, liquid, and gaseous forms were disposed or released in the year 2005 in the state of Illinois by electric utilities, of which 4,164 lbs were released to the air<sup>(2)</sup>.

In March 2005, the US EPA issued the Clean Air Mercury Ruling to permanently cap and reduce mercury emissions from coal-fired power plants in the United States (47% by 2010 and 79% by 2018). Illinois has a more stringent mercury emission control (90% reduction) for coal fired power plants in Illinois by mid-2009.

Mercury is associated mostly with pyrite in Illinois coals. During conventional and advanced physical coal cleaning processes part of the mercury in the in-ground coal is removed. Mercury remaining in cleaned coal transforms into three forms during combustion in a utility boiler: particulate mercury ( $Hg_p$ ), ionic mercury ( $Hg^{2+}$ ), and elemental mercury ( $Hg^0$ ).  $Hg_p$  is mostly associated with unburned carbon in fly ash and to a lesser extent with the bottom ash. Fly ash  $Hg_p$  is captured in particulate control devices such as an electrostatic precipitator (ESP) or a fabric filter (FF). It can also be present in the wet flue gas desulfurization (WFGD) gypsum byproduct.  $Hg^{2+}$  is highly soluble in water and can be easily captured in limestone-based WFGD processes.  $Hg^0$  is generally more difficult to capture and in the absence of a mercury control process, such as carbon injection, is mostly released to the atmosphere.

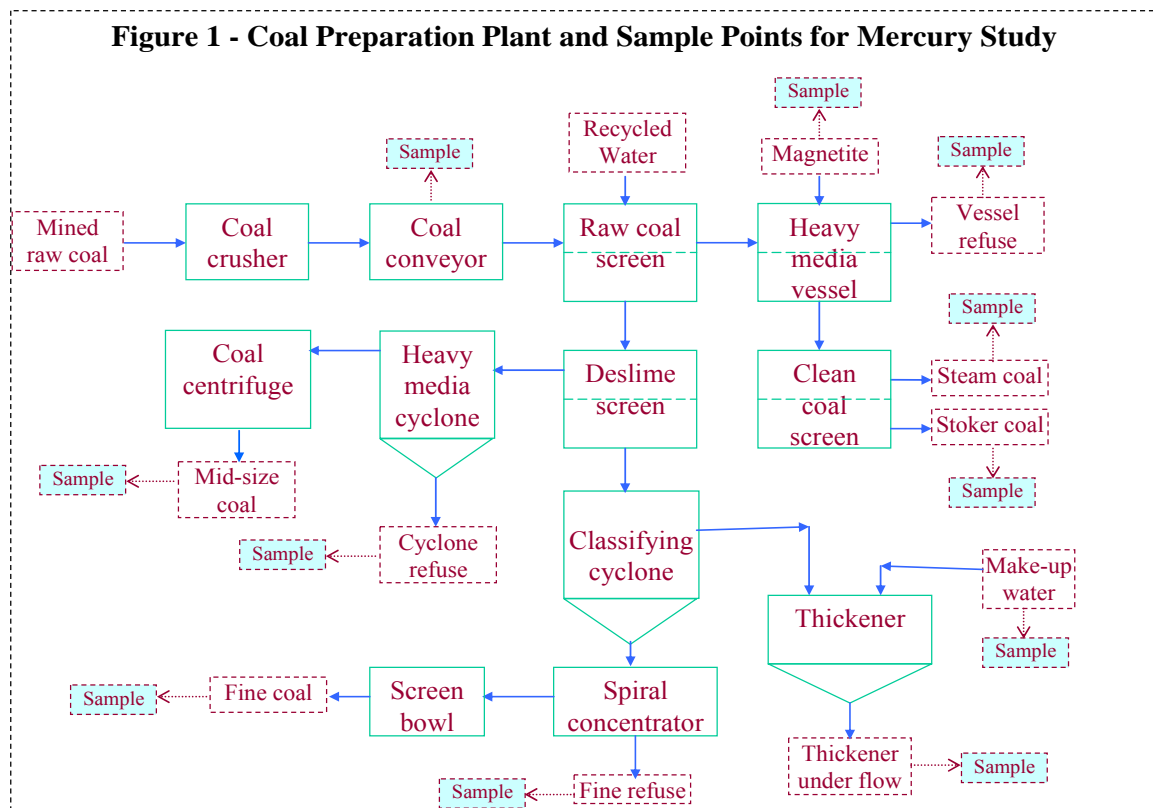
In this study about six hundred samples from a coal preparation plant (CP-1) and a power plant (PP-1) equipped with a SCR and a WFGD were collected in April 2007 (non-ozone season for the power plant) and in May 2007 (ozone season for the power plant). In addition, gas-phase mercury concentrations were measured at several locations at the power plant during this period. The data generated from characterization of the samples, gas-phase mercury measurements, and mercury mass balance calculations were used to determine the level of mercury reduction during the coal cleaning and post-combustion flue gas cleaning.

## EXPERIMENTAL PROCEDURES

### Sample Collection

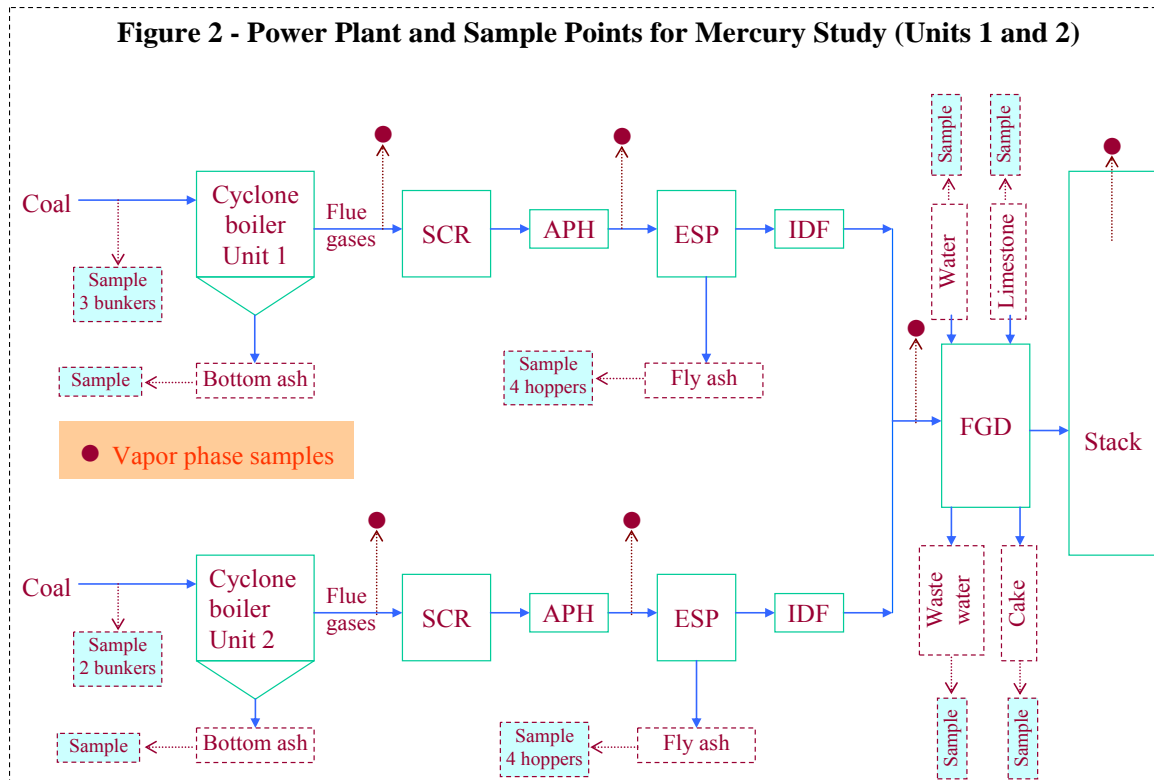
This study required collecting around six hundred samples from a coal preparation plant (CP-1) and a power plant (PP-1) located in Illinois. A major aim of the study was to ensure that the same batch of coal sampled at the coal preparation plant was burnt at the power plant during the respective sampling during ozone and non-ozone seasons.

The coal preparation plant (CP-1) employed gravity and cyclone separation. Representative samples of raw coal, magnetite, clean coal, rejects, and liquid effluents at several locations of the preparation plant were collected as shown in Figure 1. The sampling was conducted in the morning and in the afternoon for two days in April 2007 (non-ozone season for the power plant) and for two days in May 2007 (ozone season for the power plant). The sampling at CP-1 was conducted two days ahead of the sampling at PP-1 to allow adequate time for shipping the sample from the preparation plant to the power plant.



The power plant (PP-1) had two cyclone boilers, two selective catalytic reduction units (SCR), two electrostatic precipitators (ESP), and one wet flue gas desulfurization (WFGD) forced oxidation unit and one stack to treat the combined flue gases of these two units, Unit 1 and Unit 2. Representative samples of feed coal, bottom ash, fly ash, limestone, make-up water, WFGD sludge (gypsum) and liquid effluents were collected at the power plant as shown in Figure 2. The feed coal samples were collected from the

bunkers feeding coal to the respective boilers. The fly ash samples were collected from the four hoppers, two each in the front two rows of each system. The sampling at the PP-1 was conducted for three days in April 2007(non-ozone) and for three days in May 2007 (ozone).



The solid and liquid samples at PP-1 were collected while gas-phase mercury concentrations were measured by the Institute for Combustion Science and Environmental Technology (ICSET) of the Western Kentucky University (WKU) at various locations. The WKU was awarded a separate ICCI grant to perform the vapor-phase mercury measurements. After the completion of the vapor-phase mercury measurements, WKU provided the results to ISGS. The WKU has a Mobile Mercury Emission Monitoring Lab (MMEML). The MMEML contains state-of-the-art equipment needed to collect samples from flue gas, fly ash, or ambient air and analyze them for mercury. The lab contains facilities to perform both continuous emissions monitoring (CEM) of mercury and the Ontario Hydro Method (OHM) for mercury analysis.

The Relative Accuracy Test Audit (RATA) by OHM for two units 1 and 2 having common stack was conducted by WKU at PP-1 for three days in April non-ozone season. The vapor phase samples were drawn from ESP inlets of two units, FGD inlet, and at the common stack. The PSA CEM and Tekran CMM systems were in service at the stack during this period to monitor mercury and the sampling as per Appendix K to Part 75 of CFR 40 was also in service for the quality assurance for the sorbent trap monitoring systems. The RATA by OHM for units 1 and 2 having common stack was conducted by WKU at PP-1 for three days in May (ozone season). The vapor phase samples were

drawn from SCR inlets and SCR outlets of two units, FGD inlet, and at the common stack. The PSA CEM and Tekran CMM systems were in service at the stack during this period to monitor mercury and the sampling as per Appendix K to Part 75 of CFR 40 was also in service for the quality assurance for the sorbent trap monitoring systems.

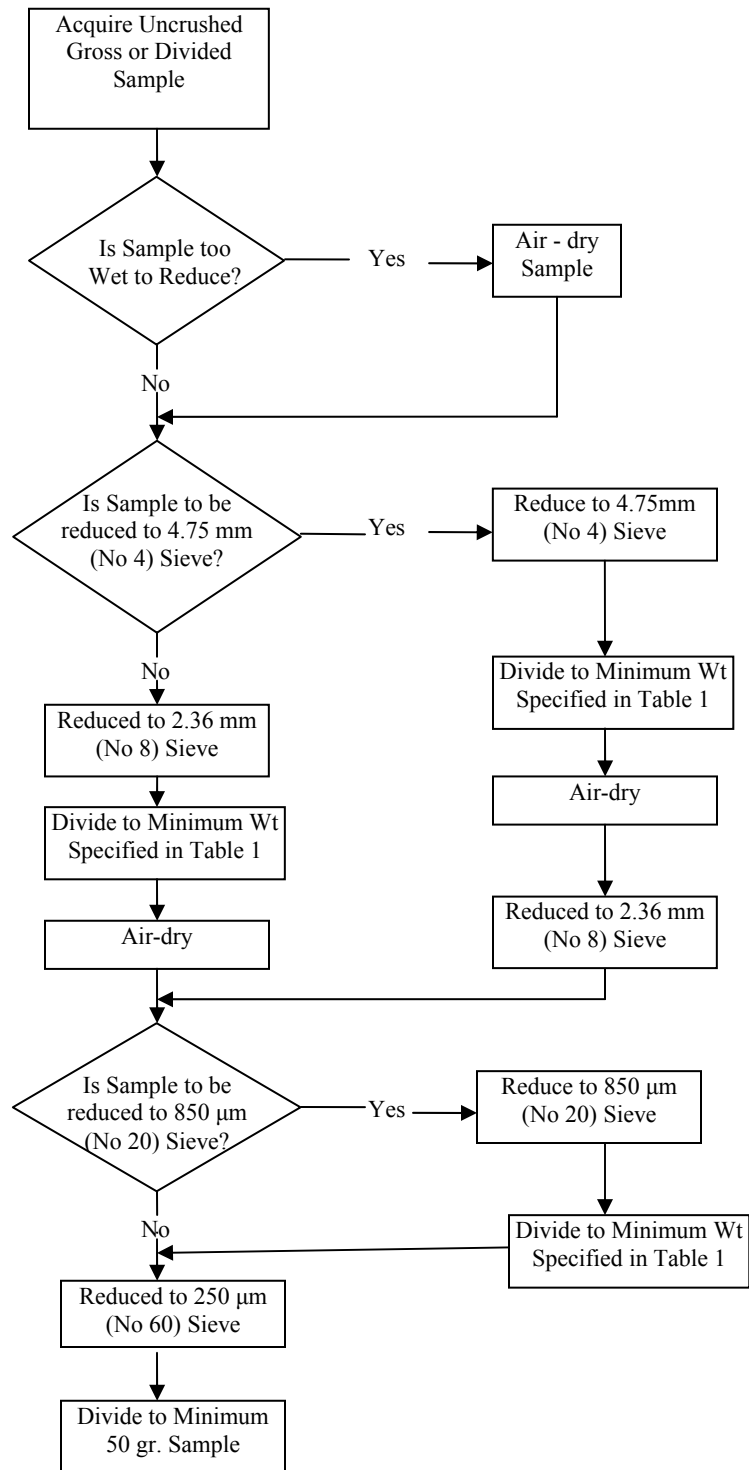
### Sample Preparation and Characterization

All the samples were stored in air tight containers. Four sets of samples, two sets collected in April 2007 and two sets collected in May 2007, each from CP-1 and PP-1 (total eight sets of samples) were selected for processing and characterization. The solid samples were air dried in an air drying oven to determine air drying loss as per ASTM D 3302 - Standard Test Method for Total Moisture in Coal. The air-dried samples were crushed and divided to prepare representative samples for analysis as per ASTM D 2013 - Standard Practice for Preparing Coal samples for Analysis<sup>(3)</sup>. The standard describes the details of reduction and division of gross sample with the help of a flowchart presented in Table 1 and Figure 3. The prepared samples were analyzed for mercury content and proximate analysis. The proximate analysis determined the residual moisture, volatiles, and ash contents of the sample. The coal samples were further analyzed for heating value and sulfur content. The total moisture of the solid samples was calculated using the formula given in the standard ASTM D 3302 from the data of the air dry loss and the residual moisture. The sludge samples were filtered to separate solid and liquid. The solids were further processed and analyzed as other solid samples. The liquid samples were analyzed for mercury content.

<b>Table 1 - Preparation of Laboratory Sample</b>		
Crush to pass at least 95% through sieve	Divide to a minimum weight of, gram*	
	Group A (Cleaned Coal)	Group B (All other Coals)
No. 4 (4.75 mm)	2000	4000
No. 8 (2.36 mm)	500	1000
No. 20 (850 µm)	250	500
No. 60 (250 µm) (100% through)	50	50

\* If a moisture sample is required, increase the quantity of No. 4 (4.75 mm) or No. 8 (2.36mm) sieve sub-sample by 500 gram.

The mercury content of solid samples was analyzed with a LECO AMA254 instrument of LECO Corporation which uses approved ASTM Method D 6722 and complies with EPA Method 7473. The AMA254 technique of direct combustion features a combustion/catalyst tube that decomposes the sample in an oxygen rich environment and removes interfering elements. A gold amalgamator trap collects all mercury from the evolved gases and a dual-path length cuvette/atomic absorption spectrophotometer specifically determines mercury over a wide dynamic range. The liquid samples were analyzed for mercury content with a PS Analytical Millennium system which uses cold vapor atomic fluorescence spectroscopy and follows USEPA method 245.7. The proximate analysis was performed with a LECO MAC-400. The heating value was determined with a Parr oxygen bomb calorimeter No. 1281 and the total sulfur was analyzed with a LECO SC-32 microprocessor based instrument.



**Figure 3 - Sample Preparation Flowchart (ASTM D2013-03)**

During the preparation of the first draft of this report, mercury mass balance calculations for the power plant showed a higher mercury input than output in the most cases. In one monitoring day, the difference of mercury input and output reached as much as 40%. Besides, mercury contents measured for the collected coal samples were generally lower



than a typical level of mercury in the Illinois coals. Further examination of data excluded the possibility of any significant errors incurred from sampling and sample preparation. It was concluded that mercury content of the solid samples were not accurately measured.

To assure the reliability of mercury measurement, ten samples were selected for analysis by an independent laboratory, where a Leeman Hydra C Mercury Analyzer was used for mercury analysis following ASTM Method D 6722. These samples included a feed coal, a steam coal, a mid-size coal, a fine coal and a refuse from the coal preparation plant, and a feed coal, a bottom ash, a fly ash, and two FGD cakes from the power plant. They covered a wide range of mercury content occurring in the solid samples collected in this study.

Meanwhile, the ISGS staff also examined the calibration standard and operating protocol employed in the analysis using the LECO AMA254 analyzer. It was concluded that the error was due to that a standard sample was calibrated to the value of a different standard. Mercury contents of the samples sent to the independent laboratory were measured using the recalibrated LECO AMA245 at the ISGS.

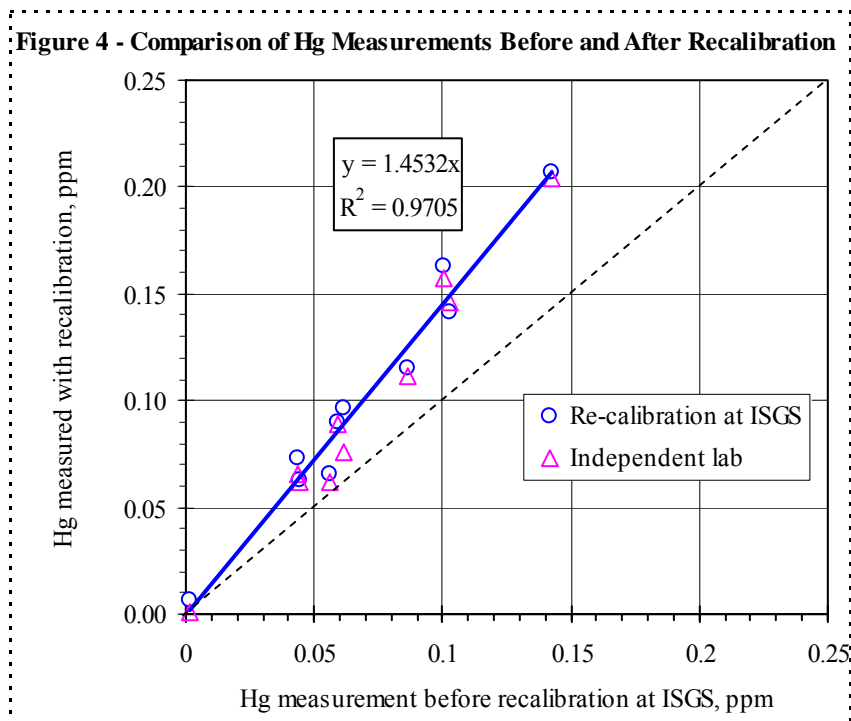


Figure 4 shows that the mercury content measured at the ISGS using the corrected approach and at the independent lab were almost identical (R square of 0.99). The new mercury data for the selected ten samples measured at the ISGS could also be well correlated with the old measurements, with an R square of 0.97 (Figure 4). A regression equation was obtained between these two sets of data, i.e.,  $y = 1.4532x$ . This equation was used to correct the mercury measurement for all the solid samples analyzed prior to the upgraded calibration. The following results and discussion are based on the corrected mercury measurement data.

### Data analysis and mass balance calculations

Data generated were analyzed and interpreted using statistical models to establish consistency of the results. Excel 2003 data analysis software was used to determine mean and standard deviation. Excel's descriptive statistics were used to establish confidence levels within each sample set. Statistical t-test was used to compare mean values and to determine dataset independence. P (two-tail) values of less than 0.05 were used to establish the independence of each sample. The values above 0.05 indicated that the mean values were consistent with a single mean value.

Detailed mass balance calculations were performed on Excel spread sheets to quantify the amount of mercury in various stages of processing and combustion. The flow rate data of various streams were acquired from the respective plants. Considering these flow rates with the total moisture and the mercury content, the mass balance calculations were completed. The respective mercury content on lb/trillion BTU and lb/GWh was calculated on spread sheet with heating value and power generation data and % mercury reduction in various processes was determined.

### Preliminary techno-economic study

A preliminary cost study was performed to determine the cost of the mercury emission control with activated carbon injection. The Integrated Environmental Control Model (IECM, May, 2007) developed by Carnegie Mellon University, was used for the cost estimations. The power plant configuration included a cyclone boiler, a hot side SCR, a cold side ESP and a wet FGD. Power plant performance was maintained constant as were fuel property values. Operational parameters of flue gas temperatures, percent ash entering the flue stream, and SCR, ESP and FGD performance variables were held constant. Four different scenarios based on varying plant gross electrical output (100, 300, 500 and 750 MW) were considered. The results from the cost analysis study were also used to assess the relative cost benefit of additional coal cleaning to achieve the same level of mercury control with activated carbon injection (ACI). The IECM calculations provided a potential range of market value for coal sufficiently free of mercury to meet emission rules.

## RESULTS AND DISCUSSION

### Samples and Characterization (Tasks 1, 2, and 3)

Table 2 shows the mercury content in the samples of the coal preparation plant. The liquid mercury contents are reported in ppb ( $\mu\text{g/liter}$ ) units and all others are in ppm units. The results show consistency in mercury content of each sample though the samples were collected at an interval of more than one month. As expected, all the three refuse flows from the plant contained more mercury than the clean coals.

<b>Table 2 - Coal Preparation Plant Samples Mercury Content</b>				
Hg content (dry basis), ppm/ppb				
Sample Location/Description	April 2007	April 2007	May 2007	May 2007
Plant Feed Coal	0.0891	0.0748	0.0766	0.0873
Coarse Coal (Steam)	0.0639	0.0667	0.0773	0.0652
Coarse Coal (Stoker)	0.0619	0.0709	0.0671	0.0782
Magnetite	0.0039	0.0039	0.0029	0.0035
Vessel/Coarse Refuse	0.1253	0.1734	0.1242	0.1145
Cyclone Refuse	0.1292	0.1068	0.1107	0.0956
Mid-size Coal	0.0812	0.0458	0.0562	0.0712
Fine Coal	0.0573	0.0555	0.0564	0.0680
Fine Refuse	0.1494	0.1436	0.1674	0.1359
Make-up Water      ppb	<b>0.4200</b>	<b>&lt;0.0800</b>	<b>&lt;0.0800</b>	<b>&lt;0.0800</b>
Thickener Under Flow				
Solid	0.0657	0.0622	0.0695	0.0545
Liquid, ppb	<b>&lt;0.0800</b>	<b>&lt;0.0800</b>	<b>&lt;0.0800</b>	<b>&lt;0.0800</b>

<b>Table 3 - Power Plant Samples Mercury Content</b>				
Hg content (dry basis), ppm/ppb				
Sample Location/Description	Non-ozone (SCR off)		Ozone (SCR on)	
	April 2007	April 2007	May 2007	May 2007
<b>Unit 1</b>				
Feed Coal	0.0607	0.0591	0.0663	0.0619
Bottom Ash	0.0023	0.0017	0.0019	0.0019
Fly Ash	0.0539	0.0841	0.0715	0.0670
<b>Unit 2</b>				
Feed Coal	0.0597	0.0613	0.0503	0.0638
Bottom Ash	0.0017	0.0020	0.0019	0.0022
Fly Ash	0.0436	0.0695	0.0727	0.0330
<b>Units 1/2 combined</b>				
Limestone	0.0023	0.0023	0.0026	0.0019
Make-up Water      ppb	<b>&lt;0.0800</b>	<b>&lt;0.0800</b>	<b>&lt;0.0800</b>	<b>&lt;0.0800</b>
Cake	0.2074	0.2219	0.1463	0.1488
Waste Water          ppb	<b>0.3000</b>	<b>0.2000</b>	<b>0.7100</b>	<b>1.4000</b>
Flue Gas (Stack)    µg/dscm	<b>1.7000</b>	<b>2.0800</b>	<b>3.6600</b>	<b>2.3100</b>

Table 3 shows the mercury content in the samples collected at the power plant. The mercury contents of the liquid samples are reported in ppb ( $\mu\text{g/liter}$ ) units, that of flue gas in  $\mu\text{g/dscm}$  and all others are in ppm. The results show consistency in mercury content of each coal sample though the samples were collected at an interval of more than one

month. No significant difference of mercury content in the fly ash during the ozone or the non-ozone season was observed. The concentration of mercury in the FGD waste water was higher during the ozone season and the mercury content of the WFGD cake (gypsum) was higher during the non-ozone season. The concentration of mercury in the flue gas at the common stack, shown in the Table 3, are the measurements performed by the WKU. The mercury concentration on day one of the monitoring in the ozone season was higher than that on the other days of monitoring both in the non-ozone and the ozone seasons.

In a previous ICCI project by Vivak Malhotra <sup>(4)</sup>, the mercury concentration in the feed coal, fly ash, bottom ash, and FGD cake from two different power plants using Illinois coal were monitored on a weekly basis over a one-year period <sup>(4)</sup>. The configuration of the PP-A power plant studied by Vivak is similar to the configuration of the power plant PP-1 investigated in this study except the boiler types. The PP-A had a PC boiler and PP-1 had two cyclone boilers. A comparison of the results is presented in Table 4.

Hg in ppm	Malhotra's study		This study
	PC boiler (PP-A)	Cyclone boiler (PP-B)	Cyclone boiler (PP-1)
	IL coal	IL coal - petroleum coke blend	IL coal
Coal	0.088±0.011	0.095±0.009	0.060±0.005
Fly ash	0.024±0.002	0.022±0.002	0.062±0.017
Bottom ash	0.039±0.008	0.001±0.0003	0.002±0.0002
FGD cake	Gypsum 0.165±0.052	Sulfite-rich 0.370 (non-O <sub>3</sub> season) 0.626 (O <sub>3</sub> season)	Gypsum 0.215 (non-O <sub>3</sub> season) 0.148 (O <sub>3</sub> season)
Limestone	<0.004	<0.004	0.002

The results showed that the Hg contents of the coal burned in the PP-A differed from that of the coal burned in PP-1. A higher Hg concentration in fly ash was observed in this study compared to the previous study. In both the studies, however, no significant difference was observed during the ozone and the non-ozone seasons. The Hg content of bottom ash in the PP-A plant in the Malhotra's study was extremely high, and it was claimed that this high concentration was due to the operation problems associated with the fireball in the boiler. The Hg concentration in gypsum cake is comparable between the two studies. Malhotra's study showed no significant difference of Hg concentration of cake during the non-ozone and ozone seasons, while this study showed a lower concentration of mercury in the scrubber cake when the SCR was in operational during the ozone season.

#### Data Analysis, Mass Balance Calculations, and Mercury Assessment (Task 4)

As previously indicated, statistical models were used for data analysis. Values of P (two-tail) less than 0.05 were used to establish the independence of each sample. Mercury contents of the processed samples were compared to that of the plant feed coal with p (two tail) values of coarse coal (steam) 0.0283, mid-size coal 0.1015, coarse coal (stoker) 0.0474, and fine coal 0.0028. The P value for the mid size coal is larger than the threshold (0.05) because it comprises of about half of the coal products from the feed

coal. Values above 0.05 indicated that the mean values were consistent with a single mean value as found in comparison of fly ash from unit 1 and unit 2 ( $p = 0.2662$ ) and bottom ash from unit 1 and unit 2 ( $p = 1$ ).

Figure 5 shows the statistical analysis of the data from the coal preparation plant.

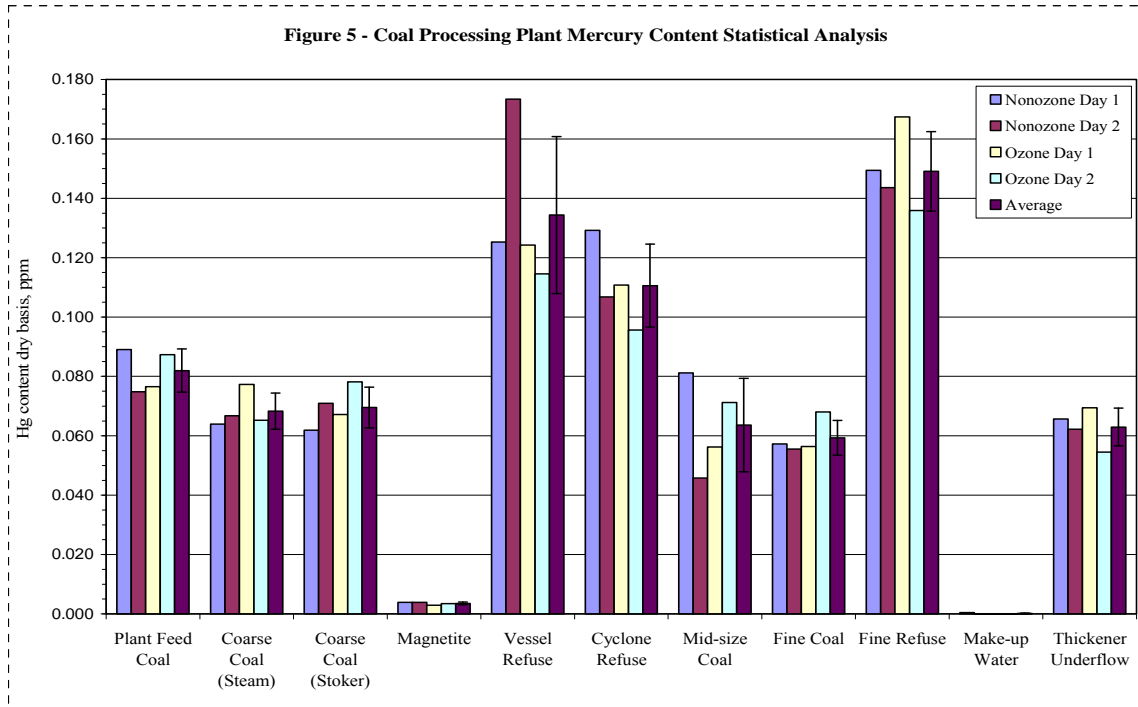
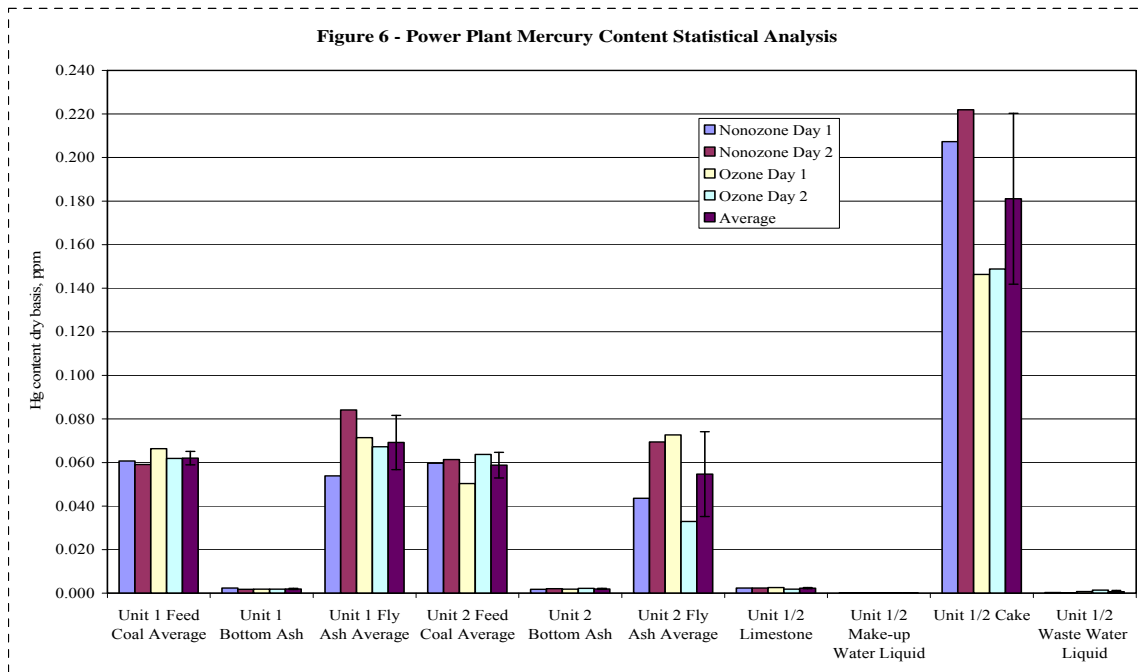


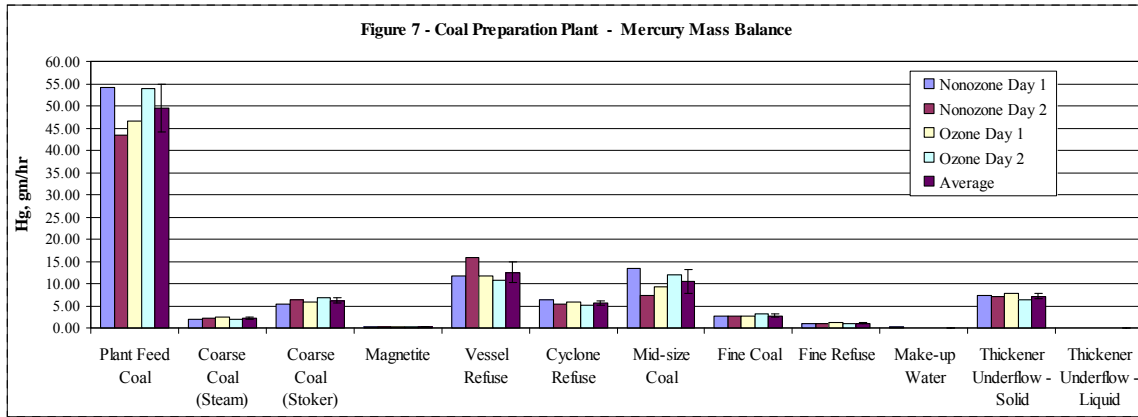
Figure 6 shows the statistical analysis of the data from the power plant.



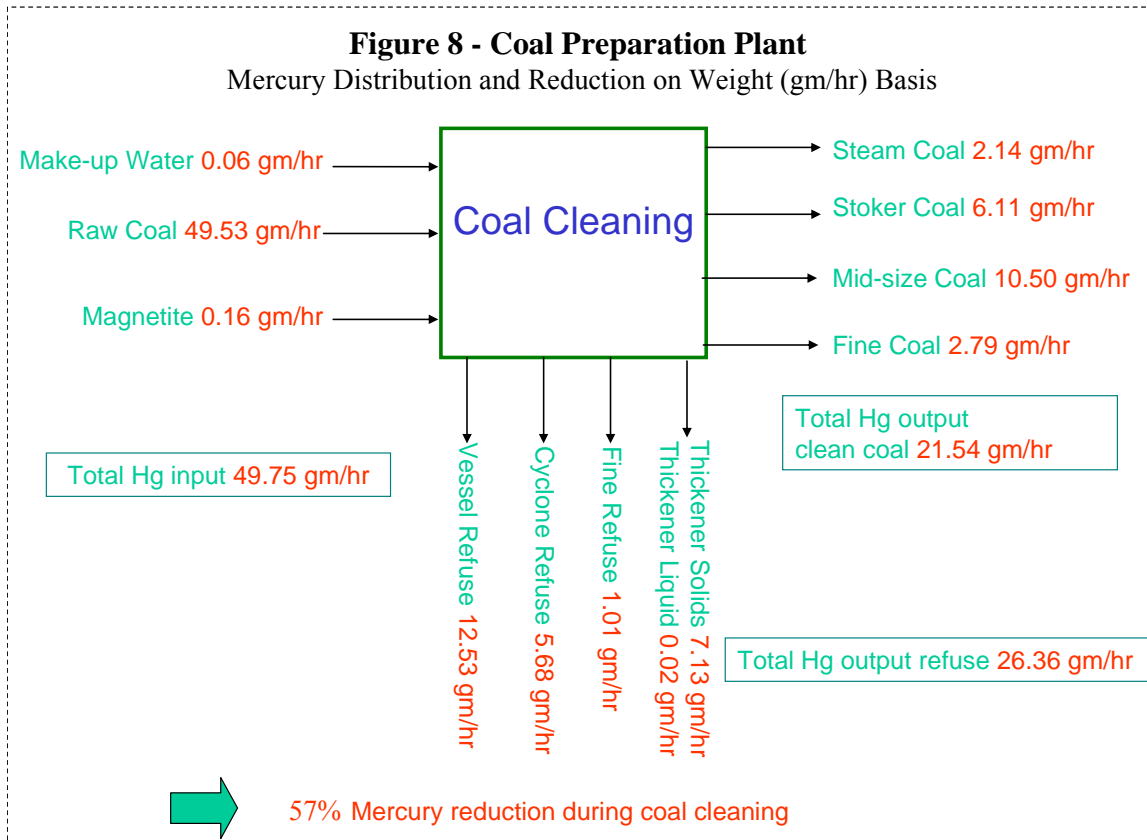
Each bar graph illustrates the four sets of samples analyzed for each sampling location, i.e. plant feed coal, coarse coal (steam), coarse coal (stoker), etc. An average value is also shown with each set of data points. The first standard deviation is shown using error whiskers on the average bar for those data points. In some cases one or more points are outside the first standard deviation. For the coal preparation plant, as shown in Figure 4, although the data points of vessel refuse on non-ozone day 2, cyclone refuse on non-ozone day1, and fine refuse on ozone day1 are outside the first standard deviation, but they are still well within the normal 95% confidence interval. All of the samples except the FGD waste water represent normal variability within 95% confidence interval of the sample mean.

Mercury mass balance for the coal preparation plant was calculated using Hg content, moisture content, and the mass flow rate of each sample stream (Table 5). Figure 7 shows graphical presentation of the mercury mass balance for the coal preparation plant with mean and the first standard deviation. The mass flow rates were obtained from the plant flow sheet provided by the CP-1. The difference between the total input and the total output observed was between -10 to 13%. Considering the number of process stages in the plant, this variation may not be very significant statistically. Although the concentration of mercury (ppm) in the mid-size coal was not high, it carried more mercury on a gm/hr basis because its output flow rate was very high compared to other clean coal fractions. The fine refuse fraction having the highest concentration of mercury carried the least amount in gm/hr because of its very low mass flow rate. The vessel/course refuse fraction carried the largest amount of mercury. The combined contents of the four fractions of clean coal indicated an average of around 57% on weight basis mercury reduction during the cleaning process at the CP-1 plant.

Sample Description	April 2007		April 2007		May 2007		May 2007	
	Input gm/hr	Output gm/hr	Input gm/hr	Output gm/hr	Input gm/hr	Output gm/hr	Input gm/hr	Output gm/hr
Plant Feed Coal	54.20		43.35		46.63		53.96	
Coarse Coal (Steam)		2.00		2.11		2.43		2.04
Coarse Coal (Stoker)		5.42		6.22		5.96		6.86
Magnetite	0.18		0.18		0.13		0.16	
Vessel/Coarse Refuse		11.76		15.91		11.82		10.61
Cyclone Refuse		6.32		5.42		5.88		5.08
Mid-size Coal		13.47		7.42		9.24		11.86
Fine Coal		2.67		2.58		2.67		3.24
Fine Refuse		0.99		0.95		1.18		0.91
Make-up Water	0.14		0.03		0.03		0.03	
Thickener/Under Flow								
Solid		7.41		7.12		7.75		6.26
Liquid		0.02		0.02		0.02		0.02
<b>Total</b>	<b>54.52</b>	<b>50.07</b>	<b>43.55</b>	<b>47.75</b>	<b>46.79</b>	<b>46.94</b>	<b>54.14</b>	<b>46.88</b>
<b>% Diff. Input to Output</b>	<b>8.16</b>		<b>-9.64</b>		<b>-0.31</b>		<b>13.41</b>	



A summary of mercury distribution and reduction on weight basis at the CP-1 is shown in Figure 8.



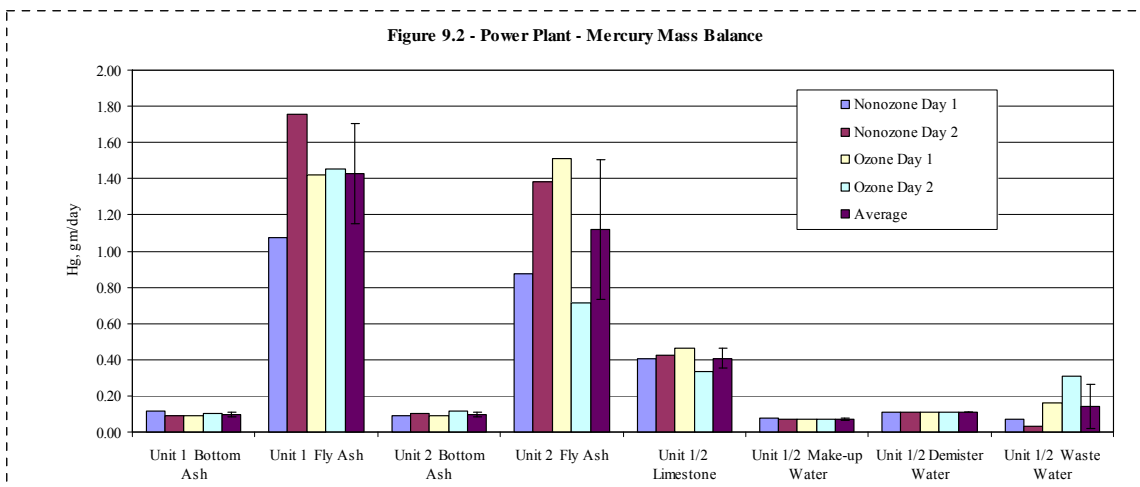
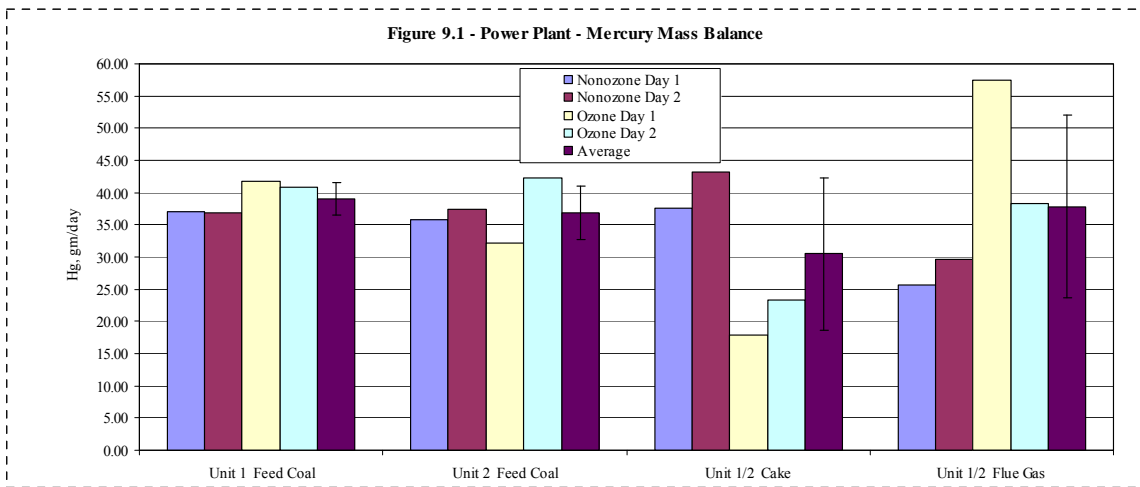
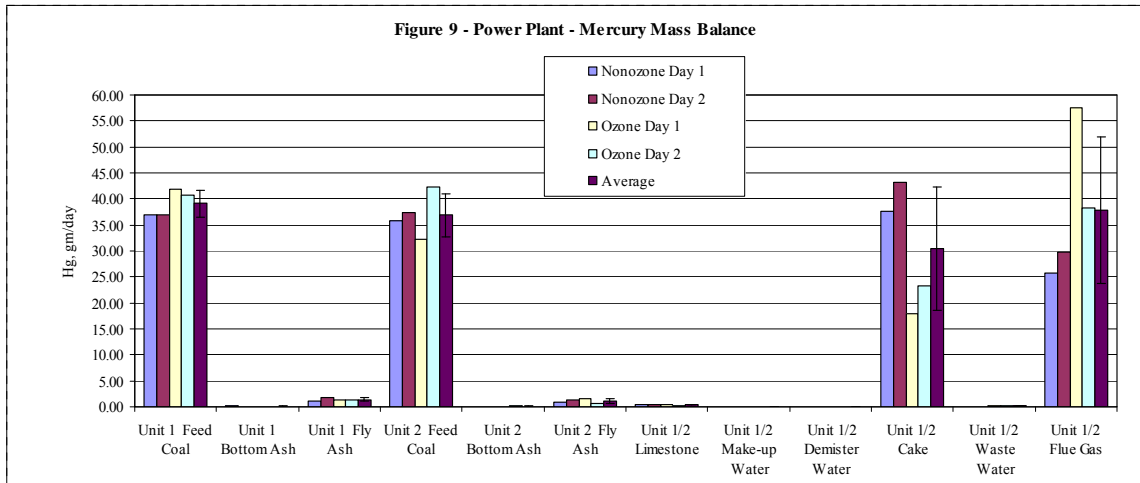
Mercury mass balance for the power plant was calculated using Hg content, moisture content, and the mass flow rate of each sample, Table 6. Figure 9 shows the graphical presentation of the mercury mass balance with mean and the first standard deviation. Because the mercury mass flow for some of the inputs and outputs are very small and can not be seen on this plot, data for feed coal, cake, and flue gas are shown separately in Figure 9.1 and all other inputs and outputs are shown in Figure 9.2. The feed coal mass

flow rates were from the daily coal usage reports from PP-1. The fly ash and the bottom ash data were estimated from the coal usage, their ash contents, and the mass ratios of fly ash to bottom ash ratio (30%:70%) for the cyclone boilers. The limestone data were estimated from the average coal usage and its sulfur content. The power plant also supplied flow rates of make-up water, demister water, gypsum cake and waste water. The demister water was not sampled, as its source was the same as that of the make-up water. The flue gas flow rates and gas-phase mercury concentrations were available from the measurements conducted by the Institute of Combustion Science and Environmental Technology (ICSET) of the WKU.

<b>Table 6 - Power Plant Mercury Mass Balance in gm/day</b>								
Sample Description	Non-Ozone Season (SCR off)				Ozone Season (SCR on)			
	April 2007		April 2007		May 2007		May 2007	
	Input	Output	Input	Output	Input	Output	Input	Output
	gm/day	gm/day	gm/day	gm/day	gm/day	gm/day	gm/day	gm/day
<b>Unit 1</b>								
Feed Coal	37.00		36.84		41.78		40.76	
Bottom Ash		0.12		0.09		0.09		0.10
Fly Ash		1.08		1.76		1.42		1.45
<b>Unit 2</b>								
Feed Coal	35.84		37.36		32.20		42.24	
Bottom Ash		0.09		0.10		0.09		0.12
Fly Ash		0.87		1.38		1.51		0.71
<b>Units 1/2 Combined</b>								
Limestone	0.41		0.42		0.47		0.33	
Make-up Water	0.08		0.07		0.07		0.07	
Demister water	0.11		0.11		0.11		0.11	
Cake		37.55		43.23		17.80		23.24
Waste Water		0.07		0.03		0.16		0.31
Flue Gas (Stack)		25.73		29.67		57.56		38.33
<b>Total</b>	<b>73.43</b>	<b>65.50</b>	<b>74.80</b>	<b>76.26</b>	<b>74.63</b>	<b>78.63</b>	<b>83.52</b>	<b>64.26</b>
<b>% Diff. Input to Output</b>	<b>10.80</b>		<b>-1.95</b>		<b>-5.37</b>		<b>23.06</b>	

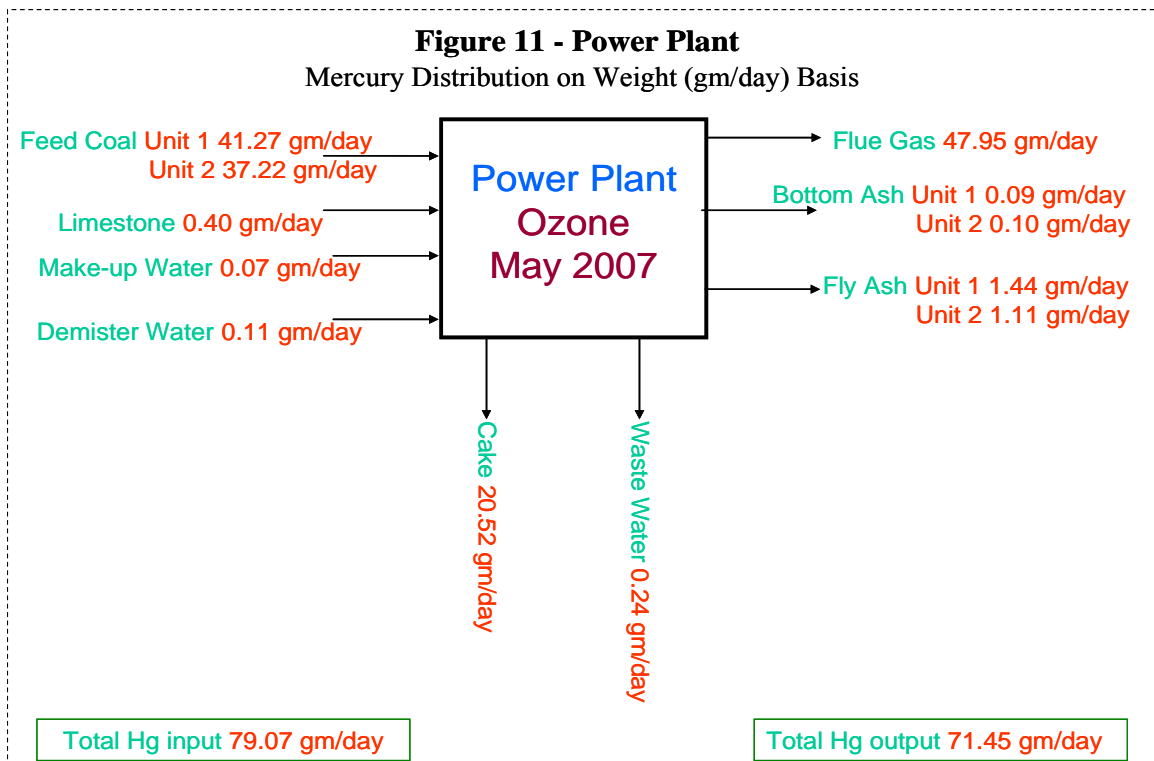
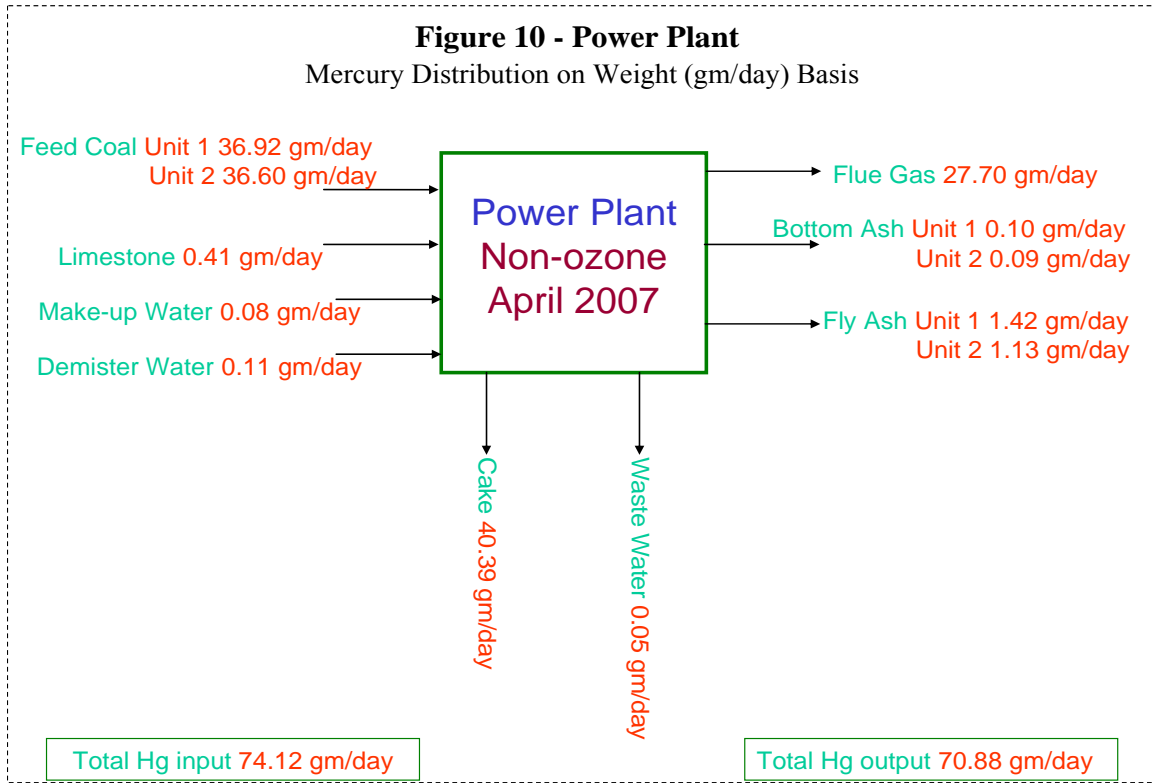
As presented in Table 6, based on the mass balance calculations, the difference between the total mercury input and the total mercury output ranged between -5 and 23 %. The highest variation (23%) was observed on the day two of the monitoring in the ozone season. The mercury concentration and the flow rate in the stack flue gas on the day one of the monitoring in the ozone season were unusually high compared to the mercury concentration and the flow rate during other days of monitoring in the ozone and the non-ozone seasons. During the non-ozone season, more than 50% of the mercury removed was contained in the FGD cake. Also, during the non-ozone season, the concentration of mercury in the FGD waste water was lower (2 to 10 times) than during the ozone season. No statistically significant variation was observed in the mercury flow with fly ash and bottom ash in the non-ozone and ozone seasons. The concentration of mercury in the flue gas at the stack was higher during the ozone season in part because some of the oxidized mercury could have been reduced in the WFGD forced oxidation which resulted in the mercury re-emission.





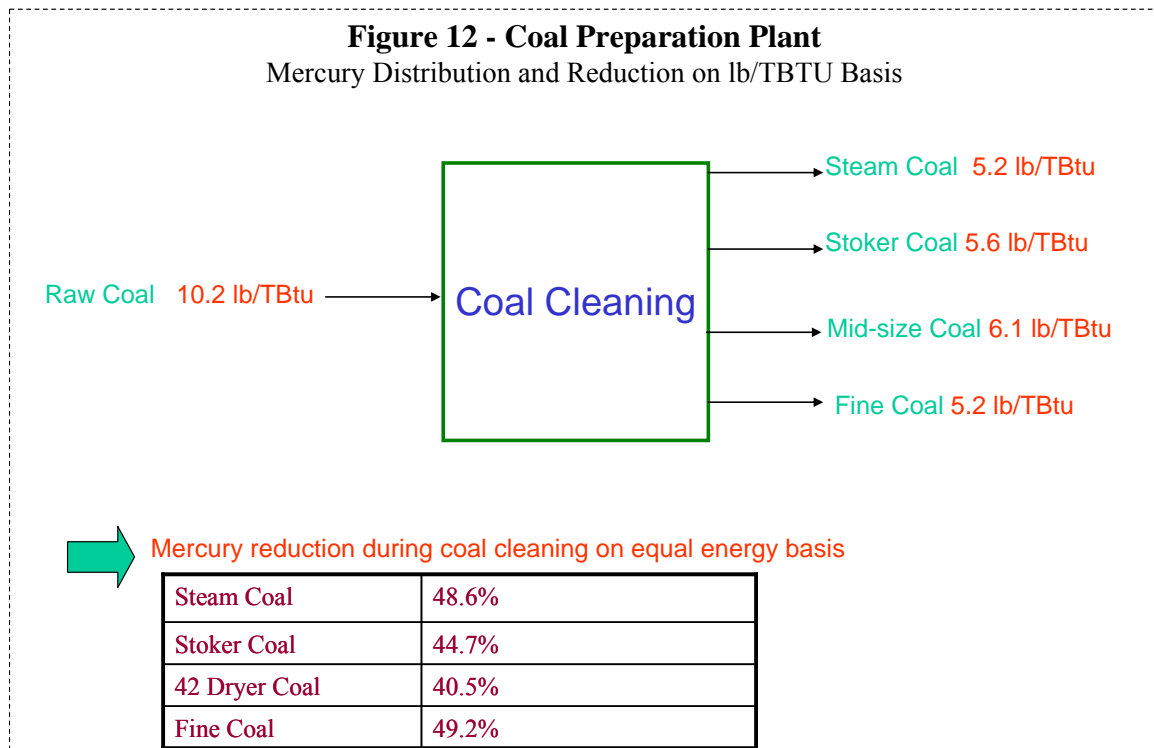
The distribution of mercury (the average of two sets of measurements presented in Table 6) from the feed coal to various coal combustion products at the power plant is presented in Figure 10 for the non-ozone season and in Figure 11 for the ozone season. The average

variation between the mercury input and the mercury output in the non-ozone season was 4% and that in the ozone season was 10%.



Mercury contents (pounds per trillion BTU, lb/TBTU) of the as-mined coal and the clean coal products from the coal preparation plant are presented in Table 7 and Figure 12. Mercury concentrations (ppm) and the heating values (Btu/lb) are the average for the samples collected on day 1 of April 2007 and day 2 of May 2007. The reduction in mercury was around 40 to 50 % on lb/TBTU basis as shown for the clean coal products.

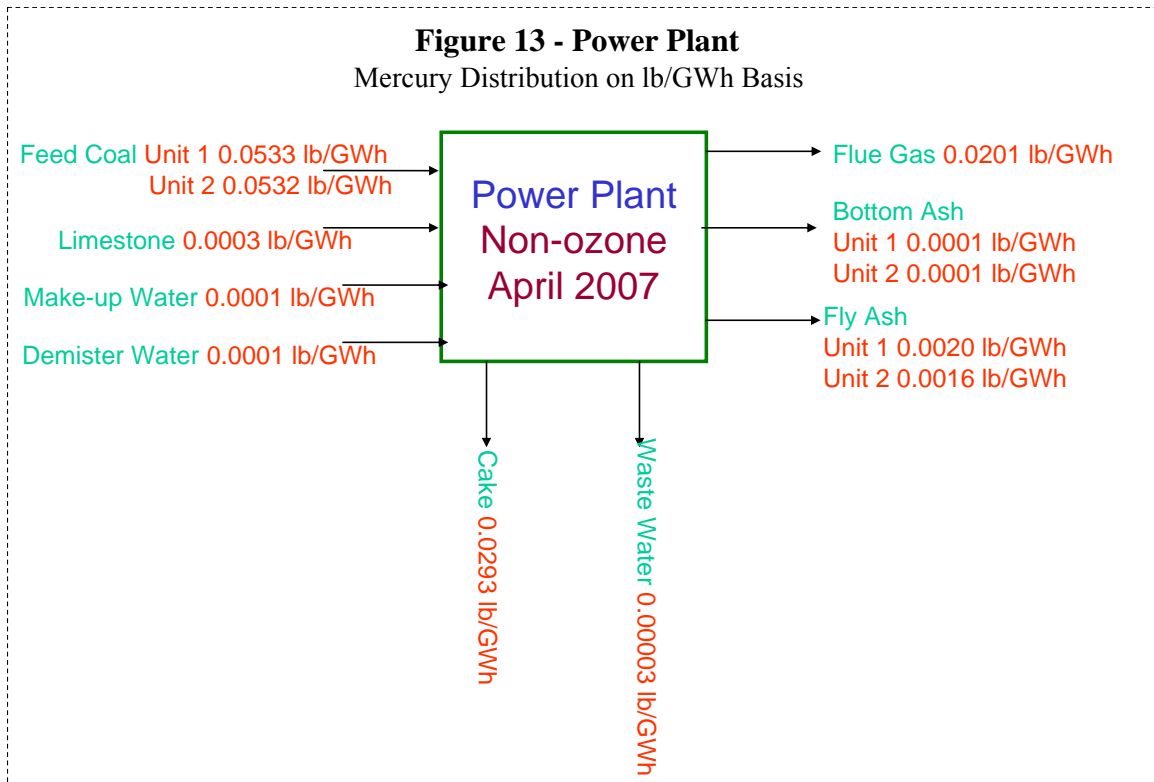
<b>Table 7 - Coal Preparation Plant</b>				
<b>Mercury Reduction on Equal Energy Basis, lb/TBTU</b>				
	Hg, Dry	Heating Value, Dry	Hg Reduction on Equal Energy	Hg
	ppm	Btu/lb	%	lb/TBTU
Plant Feed Coal	0.0882	8678.60		10.16
Coarse Coal (Steam)	0.0646	12357.91	48.57	5.23
Coarse Coal (Stoker)	0.0700	12452.21	44.66	5.63
Mid-size Coal	0.0762	12607.65	40.52	6.05
Fine Coal	0.0626	12120.18	49.16	5.17

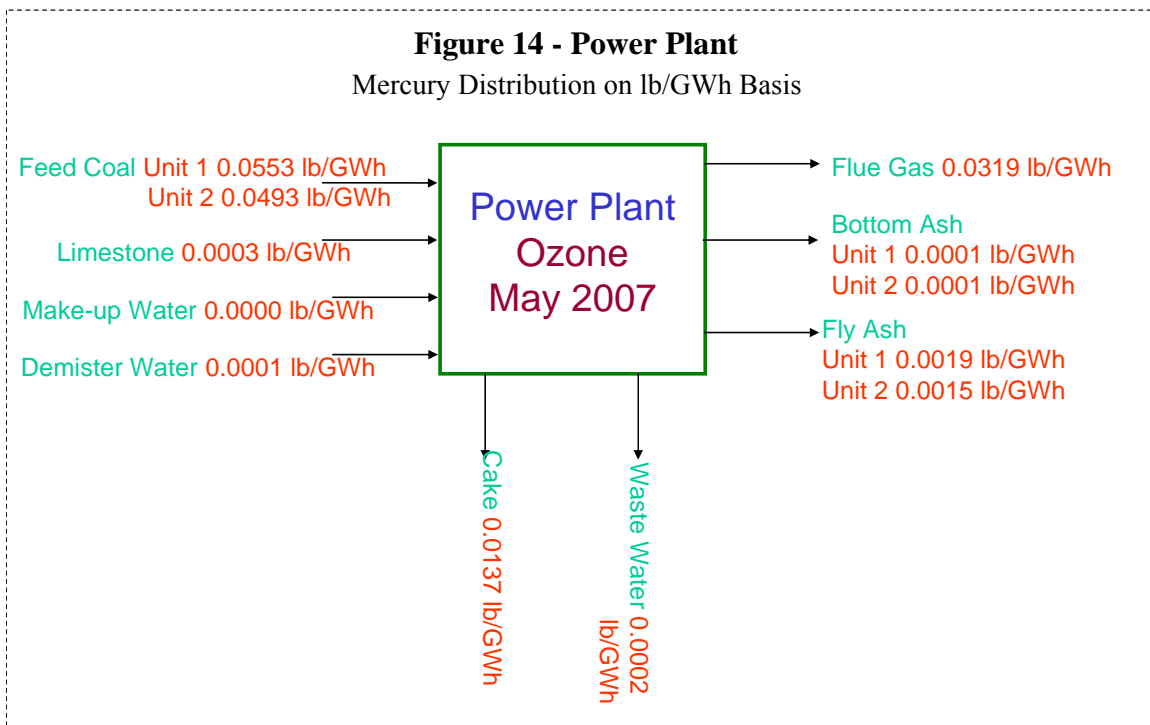


In a 2005 ICCI supported study, the washability and mercury removal efficiencies of five Illinois coals were investigated <sup>(5)</sup>. The results of that study showed that the mercury removal of 45%, 30% and 55% for three size fractions of Illinois #5 coal examined (+16 mesh, 16x48 mesh, 48x100 mesh). Based on the dry Btu basis (lb/TBTU dry), the overall Hg removal reached about 80% for the Illinois #5 coal. In this study, samples of Illinois #5 coal collected at the preparation plant showed that gravity and cyclone coal washing processes, removed about 57% on weight basis and from 40 to 50% on lb/TBTU basis.

A summary of the mercury balances (lb/GWh) for the power plant during the non-ozone and the ozone seasons on pound per gigawatt hour is presented in Table 8 and Figure 13 and Figure 14.

Table 8 - Mercury Emissions on Power Generation Basis, lb/GWh					
Non-ozone Season			Ozone Season		
	Hg Emissions			Hg Emissions	
	lb/GWh			lb/GWh	
	Input	Output		Input	Output
<b>Unit 1 (Average 63.60MW)</b>			<b>Unit 1(Average 68.59MW)</b>		
Feed Coal	0.0533		Feed Coal	0.0553	
Bottom Ash		0.0001	Bottom Ash		0.0001
Fly Ash		0.0020	Fly Ash		0.0019
<b>Unit 2 (Average 63.15 MW)</b>			<b>Unit 2 (Average 69.40MW)</b>		
Feed Coal	0.0532		Feed Coal	0.0493	
Bottom Ash		0.0001	Bottom Ash		0.0001
Fly Ash		0.0016	Fly Ash		0.0015
<b>Units 1/2 Combined</b>			<b>Units 1/2 Combined</b>		
Limestone	0.0003		Limestone	0.0003	
Makeup Water	0.0001		Makeup Water	0.0000	
Demister Water	0.0001		Demister Water	0.0001	
Cake		0.0293	Cake		0.0137
Waste Water		0.0000	Waste Water		0.0002
Flue Gas (Stack)		0.0201	Flue Gas		0.0319





On lb/GWh basis, the average mercury removed at the power plant was around 63% in non-ozone season and around 40% in ozone season. The mercury emission observed (0.0201 and 0.0319 lb/GWh) was higher than Illinois Mercury Rule limit of (0.008 lb/GWh).

#### Preliminary Techno-Economic Study (Task 5)

To establish cost trend lines using the Integrated Environmental Control Model (IECM) parameters, a typical power plant configuration was simulated using a cyclone boiler, a hot side SCR, a cold side ESP and a wet FGD unit. Operational parameters of flue gas temperatures, percent ash entering the flue gas stream, and SCR, ESP and FGD performance variables used in the simulations were the default values from the IECM model.

An average Hg content of IL coal (0.060 ppm) was employed in the analysis. The ratio of elemental, oxidized and particulate mercury of 60%, 35% and 5% in the flue gas were adopted in the simulation. Without mercury control, it was assumed that 20% of mercury is removed through ESP, and 95% of the oxidized mercury is removed in the wet FGD. This resulted in about 60% of the mercury removal through the wet FGD, and about 70% overall through the power plant. These assumptions are consistent with the long-term gas-phase mercury measurement performed by the WKU team during ozone season at the PP-1 plant.

The results from the simulation showed that mercury emitted at PP-1 with SCR+WFGD is about 0.0133 lb/GWh. To meet the Illinois mercury emission limit of 0.008 lb/GWh, an overall removal of about 85% (or an additional 40% removal) is required.

Four different scenarios were considered based on plant gross electrical output: 100, 300, 500 and 750 MW. The costs to operate the carbon injection for mercury control are shown in Table 9. The price of activated carbon was assumed to be 0.50 \$/lb. The cost of mercury control ranged from \$55,000-70,000/lb Hg removed. As the plant size increased, the difference in mercury control cost only slightly decreased. This nominal change is mainly due to the cost of activated carbon.

Plant Capacity	Cost of Hg Control	
Gross Output	\$/MWh	\$/lb Hg
100 MW	1.74	42,104
300 MW	1.56	38,155
500 MW	1.52	37,046
750 MW	1.49	36,365

The costs of purchasing a mercury-compliance clean coal as opposed to installing an activated carbon injection process to achieve the 0.008 lb/GWh mercury emission limit are presented in Table 10. In the analysis, the base coal rate of \$35 was assumed based on the current market price.

Plant Capacity	Cost of Hg Control	Base Coal Price	Parity Coal Price w/o Hg Control	Difference of Coal price
	\$/MWh	\$/ton	\$/ton	%
100 MW	1.74	35	38.70	10.58%
300 MW	1.56	35	38.35	9.58%
500 MW	1.52	35	38.26	9.31%
750 MW	1.49	35	38.20	9.14%

The above results showed that the cost difference between the current coal (\$35/ton) and clean coal (\$38.20 - 38.70/ton) is around 10% and only slightly varies with the plant size. Therefore, a pre-combustion process that could reduce the mercury concentration in coal from 0.060 ppm to 0.035 ppm at a cost less than \$3.2-3.7/ton would provide an economic alternative to installation of a carbon injection process for mercury emission control at this power plant.

## CONCLUSIONS AND RECOMMENDATIONS

The objective of the study was to quantify the fate of mercury in Illinois coal during physical cleaning, combustion, particulate control, flue gas cleaning in a wet flue gas desulfurization (WFGD), and byproducts disposal. To achieve this goal, around six hundred samples of raw as-mined coal, magnetite, clean coal, refuse, make-up water, coal cleaning sludge, power plant feed coal, bottom ash, fly ash, limestone, make-up water, FGD sludge, and waste water were collected from a coal cleaning plant and a power plant located in Illinois. The following conclusions were observed:

1. There was no statistically significant variation in the mercury contents of the respective samples though the various sets of samples were collected over an interval of more than one month.
2. The mercury mass balance for the coal preparation plant showed that the difference between the total mercury input and the total mercury output was between -10 to 13%. Considering the number of process stages in the coal cleaning plant, this variation may not be very significant statistically.
3. The mercury mass balances for the power plant showed that the difference between the total mercury input and the total mercury output was -5 to 23 %. The average variation between the mercury input and the mercury output in the non-ozone season was 4% and that in the ozone season was 10%.
4. The reduction of mercury at the coal processing plant was on an average 57% on weight basis and 40 to 50% on energy basis (lb/TBTU).
5. The average mercury reduction observed at the power plant was around 63% in non-ozone season (ESP + WFGD) and around 40% in ozone season (SCR + ESP + WFGD) on lb/GWh basis. The mercury emission observed was higher than the Illinois Mercury Rule limit of 0.008 lb/GWh.
6. Purchasing coal sufficiently low in mercury to achieve emission rules at 9-11% higher cost (compared to \$35/ton base coal) could be more cost effective than installation of a carbon injection process for mercury emission control.
7. Further studies are required to evaluate the technical and economic feasibilities of improving existing coal cleaning processes for sufficient removal of mercury from as-mined coal to meet the Illinois mercury emission standards.

## ACKNOWLEDGEMENT

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## REFERENCES

- (1) U.S. Environmental Protection Agency - U.S. EPA Toxic Release Inventory (TRI) - 2005 TRI Public Data Release eReport - March 2007.
- (2) U.S. Environmental Protection Agency - EPA TRI Explorer - Chemical Release Reports.
- (3) American Society for Testing and Materials, Annual book of ASTM standards:  
ASTM D 2234/D 2234M -03 - Standard practice for collection of a gross sample of coal  
ASTM D 2013 - 03 - Standard practice for preparing coal samples for analysis.
- (4) Vivak Malhotra, 2006 - The Role of Mercury in Enhanced Utilization of Coal Combustion Byproducts, Final Technical Report to the Illinois Clean Coal Institute.
- (5) John Crelling, B. C. Paul, Ron Carty, 2005 - Prediction of Mercury Removal Efficiencies with Current Coal Washing Practices, Final Technical Report to the Illinois Clean Coal Institute.

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EQUIPMENT INVENTORY REPORT  
September 1, 2006, through December 31, 2007

Project Title: **LIFE CYCLE ASSESSMENT OF MERCURY IN ILLINOIS COALS**

ICCI Project Number: 06-1/10.1A-7  
Principal Investigator: Vinodkumar A. Patel, Illinois State Geological Survey (ISGS)  
Other Investigator: Yongqi Lu, David Ruhter, and Massoud Rostam-Abadi, ISGS  
Project Manager: Dr. Francois Botha, Illinois Clean Coal Institute

LIST OF EQUIPMENT PURCHASED

<b>Account Number</b>	<b>Date Acquired</b>	<b>Short Description</b>	<b>Cost</b>	<b>Tag Number</b>	<b>Location (Bldg. &amp; Room)</b>

No equipment was purchased for this project.

PUBLICATIONS AND PRESENTATIONS REPORT  
September 1, 2006, through December 31, 2007

Project Title: **LIFE CYCLE ASSESSMENT OF MERCURY IN ILLINOIS COALS**

ICCI Project Number: 06-1/10.1A-7  
Principal Investigator: Vinodkumar A. Patel, Illinois State Geological Survey (ISGS)  
Other Investigator: Yongqi Lu, David Ruhter, and Massoud Rostam-Abadi, ISGS  
Project Manager: Dr. Francois Botha, Illinois Clean Coal Institute

PUBLICATIONS AND PRESENTATIONS

No presentations were given or publications submitted.