

FINAL TECHNICAL REPORT
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Project Title: **CORRELATE COAL/SCRUBBER PARAMETERS WITH Hg REMOVAL AND Hg SPECIES IN FLUE GAS**

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ABSTRACT

The U.S. EPA is collecting information on mercury (Hg) emissions from coal-fired utilities to determine if Hg control for this source category is warranted. Presently, there is no proven Hg removal process for coal-fired utility boilers. The demonstration of multi-pollutant control by commercial flue gas desulfurization (FGD scrubbers) systems could provide utilities with an attractive control option that would help keep high-sulfur Illinois coal competitive with compliance coal. The objective of this study was to document the Hg reduction achieved by commercial FGD systems installed and operated by Illinois utilities firing Illinois coal. The simultaneous removal of HCl and HF also was determined.

Phase I (9/1/96 - 8/31/97) sampling results from two Illinois-based FGD-equipped coal-fired utility boilers showed 48% to 58% Hg removal across the scrubber and 56% to 72% total plant removal. Phase II (12/1/97 - 11/30/98) sampling from two additional Illinois-based FGD-equipped systems showed 46-57% Hg removal across the scrubber and 67-75% total plant removal. The average Hg removal across the FGD for the four units tested was 52%. The total system removal averaged 68%. The Hg removal due to adsorption on the ESP/bottom ash ranged from 7% to 13% for three of the plants. The remaining plant showed an almost 50% Hg reduction, which was a result of very high carbon in the ash and a lower operating ESP temperature. The material balance closures were within the data quality objectives and validate the gas phase Hg measurements. The data obtained in these studies will provide the Illinois coal and utility industries and emissions-regulating authorities valuable information on the effectiveness of wet FGD scrubbers for mercury removal.

A statistical analysis of the process parameters influencing Hg removal was conducted by the Illinois State Geological Survey (ISGS). Hg removal showed a strong correlation with scrubber slurry pH, with higher pH resulting in increased removal. A suspected correlation between Hg removal and the chlorine concentration of the coal was not apparent.

The average HCl removals for the Phase II test sites were 97% and 99%. The HF removals for these sites were >95%. This program showed that wet FGDs are effective for multi-pollutant control and can provide utilities with a valuable control option as air regulations become increasingly more stringent.

EXECUTIVE SUMMARY

The Environmental Protection Agency (EPA), the U.S. Department of Energy (DOE), the Electric Power Research Institute (EPRI), and their contractors have studied the partitioning of Hazardous Air Pollutants (HAPs) at coal-fired utility plants. The majority of the HAPs were captured with the fly ash in existing particulate collection devices (ESPs, fabric filters). The exceptions are the elements or compounds denoted as Class III (Hg, Se, HF, HCl) which, because of their volatility, are vapors at the exit of conventional particulate control equipment. Potential HAP control regulations could have an adverse effect on the Illinois coal and utility industries.

In a series of EPA Reports to Congress, EPA has identified potential health concerns related to Hg emissions from coal fired utilities. EPA has identified this source category as the largest national single source contributor of anthropogenic Hg emissions (~50 tpy for coal-fired utilities versus 150 total tpy from all anthropogenic sources). EPA is in the process of collecting additional Hg-related information from these sources to determine if Hg control is warranted. Currently, there is no demonstrated Hg control technology for coal-fired utilities. Carbon injection has been studied at the pilot scale with some limited success. However, the control costs for this technology have been estimated as high as \$40,000 to \$50,000 per lb of Hg removed.

Earlier studies at coal-fired utilities have shown that wet scrubbers can remove mercury. However, these studies show a wide variation in removal (0 to 100%), indicating the need for additional data to define the cause of this variation. The goal of this program was to develop more precise mercury removal data and other volatile HAPs, hydrofluoric acid (HF), and hydrochloric acid (HCl), by wet FGD systems. These data will supply the Illinois utility industry with information to evaluate SO₂ scrubbers as volatile HAP control devices. The data will be used to develop a model to predict HAP removal by SO₂ scrubbers.

In this program, CONSOL R&D and the Illinois State Geological Survey:

1. Determined the mercury and acid gas removal at four scrubber-equipped boilers firing Illinois coal (two in Phase I and two more in Phase II).
2. Completed correlation analysis of mercury removal with coal properties and/or scrubber operating parameters,
3. Evaluated the stability of the Hg contained in the FGD by-product solids.

The project team contacted the owner/operators of all of the scrubber-equipped boilers operating in Illinois. Four of the owners agreed to participate in the program. Two units were tested in Phase I (9/1/96 - 8/31/97) and the results of this program were previously reported. Two additional units were evaluated in June and July 1998. The results of this test work are documented in this report.

Phase I Results - Sites 1 and 2 (1996 testing previously reported)

The first sampling program was completed during the week of October 21, 1996, and the second sampling program was completed the week of October 28, 1996. Testing at both plants consisted of triplicate flue gas Hg measurements across the FGD scrubber. Process stream samples (i.e., feed coal, fly ash, bottom ash, limestone, FGD sludge/product, etc.) were obtained to conduct a mercury material balance to verify data quality.

The average Hg emissions for the two sites were 2.5 and 2.9 $\mu\text{g}/\text{m}^3$ (0.005 and 0.004 lb/hr or ~30 lb/year). The Hg removals across the ESP and FGD system averaged 56% and 72%. The average Hg removals across the FGDs were 48% and 58%. The Hg material balance closures for four tests conducted at the first plant ranged between 75% and 104%, and averaged 92%. The Hg material balance closures for three tests conducted at the second plant ranged from 108% to 125% and averaged 116%. Of the total Hg in the coal, 7% to 14% reported to the ESP ash and 35% to 70% to the FGD solids. No measurable Hg was found in the ash samples obtained upstream of the air preheater (bottom ash and economizer ash), or in the FGD slurry filtrate water.

The flue gas Hg speciation data indicate that the Hg fraction collected in the KCl impingers of the Ontario Hydro sampling train at the scrubber inlet is the species that is removed across the FGD system. In this method, the KCl impingers collect the oxidized fraction of the flue gas Hg (Hg^{++}). The inlet Hg speciation estimated from the KCl sampling method showed between 80% and 90% oxidized Hg at the ESP inlet. Outlet speciation data showed measurable particulate Hg emissions that are thought to be an artifact formation from a gas phase reaction of Hg with the filter media used in the sampling train.

The Illinois State Geological Survey conducted a literature search to identify available flue gas Hg sampling data from scrubbed units. It became evident, based on this literature search, that little reliable data existed. Statistical analyses performed on data obtained at the EPRI High Sulfur Test Center (HSTC) showed no statistical significance at the 95% level for Hg removal with any of the observed process parameters. The information collected in this study and other CONSOL in-house test data from an eastern coal-fired, scrubber-equipped utility were used to assist in this activity. A statistical analysis of these data showed no strong correlation between scrubber parameters and Hg removal. Some minor coal quality parameters appeared to correlate with Hg removal across the ESP.

The average HCl emissions at the two sites were 66 lb/hr and 26 lb/hr (~200 and ~80 tons per year). The average HCl removal across the FGD scrubber at both sites was ~82%. The HF emissions at the first site were below the detection limit of 2 lb/hr. The HF emissions at the second site averaged 6 lb/hr (~20 tons per year) with an average FGD scrubber removal of 79%. However, due to the sampling method used, we believe that the reported acid gas removal rates are biased low.

Phase II Results - Sites 3 and 4 (New Data)

The third sampling program was completed during the week of June 22, 1998, and the fourth sampling program was completed the week of July 14, 1998. Testing at the third plant consisted of four replicate flue gas Hg measurements at the ESP Inlet, the FGD inlet and the FGD outlet. Testing at the fourth plant consisted of triplicate flue gas Hg measurements at the ESP inlet and the FGD outlet. Process stream samples (i.e., feed coal, fly ash, bottom ash, limestone, FGD sludge/product, etc.) were obtained at both plants to conduct a mercury material balance to verify data quality.

The average Hg emissions for the two Phase II sites were 1.9 and 2.8 $\mu\text{g}/\text{m}^3$ (0.0006 and 0.007 lb/hr). The total Hg removal across the entire system (ESP and FGD) averaged 75% and 67%. The average Hg removals across the FGDs were 46% and 57%. The Hg material balance closures for four tests conducted at the third plant ranged between 79% and 118%, and averaged 97%. The Hg material balance closures for three tests conducted at the fourth plant ranged from 99% to 108%, and averaged 104%. Of the total Hg in the coal, for Plant 3, 35% reported with the ESP ash and only 5% was associated with the FGD solids. However 13% of the Hg reported with the bottom ash, and another 17% was found in the pre-scrubber blowdown water. For Plant 4, 8% of the Hg reported with the ESP ash and 58% reported with the FGD solids.

As in the Phase I results, the flue gas Hg speciation data indicate that the Hg fraction collected in the KCl impingers of the Ontario Hydro sampling train at the scrubber inlet is the species that is removed across the FGD system. If it is assumed that the Hg adsorbed on the solid samples (ESP and bottom ash) and in the KCl impingers is in the oxidized form, then ~90% of the oxidized fraction is being removed by a combination of solid adsorption and removal across the FGD.

The information collected in this study and another CONSOL in-house test data from an eastern coal-fired, scrubber-equipped utility was added to the existing ISGS database for additional correlation analysis. A statistical analysis of these data showed a strong correlation between scrubber slurry pH and Hg removal where higher pH showed higher Hg removal.

The average HCl removal across the FGD scrubber at the third and fourth site were 99% and 97% respectively. The HF removals for these plants were >95% and >96% respectively.

The results of both the Phase I and II testing demonstrated that wet FGD systems installed and operated for SO₂ control are capable of removing 50-60% of the flue gas Hg. The total Hg removal ranged from 56% to 75% for the ESP-FGD combination. This information will provide utilities with a low-cost compliance option if EPA proposes a Hg emission reduction program.

OBJECTIVES

The goal of the project was to determine the percentage of removal of selected HAPs by wet FGDs at Illinois coal-fired utility boilers. The HAPs of concern are mercury and acid gases (HCl, HF). These species, because of their volatility, are not captured with the fly ash and remain in the vapor state at the exit of the particulate collection devices (ESPs, fabric filters). A secondary objective was to correlate Hg removal with boiler/scrubber operating parameters. To accomplish these goals, CONSOL completed two, one-week sampling programs at two Illinois coal-fired utilities equipped with wet FGD scrubbers. These test programs consisted of flue gas Hg measurements at the ESP inlet, the scrubber inlet, and the scrubber outlet, in conjunction with obtaining a variety of process stream samples. The sampling programs were conducted by the CONSOL Research & Development field services staff. The test data were evaluated by personnel from the Illinois State Geological Survey (ISGS) in an effort to develop a correlation between HAP removal and boiler/scrubber operating parameters. The potential HAP regulations are a concern to the Illinois coal and utility industries. The data from this study will help to determine the effectiveness of wet FGD systems in removing volatile HAPs. Two utility plants were evaluated and reported in 1996-1997. Two additional plants were evaluated in 1998 (Phase II). The results of the Phase II testing are documented in this report.

INTRODUCTION AND BACKGROUND

The Environmental Protection Agency (EPA), the U.S. Department of Energy (DOE), the Electric Power Research Institute (EPRI), and their subcontractors have extensively studied the partitioning of Hazardous Air Pollutants (HAPs) at coal-fired utility plants. The majority of HAPs were captured in existing particulate collection devices (ESPs, fabric filters). The exceptions are the elements or compounds denoted as Class III (Hg, Se, HF, HCl), which remain in the vapor state at the ESP or fabric filter exit. Potential HAP regulations could impact the Illinois coal industry.

In a series of EPA Reports to Congress, EPA has identified a "plausible link" between utility Hg emissions from coal-fired boilers and health and ecological impacts. EPA has identified this source category as the largest single source contributor of anthropogenic Hg emissions (~50 tpy for coal-fired utilities versus 150 total tpy from all anthropogenic sources). EPA is in the process of collecting additional Hg emissions information from these sources to determine if Hg control is warranted. Currently, there is no proven Hg control technology for this source category. Carbon injection has been studied at the pilot scale and control costs for this technology have been estimated as high as \$40,000 to \$50,000 per lb of Hg removed.

Studies at coal-fired utilities have shown that wet scrubbers can remove mercury. However, these studies show a wide variation in removal (0 to 100%), indicating the need for additional data to define the cause of the reported variation. The goal of this program is to develop more precise data regarding the removal of mercury and other volatile HAPs (HF,

HCl) by wet FGD systems. These data, along with EPA and DOE emission assessment results, will provide the Illinois utility industry with the information necessary to evaluate wet FGD systems to remove volatile HAPs. Because of recent acid deposition legislation, the Illinois coal industry is losing a significant market share to lower sulfur Western coal. This coal can meet SO₂ emission compliance levels without the addition of wet scrubbers. However, the volatile HAP emissions are uncontrolled. If FGD scrubbers, designed and operated for SO₂ removal, are also effective for HAP control, and if HAP regulations are instituted, there may be a cost advantage to using in-state coal and incorporating a wet FGD system. The data developed in this test program will be used to develop a model to predict HAP removal by wet FGD systems.

EXPERIMENTAL PROCEDURES

Four Illinois utility stations equipped with wet scrubbers agreed to participate with CONSOL on the sampling test program. Two stations were tested in the 1996-1997 test program (Phase I) and are identified as sites 1 and 2. Two additional stations were evaluated in 1998 (Phase II) and are identified as sites 3 and 4. Site visits were conducted at sites 3 and 4 by the CONSOL sampling team in early 1998. During the site visits, program requirements were discussed with plant operating personnel, sampling locations were identified, and arrangements were made with plant personnel for assistance during the sampling.

Four material balance tests were conducted at the third station and three material balance tests were conducted at the fourth station. Each test period included simultaneous flue gas sampling at the ESP inlet and at FGD outlet. In addition to these locations, gas sampling was also conducted at the FGD inlet of Site 3. These samples were obtained by using the Ontario Hydro sampling train. The Ontario Hydro sampling train is capable of speciating Hg into three fractions; 1) Hg adsorbed on particulate, 2) oxidized Hg, and 3) elemental Hg. Acid gas (HCl and HF) sampling was conducted at the ESP inlet and FGD outlet at each test site. In addition to flue gas samples, representative process stream samples were obtained during the test period. Process stream samples included: coal, ash (bottom, economizer, ESP), limestone slurry, scrubber make-up water, scrubber by-product (gypsum, sludge), and scrubber discharge water. The analyses of these samples were used to calculate material balances. Diagrams showing the sampling locations utilized at each test site are presented in Figures 1 and 2.

During the test periods, pertinent boiler and scrubber operating data were periodically obtained to ensure steady-state plant operation. Both stations provided complete logs of boiler and scrubber operating data for the test periods.

Utility Operating Conditions

One objective of the test program was to determine the accuracy and reliability of existing mercury-in-flue-gas measurement techniques. This required repetitive measurements taken under similar conditions. The operating staffs at both utilities were asked to maintain similar boiler and scrubber operating conditions for each test period. The third test site is a 40 MWe equivalent steam plant consisting of three spreader-stokers, of which two were operating during the test period. Each boiler has a dedicated ESP and each ESP has three collection fields. This plant is equipped with a Chiyoda scrubber that incorporates a water spray pre-scrubber upstream of the FGD module. The fourth test site is a 400 MWe PC-fired boiler equipped with a natural oxidation limestone slurry scrubber. Particulate removal is accomplished by a three-field ESP. The following tables show the operating parameters maintained at both sites during the sampling programs.

BOILER/SCRUBBER OPERATING PARAMETERS AT SITE 3

Plant Parameter	Test 1	Test 2	Test 3	Test 4	Average
lb/hr Steam (x 1000)	295	294	298	265	288
Equivalent MWe	39	39	39	35	38
Coal Feed, lb/hr (dry)	29320	29830	30060	25470	28670
% O ₂ @ Economizer	7.8	7.9	7.4	7.6	7.7
Drum Pres, psi	840	840	840	830	838
Steam Pres, psi	810	810	810	800	808
Flue Gas Parameters					
Flow, dscfm	99400	99200	99200	91700	97375
% CO ₂	11.0	11.4	11.5	10.4	11.1
SO ₂ , ppmv	290	328	320	331	317
SO ₂ , lb/MM Btu	0.77	0.86	0.83	0.94	0.85
Scrubber Parameters					
Limestone Use, tph	~1.7	~1.8	~1.8	~1.5	~1.7
FGD Slurry Density	1.17	1.13	1.17	1.18	1.15
FGD Slurry pH	4.6	5.1	5.3	4.9	5.0
SO ₂ Removal, %	88	87	87	86	87

These data indicate that steady-state boiler and scrubber operations were maintained over the three-day test period with just a slight drop in load (~10%) for the fourth test period.

BOILER/SCRUBBER OPERATING PARAMETERS AT SITE 4

Plant Parameter	Test 1	Test 2	Test 3	Average
Megawatts	374	375	375	375
Coal Feed, lb/hr (dry)	310600	315600	305300	310500
%O ₂ @ Economizer	2.5	2.2	2.6	2.4
Flue Gas Parameters				
Flow, dscfm	866300	874900	853200	864800
%O ₂	5.2	4.7	5.1	4.9
%CO ₂	13.5	13.6	13.4	13.5
NO _x , ppmv	387	373	381	380
SO ₂ , ppmv	540	500	535	524
SO ₂ , lb/hr	4674	4373	4563	4537
Scrubber Parameters				
Limestone Use, tph	~16	~16	~16	~16
FGD Slurry % Solids	NA	NA	NA	NA
Absorber Slurry pH	5.8	5.8	5.8	5.8
SO ₂ Removal, %	82	83	82	82

These data show consistent plant operation over the three-day test period.

Coal Analyses

The literature suggests that coal composition can influence Hg speciation in the flue gas. Both utilities were firing coal from the State of Illinois. Comprehensive coal analyses were completed on daily test coal samples from each plant. The coal analyses from samples collected at the test sites are presented in Tables 1 and 2 and summarized as follows.

ANALYSES OF COAL FEED SAMPLES AT SITE 3

(Units are % dry basis unless noted)

	Test 1	Test 2 & 3	Test 4	Avg
Volatile Matter	42.33	42.66	42.46	42.48
Ash	9.83	10.15	10.40	10.13
Carbon	70.42	70.51	70.39	70.44
Hydrogen	4.99	5.11	4.90	5.00
Nitrogen	1.25	1.29	1.29	1.28
Oxygen	9.14	8.48	8.54	8.72
Total Sulfur	4.14	4.24	4.24	4.21
Chlorine	0.23	0.22	0.23	0.23
Fluorine, ppm	115	106	120	114

Mercury, ppm	0.08	0.09	0.09	0.09
Heating Value, Btu/lb	12775	12754	12665	12731

The Hg concentration in the coal showed little variability and averaged 0.09 ppm ($\mu\text{g/g}$) on a dry basis. Assuming that all the Hg in the coal volatilizes during combustion, the mercury concentrations would result in a nominal Hg flue gas concentration of $\sim 8 \mu\text{g/m}^3$. A number of studies have linked the chlorine concentration of the coal with flue gas Hg speciation. The chlorine content of this coal would result in a theoretical flue gas HCl concentration of ~ 120 ppmv. Actual measurements at the ESP inlet showed HCl concentrations of ~ 70 ppmv. The fluorine content of this coal would result in a theoretical flue gas HF concentration of $\sim 6-8$ ppmv. The three flue gas HF measurements at the ESP inlet averaged 6 ppmv.

ANALYSES OF COAL FEED SAMPLES AT SITE 4

(Units are % dry basis unless noted)

	Test 1	Test 2	Test 3	Avg
Volatile Matter	42.16	42.31	42.48	42.32
Ash	10.08	10.02	9.82	9.97
Carbon	70.64	70.85	70.76	70.75
Hydrogen	4.85	4.77	4.68	4.77
Nitrogen	1.37	1.35	1.33	1.35
Oxygen	8.81	8.82	9.13	8.92
Total Sulfur	4.09	4.05	4.14	4.09
Chlorine	0.15	0.14	0.14	0.14
Fluorine, ppm	104	116	95	105
Mercury, ppm	0.08	0.08	0.08	0.08
Heating Value, Btu/lb	12748	12734	12777	12753

The Hg concentration in the coal showed no variability and averaged 0.08 ppm ($\mu\text{g/g}$) on a whole coal basis. Assuming that all the Hg in the coal volatilizes during combustion, the flue gas mercury concentration would be $\sim 9 \mu\text{g/m}^3$. The chlorine content of this coal would result in a theoretical flue gas HCl concentration of ~ 100 ppmv. At the ESP inlet, the measured HCl concentration was between 60-70 ppmv. The fluorine concentration of this coal would result in a theoretical flue gas HF concentration of ~ 16 ppmv. The three flue gas HF measurements at the ESP inlet indicated HF concentrations of 9, 15, and 8 ppmv.

Process Flow Rates

Coal Feed to Boiler. The only input stream required for the material balance calculation at both plants was the coal fed to the boiler. The coal firing rate was determined by two methods: the F-factor calculations and the volumetric feeders. The F-factor calculation uses the measured flue gas flow rate, flue gas composition, and coal quality data to determine the amount of coal combusted. The accuracy of this method is a function of how accurately these parameters can be measured. The volumetric feeders give a direct readout of the volume of coal fed into the system, and the accuracy of this measurement is a function of the bulk coal properties and feeder calibrations. The difference in calculated coal feed rate using both methods was less than 4% at both test sites. For this study, all results are based on the coal feed rate from the F-factor calculations.

Bottom Ash, Economizer Ash, and ESP Ash. The primary split between the combination of the bottom ash with the ESP ash at both plants was determined by forcing an ash material balance. The total ash was determined based on the coal firing rate and the ash content of the coal. The ESP fly ash rate was measured using isokinetic sampling techniques (EPA Method 5) at the inlet plane of the ESP. The ESP fly ash flow rate accounted for ~15% of the total ash flow at the third test site (spreader-stoker boiler). It then was estimated that the bottom ash accounted for ~85%. There are no economizer hoppers at this site.

The ash split at the fourth test site (PC-fired boiler) showed ~60% ESP ash, 38% bottom ash, and only 2% economizer ash.

Carbon analysis of the ash samples for the two plants showed a wide range of variability. A summary of the carbon and Hg analyses performed on the bottom ash samples are shown in the following tables.

BOTTOM ASH SAMPLES - CARBON AND Hg RESULTS

	Plant No. 3	Plant No. 4
% Carbon in Bottom Ash		
Test 1	2.58	9.39
Test 2	3.23	6.76
Test 3	3.23	19.31
Test 4	2.84	----
Average	2.88	11.82
ppm Hg in Bottom Ash		
Test 1	0.21	<0.01
Test 2	0.13	0.05
Test 3	0.13	0.05
Test 4	0.08	----
Average	0.14	0.04

Summaries of the analyses performed on these samples are presented in Tables 3 and 4.

Plant 3 is not equipped with economizer ash hoppers. The results of the economizers ash samples obtained at Plant 4 are shown as follows.

ECONOMIZER ASH SAMPLES - CARBON AND Hg RESULTS

	Plant No. 3	Plant No. 4
% Carbon in Economizer Ash		
Test 1	No Sample	25.80
Test 2		27.89
Test 3		51.50
Average		35.06
ppm Hg in Economizer Ash		
Test 1	No Sample	0.03
Test 2		0.06
Test 3		0.04
Average		0.04

A summary of the analyses performed on these samples is presented in Table 5.

Each plant was equipped with a multi-field ESP for particulate collection. Separate samples were collected and analyzed from each field. The composite average value for each plant and test are shown below.

ESP HOPPER ASH SAMPLES - CARBON AND Hg RESULTS

(Composite Values from the Individual Fields)

	Plant No. 3	Plant No. 4
% Carbon in ESP Hopper Ash		
Test 1	42.43	3.79
Test 2	41.78	2.15
Test 3	41.78	4.87
Test 4	44.29	----
Average	42.84	3.60
ppm Hg in ESP Hopper Ash		
Test 1	1.25	0.10
Test 2	1.02	0.11
Test 3	1.02	0.11
Test 4	0.87	---
Average	1.05	0.11

Plant 3 had two precipitators, and each precipitator had three hoppers operated in series. Separate ESP ash samples were obtained from each hopper. A summary of the analyses performed on each sample is presented in Table 6.

The Plant 4 ESP consists three fields, and individual samples were collected from selected hoppers representative of each field. A summary of the analyses performed on each sample is presented in Table 7.

FGD Solids. Neither plant was equipped with flow measuring devices for this stream; therefore, the FGD solids production was estimated based on the FGD SO₂ removal rate, scrubber chemistry, and FGD solids analysis. The third test site used forced oxidation in the FGD to convert the SO₂ to a CaSO₄ product. The assumptions used in this estimate are that limestone is used in a 2% excess and the product is CaSO₄·2H₂O. Analyses of these samples indicate that this is the primary constituent. The data used in calculating the individual FGD production and Hg mass flow rates are summarized below.

MASS FLOW RATE OF FGD SOLIDS FOR TEST SITE 3

	Test 1	Test 2	Test 3	Test 4
SO ₂ Produced, lb/hr	2428	2530	2549	2165
FGD SO ₂ Removal Eff, %	88.1	87.1	87.6	86.0
SO ₂ Removed, lb/hr	2140	2204	2232	1862
SO ₂ Removed, lb-moles	33	34	35	29
CaSO ₄ ·2H ₂ O Produced, lb/moles	34	35	36	30
Mol. wt of CaSO ₄ ·2H ₂ O	172	172	172	172
CaSO ₄ ·2H ₂ O Produced, lb/hr	5848	6020	6192	5160
ppm of Hg in FGD Solids, dry	0.03	0.03	0.03	0.03
lb/hr of Hg in FGD Solids	0.00017	0.00018	0.00019	0.00014
mg/sec of Hg in FGD Solids	0.02	0.02	0.02	0.02

The fourth test site does not use forced oxidation in the FGD. The assumptions used in this estimate are that no excess limestone is used and the product is CaSO₃·½H₂O. Analysis of these samples indicate that this is the primary constituent. The data used in calculating the individual FGD production and Hg mass flow rates are summarized below.

MASS FLOW RATE OF FGD SOLIDS FOR TEST SITE 4

	Test 1	Test 2	Test 3
SO ₂ Produced, lb/hr	25407	25564	25279
FGD SO ₂ Removal Eff, %	81.6	82.9	82.0
SO ₂ Removed, lb/hr	20731	21191	20716
SO ₂ Removed, lb-moles	324	331	324
CaSO ₃ ·½H ₂ O Produced, lb/moles	324	331	324
Mol. wt of CaSO ₃ ·½H ₂ O	129	129	129
CaSO ₃ ·½H ₂ O Produced, lb/hr	41800	42700	41800
ppm of Hg in FGD Solids, dry	0.35	0.35	0.35
lb/hr of Hg in FGD Solids	0.015	0.015	0.015
mg/sec of Hg in FGD Solids	1.84	1.88	1.84

Comprehensive analyses were completed on the FGD solid/sludge samples obtained at each plant. These data are presented in Tables 8 and 9. At the third site, the FGD solids were collected as a filter cake and analyzed as a solid sample. At the fourth site, FGD slurry samples were obtained from the recycle line servicing each of the scrubber modules. The liquid portion was decanted from the solids and analyzed separately. No significant concentration of Hg was found in the decant water. The FGD solids were air-dried to retain the Hg and then analyzed.

Limestone, Make-up Water to FGD, and FGD Slurry Filtrate. Analyses conducted on these samples indicated no significant Hg contribution to the system. Because these streams do not contribute to the overall Hg balance, their mass flowrates are not required. The results of the analyses performed on the limestone samples from each plant are shown in Tables 10 and 11.

Pre-Scrubber Blowdown Water for Plant 3. Plant 3 was equipped with a pre-scrubber spray tower prior to the Chiyoda FGD scrubber. The gas is contacted with a fine liquid spray consisting of make-up water and recirculated cooling water. The liquid cools and humidifies the gas to its adiabatic saturation temperature. The liquid has a secondary function of removing impurities including particulate and soluble chlorides. These impurities are removed in a blowdown stream. Representative samples of this blowdown stream were taken for each test period. The liquid flow rate of this stream is 20 gpm, as determined by plant personnel. The Hg concentration for the four test samples were 56, 38, 38, and 42 ng/mL. This calculates to a mass flow rate of 0.07, 0.05, 0.05, and 0.05 mg/sec, and accounts for 14% to 21% Hg removal.

Waste Water Solids and Filtrate Water for Plant 3. Plant 3 was equipped with a waste water treatment system. The primary feed to this system is the pre-scrubber blowdown liquor, the water from the gypsum dewatering filter, and liquid slurries from a variety of plant drains/sumps. The waste water is treated with chemical flocculent, which serves to coagulate the solids. The solids are pressed and removed as a dense filter cake. Analyses performed on the solids indicate that they consist mostly of coal particles. The Hg content of this waste stream ranged from 0.10 to 0.15 wt %. The primary source of this Hg is the pre-scrubber blowdown stream. The Hg concentration of the filtrate water was <0.01 ppm. The waste water treatment plant is doing an excellent job in removing the Hg from the liquid streams and sequestering it in the solid sludge. The analytical data for the discharge water is shown in Table 12 while the results of the solids are shown in Table 13.

Flue Gas Sampling Data

The flue gas sampling matrix for the third plant is shown below.

	ESP Inlet	ESP Outlet	FGD Outlet
Hg Speciation	Traverse	Middle of Duct	Middle of Duct
Acid Gases	NA	Middle of Duct	Middle of Duct

Particulate	Traverse	Middle of Duct	NA
Velocity	Traverse	Traverse	NA

There were two ESP inlet and outlet ducts and these were treated as a common duct. The ESP outlet ducts provided the optimum location for the measurement of the gas flow rate. A daily velocity traverse was conducted at this location, and the results were used to calculate the gas flow rates for the other locations. Velocity traverses were conducted on the ESP inlet ducts, but, due to the proximity of upstream and downstream disturbances, these results are not as reliable as the ESP outlet duct measurements. Single point (mid-point of the sampling ducts) measurements were used for the Hg and acid gas sampling at the ESP outlet (two ducts) and FGD outlet (single duct). It is reasonable to assume that the gas species are homogeneously distributed at these sampling location. The key flue gas sampling parameters measured at these locations are summarized in the following tables.

SUMMARY OF FLUE GAS MEASUREMENTS FOR THE THIRD TEST SITE

ESP Inlet Measurement

	Test 1	Test 2	Test 3	Test 4
Sample Time, min	110	115	120	130
Bar. Pres., inches of Hg	29.15	29.12	29.14	29.05
Static Pres., inches of H ₂ O	-15.1	-17.8	-14.4	-12.1
% O ₂	7.8	7.9	7.4	7.6
% H ₂ O	11.0	10.2	10.2	9.8
Flue Gas Temp, °F	340	339	343	346
Gas Sample Volume, dry std cubic feet	70.21	70.23	69.08	77.16
Flue Gas Velocity, feet/sec	56.2	57.8	56.1	52.5
Flue Gas Flow, actual cubic feet/min	175200	179800	175000	150000
Flue Gas Flow, dry std cubic feet/min	96400	100000	97000	83400
Particulate Rates: gr/dry standard cubic feet lb/hr	1.099 908	1.100 942	1.117 929	0.999 715
% Isokinetic	101.1	93.1	90.7	99.6

ESP Outlet (FGD Inlet) Measurement

	Test 1	Test 2	Test 3	Test 4
Sample Time, min	120	110	110	120
Bar. Pres., inches of Hg	29.15	29.12	29.14	29.05
Static Pres., inches of H ₂ O	-0.65	-0.88	-0.90	-0.86
% O ₂	8.2	7.8	7.7	8.8
% H ₂ O	10.2	10.0	9.8	9.4
Flue Gas Temp, °F	343	344	346	346
Gas Sample Volume, dry std cubic feet	90.53	80.02	80.59	80.22
Flue Gas Velocity, fps	53.0	52.6	52.6	47.6
Flue Gas Flow, actual cubic feet/min	173100	172800	172800	159600

Flue Gas Flow, dry std cubic feet/min	99400	99200	99200	91700
Particulate Rates: gr/dry standard cubic feet lb/hr	0.007 6	0.017 15	0.020 17	0.023 18
% Isokinetic	103.9	101.1	101.8	102.6

FGD Outlet Measurement

	Test 1	Test 2	Test 3	Test 4
Sample Time, min	100	100	100	100
Bar. Pres., inches of Hg	29.15	29.12	29.14	29.05
Static Pres., inches of H ₂ O	-0.35	-0.30	-0.25	-0.35
% O ₂	8.4	8.3	9.0	8.6
% H ₂ O	17.4	16.4	16.5	17.2
Flue Gas Temp, °F	178	179	179	183
Gas Sample Volume, dry std cubic feet	83.66	76.62	75.12	80.52
Flue Gas Velocity, fps	49.9	46.3	45.9	44.0
Flue Gas Flow, actual cubic feet/min	152000	153600	163900	136800
Flue Gas Flow, dry std cubic feet/min	101000	103200	110100	90200
Particulate Rates: gr/dry standard cubic feet lb/hr	0.008 7	0.010 9	0.006 5	0.002 2
% Isokinetic	103.6	101.4	100.2	103.7

These data show excellent reproducibility for each test and location. The data obtained from these samples are used to calculate the Hg concentrations in the flue gas, Hg mass flow rate, Hg removal across the scrubber and system, and the fate of Hg in the utility system.

The flue gas sampling matrix for the fourth plant is shown below.

	ESP Inlet	FGD Outlet
Hg Speciation	Traverse	Middle of Duct
Acid Gases	Middle of Duct	Middle of Duct
Particulate	Traverse	Middle of Duct
Velocity	Traverse	Traverse

There were two ESP inlet ducts, and these were treated as a common duct. A single point measurement was used for the acid gas sample at this location. Due to safety considerations, no samples were obtained on the ESP outlet/FGD inlet duct. The FGD outlet stream was sampled at the base of the stack. A full velocity traverse was conducted at this location for every test period. Single point (mid-point of the sampling duct) measurements were used for the Hg and acid gas sampling at this location. Again, it is reasonable to assume that the gas

species are homogeneously distributed at this sampling location. The key flue gas sampling parameters measured at these locations are summarized in the following tables.

SUMMARY OF FLUE GAS MEASUREMENTS FOR THE FOURTH TEST SITE

ESP Inlet Measurement

	Test 1	Test 2	Test 3
Sample Time, min	120	120	120
Bar. Pres., inches of Hg	29.19	29.20	29.28
Static Pres., inches of H ₂ O	-10.0	-10.0	-10.0
% O ₂	3.9	3.8	4.2
% H ₂ O	11.1	11.7	11.3
Flue Gas Temp, °F	314	311	314
Gas Sample Volume, dry std cubic feet	52.78	42.98	44.04
Flue Gas Velocity, fps	30.4	30.8	30.3
Flue Gas Flow, actual cubic feet/min	1368800	1387200	1363200
Flue Gas Flow, dry std cubic feet/min	789800	798100	786800
Particulate Rates: gr/dry standard cubic feet lb/hr	2.84 19215	2.87 19650	2.80 18909
% Isokinetic	101.8	103.7	101.3

FGD Outlet Measurement

	Test 1	Test 2	Test 3
Sample Time, min	135	120	110
Bar. Pres., inches of Hg	29.19	29.20	29.28
Static Pres., inches of H ₂ O	-0.48	-0.50	-0.50
% O ₂	5.4	5.3	5.5
% H ₂ O	15.5	15.1	16.3
Flue Gas Temp, °F	133	133	133
Gas Sample Volume, dry std cubic feet	107.47	101.97	90.37
Flue Gas Velocity, fps	49.26	49.47	48.82
Flue Gas Flow, actual cubic feet/min	1182330	1187400	1171700
Flue Gas Flow, dry std cubic feet/min	866300	874900	853200
Particulate Rates: gr/dry standard cubic feet lb/hr	0.006 48	0.001 9	0.004 26
	99.8	105.5	104.6

As with the first plant, these data show consistent duct measurements for the three test days and serve as the basis for the Hg emission and removal calculations.

RESULTS AND DISCUSSION

Mercury Removal Due to Adsorption on Fly Ash

The Hg removal due to adsorption on the fly ash was determined by calculating the Hg input to the boiler from the amount of Hg in the coal and the coal firing rate and comparing this input value with the amount of Hg found in the ash streams. Measurable amounts of Hg were found in all of the ash streams. The Hg removals due to adsorption on the individual ash streams for each test sites are shown as follows.

Hg REMOVAL DUE TO ADSORPTION ON ASH SAMPLES
% of Total Hg Input

	Plant No. 3	Plant No. 4
BOTTOM ASH:		
Test 1	20	0
Test 2	13	3
Test 3	13	3
Test 4	8	---
Average	13	2
ECONOMIZER ASH:		
Test 1	No Sample	<0.5
Test 2		<0.5
Test 3		<0.5
Average		<0.5
ESP ASH:		
Test 1	43	8
Test 2	36	9
Test 3	35	9
Test 4	27	---
Average	35	9
TOTAL ASH:		
Test 1	63	8
Test 2	49	12
Test 3	48	12
Test 4	35	---
Average	48	11

At the third plant, 13% of the Hg in the coal reports to the bottom ash and 35% reports to the ESP ash. The total Hg removal attributed to absorption on the ash samples ranged from 35% to 63%, and averaged 48%. The fourth plant showed a 2% Hg removal with the bottom ash, insignificant removal with the economizer ash, and a 9% removal with the ESP ash. The total Hg removal attributed to absorption on the ash samples was in the range of 8% to 12%, and averaged 11%. The high Hg removal with the ash for Plant 3 may be due to the combustion system, which is a spreader-stoker. As evident by the ash analysis, there is a significant carbon concentration in the bottom ash (~3%) and a very high carbon concentration in the ESP ash (~50%). The Hg removal associated with the ash samples measured at

the fourth plant is typical of previous measurements at PC-fired utilities burning eastern bituminous coal.

Mercury Removal Across FGD System

The mercury removal across the FGD system is calculated from the FGD inlet and outlet gas phase Hg mass flow rates. The Hg removal across the FGD system was determined by two methods. In the first method, the flue gas Hg concentration at the FGD inlet was calculated based on the coal firing rate, the Hg content of the coal, and the Hg removed due to adsorption on the ash samples upstream of the FGD system. In the second method, gas phase Hg measurements at the FGD inlet were compared to the FGD outlet (stack) measurements to determine Hg removal. The results are presented in the following table.

Hg REMOVAL ACROSS THE FGD SYSTEM
% of Total Hg Input to FGD System

	Plant 3		Plant 4	
	Coal Value	Gas Samples	Coal Value	Gas Samples
Test 1	20	48	65	64
Test 2	50	45	58	54
Test 3	56	46	65	53
Test 4	74	45	---	---
Average	50	46	63	57
Standard Deviation	22	1	4	6
Percent Relative Standard Deviation	21%	3%	6%	10%

At the third test site, the average Hg removal across the FGD was 50% using the coal and ash solids data and 46% using the measured flue gas mercury data. The good agreement between the two techniques confirms the measured Hg removal. At the second site, the Hg removal was 63% using the coal and ash solids data and 57% using the gas sampling data. Again, this is fairly good agreement. The accuracy of the Hg inlet value calculated from the coal data is a function of the accuracy of the mercury-in-coal analysis, the calculated coal firing rate, and the measured bottom ash and ESP Hg removal. The accuracy of the Hg inlet value from the gas analysis is a function of the accuracy of the impinger Hg analysis. These data confirm that Hg removal across the FGD system is 46% to 50% for the first plant and 57% to 63% for the second plant.

Total Hg Removal Across Utility System

This test program confirmed Hg removal by adsorption on the bottom ash and ESP fly ash particles and gas phase Hg removal across the FGD system. The combined effects result in a total Hg removal across the entire system. The total Hg removal is calculated using the coal firing rate and Hg concentration in the coal to calculate Hg input to the system. The Hg emissions were determined from stack flue gas samples. Total Hg removals at both plants are shown in the following table.

TOTAL Hg REMOVAL ACROSS THE UTILITY SYSTEM (ESP and FGD) % of Total Hg Input

	Plant 3	Plant 4
Test 1	69	67
Test 2	74	63
Test 3	76	70
Test 4	82	---
Average	75	67
Standard Deviation	6	3
Percent Relative Standard Deviation	8%	5%

Total Hg removal averaged 75% for the third plant and 67% for the fourth plant. There was a measured variability of 5-8%. The data indicate that greater than two-thirds of the Hg in the coal is removed by a combination of adsorption on the ash particles and the action of the FGD system. These measurements were obtained on systems operating in their normal and routine mode of operation, with no adjustments to optimize Hg control.

Fate of Hg in Utility System and Material Balance Data

In addition to the measurement of Hg removal in FGD-equipped utility boilers, two other objectives were to determine the fate of the removed Hg and to calculate Hg material balance closures to assess the quality of the measurements. Representative process stream samples that augmented the flue gas measurements were obtained and analyzed to complete this task. The results of these measurements for both plants are shown below.

FATE OF Hg AND MATERIAL BALANCE DATA FOR TEST SITE 3 (Hg mass flow units are mg/sec)

	Test 1	Test 2	Test 3	Test 4	Average
Input Streams:					
Coal	0.33	0.34	0.34	0.29	0.33
Limestone	0	0	0	0	0
Make-up Water	0	0	0	0	0
Total Hg Input	0.33	0.34	0.34	0.29	0.33
Output Streams:					

Bottom Ash	0.07	0.04	0.04	0.02	0.04
ESP Ash	0.14	0.12	0.12	0.08	0.12
Pre Scrubber Blowdown	0.06	0.06	0.06	0.06	0.06
FGD Solids	0.02	0.02	0.02	0.02	0.02
FGD Filtrate	0	0	0	0	0
FGD Outlet	0.10	0.09	0.08	0.05	0.08
Total Outlet	0.39	0.33	0.32	0.23	0.32
% Hg Closure	118%	97%	94%	79%	97%

The only mercury input was from the coal. On the average, ~13% of the Hg reported with the bottom ash and ~35% reported with the ESP ash. The Hg removal attributed to absorption on the ash particles lowered the gas phase Hg concentration at the FGD inlet by ~50%. This level was further reduced by another 50% by the combined action of the pre-scrubber and the FGD. In fact, most of the Hg removal was occurring in the pre-scrubber. No mercury was detected in the FGD filtrate water. The Hg balance closures ranged from 79% to 118% and averaged 97%. At the beginning of the program, we established a $\pm 20\%$ material balance closure as a measure of data quality. These data represent acceptable Hg material balance closures.

The mercury material balances for the fourth site are presented in the following table.

FATE OF Hg AND MATERIAL BALANCE DATA FOR TEST SITE 4
(Hg mass flow units are mg/sec)

	Test 1	Test 2	Test 3	Average
Input Streams:				
Coal	3.13	3.18	3.08	3.13
Limestone	0	0	0	0
Make-up Water	0	0	0	0
Total Hg Input	3.13	3.18	3.08	3.13
Output Streams:				
Bottom Ash	0	0.08	0.09	0.06
Economizer Ash	0	0.01	0.01	0.01
ESP Ash	0.25	0.27	0.27	0.26
FGD Solids	1.84	1.88	1.84	1.86
FGD Filtrate	0	0	0	0
FGD Outlet	1.02	1.18	0.94	1.05
Total Outlet	3.11	3.42	3.15	3.24
% Hg Closure	99%	108%	102%	104%

Again, the only mercury input was from the coal. The Hg found in the bottom ash samples accounted for ~2% of the total Hg; the Hg found in the economizer ash samples accounted for less than 0.5%. Hg removal due to the ESP ash represented ~8%. The Hg concentration of the FGD solids accounts for ~60% of the Hg originally present in the coal, and this value validates the removal rate attributed to the FGD system. The outlet measurements were very consistent and represent ~33% of the Hg in the coal. As in Plant 3, an insignificant level of Hg mercury was detected in the FGD filtrate water. The Hg balance closures for this plant were 99% to 108% and averaged 104%. For this test program, a data quality objective of an average material balance closure of $\pm 20\%$ with no test greater than $\pm 30\%$ was set. These objectives were met.

Stability of Hg in FGD Solids

Another part of the CONSOL study was to determine the stability of the mercury collected with the FGD solids obtained from a magnesium-enhanced lime scrubber from an eastern utility firing eastern bituminous coal. The objective of this work was to determine the desorption and leaching potential of Hg in the FGD solids. In the first part of this evaluation, FGD solids were heated in a convection oven maintained at a temperature of 140 °F for 11 weeks to determine if some fraction of the Hg would desorb. The Hg concentration of the FGD solids before drying was $0.70 \pm 0.02 \mu\text{g/g}$ (ppm wt. basis) and $0.74 \pm 0.02 \mu\text{g/g}$ after 11 weeks of exposure. This experiment demonstrates that under normal exposure conditions, there is a limited potential for desorption. In the second part of this evaluation, 100 g of the FGD solids were placed in containers with 2 L of three leachate solutions: 1) distilled water, 2) acetic acid buffered to a pH of 4.9 with NaOH, and 3) acetic acid at a pH of 2.8. Each mixture was mechanically agitated for ~20 hours. After agitation, the solutions were filtered, and Hg analyses were performed on the solids and on the filtered leachates. No Hg was detected in the leachate solutions at a minimum detection limit of 0.01 mg/L (ppm). This is 95% below the RCRA limit of 0.2 mg/L. The Hg concentration of the FGD solids after leaching was $0.72 \pm 0.02 \mu\text{g/g}$ compared to $0.70 \pm 0.02 \mu\text{g/g}$ in the FGD solids before leaching. These data indicate that no Hg leaching occurs, as defined by the EPA Toxicity Characteristic Leaching Procedure (TCLP).

Mercury Speciation and Removal Across the ESP and FGD

Total Hg and speciated Hg at the ESP inlet, ESP outlet, and FGD outlet for the third plant are summarized as follows:

FLUE GAS Hg SPECIATION AT TEST SITE 3

	ESP Inlet	ESP Outlet (FGD Inlet)	FGD Outlet
Particulate, $\mu\text{g}/\text{m}^3$			
Test 1	1.88	0.01	<0.00
Test 2	4.08	0.04	<0.00
Test 3	2.89	0.06	<0.00
Test 4	1.67	0.05	<0.00

	ESP Inlet	ESP Outlet (FGD Inlet)	FGD Outlet
Average	2.63	0.04	<0.00
Oxidized, $\mu\text{g}/\text{m}^3$			
Test 1	1.87	3.07	0.90
Test 2	1.96	2.78	0.89
Test 3	2.31	2.41	0.54
Test 4	2.27	1.53	0.49
Average	2.10	2.45	0.70
Elemental, $\mu\text{g}/\text{m}^3$			
Test 1	2.51	1.47	1.49
Test 2	1.35	0.91	1.16
Test 3	0.74	1.01	1.35
Test 4	1.27	0.70	0.77
Average	1.47	1.02	1.19
Total, $\mu\text{g}/\text{m}^3$			
Test 1	6.26	4.55	2.39
Test 2	7.39	3.73	2.05
Test 3	5.94	3.48	1.89
Test 4	5.22	2.27	1.26
Average	6.20	3.51	1.90

The total Hg determined using the Ontario Hydro sampling train at the ESP inlet agree well with the theoretical Hg concentration calculated using the concentration of Hg in the coal and the amount of Hg reporting to the bottom ash. Hg material balance closures at the ESP inlet were 103%, 106%, 88%, and 79%, for an average of 94%. The speciation breakdown at the ESP inlet was 42% particulate, 34% oxidized in the gas phase, and 24% elemental in the gas phase. The particulate Hg is removed with the particulate that is collected in the ESP. The ESP outlet (FGD inlet) speciation showed 2.45 $\mu\text{g}/\text{m}^3$ as oxidized, which is 70% of the gas phase Hg measured at this location. This value is comparable to the gas phase oxidized fraction measured in the ESP inlet sample. Of this amount, 70% is removed by the combined action of the pre-scrubber and limestone scrubber. The gas phase elemental Hg fraction shows little change across both the ESP and the scrubber.

The Ontario Hydro Hg method sampling results show that the Chiyoda scrubber system is removing 46% of the gas phase Hg entering the system. The combined ESP-Chiyoda scrubber is removing 69% of the total Hg. When accounting for the Hg absorbed on the bottom ash upstream of the ESP, the total system Hg removal is 75%. If it is assumed that the amount of Hg absorbed on the ash material is the oxidized fraction, the calculated removal of this fraction is ~90%. Using this same assumption, the flue gas Hg speciation for this coal is 80% oxidized and 20% elemental.

Total and speciated Hg at the ESP inlet, ESP outlet, and FGD outlet at the fourth plant are as follows:

FLUE GAS Hg SPECIATION FOR TEST SITE 4

	ESP Inlet	FGD Outlet
Particulate, $\mu\text{g}/\text{m}^3$		
Test 1	1.53	0.03
Test 2	1.49	0.02
Test 3	1.57	0.02
Average	1.53	0.02
Oxidized, $\mu\text{g}/\text{m}^3$		
Test 1	5.12	1.07
Test 2	5.56	1.50
Test 3	3.52	0.61
Average	4.73	1.06
Elemental, $\mu\text{g}/\text{m}^3$		
Test 1	2.22	1.57
Test 2	1.02	1.55
Test 3	1.40	1.87
Average	1.55	1.66
Total, $\mu\text{g}/\text{m}^3$		
Test 1	8.87	2.68
Test 2	8.06	3.07
Test 3	6.50	2.50
Average	7.81	2.75

The total flue gas Hg measured with the Ontario Hydro train at the ESP inlet agree well with the theoretical Hg concentration calculated from the Hg in the coal and the amount of Hg on the bottom ash. Hg material balance closures at the ESP inlet were 99%, 92%, and 76% for an average of 89%. The speciation breakdown at the ESP inlet was 20% particulate, 60% oxidized in the gas phase, and 20% elemental in the gas phase. The amount of Hg measured on the collected particulate from the sampling train is ~50% higher than the amount of Hg measured in the ESP hopper ash. It is speculated that the sample train particulate is biased high (by 50%) as a result of absorption of gas phase Hg onto the sample train particulate during the sampling process. The FGD outlet speciation showed an insignificant amount of Hg collected in the sampling train particulate catch ($0.02 \mu\text{g}/\text{m}^3$). $1.06 \mu\text{g}/\text{m}^3$ was measured as oxidized Hg, which is 40% of the gas phase Hg measured at this location. Assuming that the particulate fraction measured at the ESP inlet is oxidized Hg adsorbed onto the fly ash, the average reduction for the oxidized Hg species is 83%. The gas phase elemental Hg fraction shows little change across both the ESP and the scrubber.

The measured gas phase values demonstrate that the FGD scrubber system is removing 57% of the gas phase Hg entering the FGD. If it is assumed that 50% of the Hg collected at the ESP inlet on the Ontario Hydro method sampling filter is actually gaseous, oxidized Hg, the gas phase removal is 61%. Using either method, the FGD system is removing 55-60% of the Hg in the flue gas. The net Hg removal from the combined ESP-FGD scrubber is 65%. When accounting for the Hg absorbed on the bottom ash upstream of the ESP, the total system Hg removal is 67%. If it is assumed that the amount of Hg absorbed on the ash material is the oxidized fraction, the calculated oxidized Hg removal is ~85%. Using this same assumption, the flue gas Hg speciation for this coal is 80% oxidized and 20% elemental.

Analysis of Hg Capture Across FGD Systems

As part of this program, personnel for the Illinois State Geological Survey (ISGS) conducted an extensive literature review of Hg emissions for scrubber-equipped coal-fired utilities. ISGS also conducted a statistical analysis of the parameters that influence Hg removal and developed an empirical model to predict Hg removal levels from other scrubbed utilities. This work is complete as a stand-alone document attached as Appendix 1. The major findings of this study are summarized as follows.

Literature Review on Mercury Capture Across FGD Systems - Flue gas desulfurization (FGD) systems are installed in power plants primarily to remove sulfur dioxide. In this process other flue gas components including mercury also are removed. The literature cited below summarizes the results of past work on the capability for mercury removal by the FGD systems.

Before the passage of the Clean Air Act Amendments of 1990, the Electric Power Research Institute (EPRI) began a study of chemical emissions from electric power plants entitled Power plant Integrated Systems: Chemical Emissions Studies (PISCES). The PISCES data show that mercury removals by wet scrubbers range from about 10% to 90%.¹ The PISCES data showed a large variability in mercury removal efficiency, which may be explained by the differences in the ratio of elemental to oxidized mercury in the different flue gases. In 1991, preliminary tests conducted at EPRI's High Sulfur Test Center (HSTC) in New York showed that the wet limestone FGD system removed about 90%.² In 1992, EPRI performed a study to determine the variability in the inlet flue gas mercury concentrations and to correlate the wet FGD scrubber operating conditions with mercury removal efficiency. The results showed that wet limestone FGD system removed about 96% of the inlet mercury which was the approximate percentage of the oxidized Hg fraction. The removal efficiency was found to be independent of the changes made in the operating conditions. Additional testing indicated that the removal efficiency for oxidized mercury seems to be limited only by gas-film mass transfer for the flue gas.

Meij and Alderliesten³ (1989) studied the effectiveness of wet FGD in removing Hg in coal-fired electric utilities in Netherlands. The results showed that although most of the inorganic

gases are removed in a wet FGD, the average Hg removal is somewhat lower (on average 60%). The results further showed that removals depend on the behavior and operating conditions of the demisters.

Gutberlet⁴ (1984) and KHM⁵ (1983) also saw similar results in their tests in West Germany (60% removal) and Sweden (75% removal). The results further showed that 50% to 70% of the Hg in the flue gases is removed by wet FGD, ~25% is emitted with the flue gas, ~60% is with the gypsum, ~10% with the sludge, and the remaining 5% in the effluent of the wastewater treatment plant.

The work of Gleiser and Felsvang⁶ (1994) showed that mercury removal in dry scrubbing systems is correlated with the chlorine content of coal.

Chu and Porcella⁷ (1994) tested the mercury removal efficiency of ESPs and FGD systems in coal-fired electric utility plants. The Hg removal efficiencies for ESP/FGD systems ranged from as low as 0% to as high as 90%. The mean Hg removal efficiency for the combined ESP/FGD system was 45%. The results revealed Hg removals up to 60% in ESP systems. The mean removal efficiency for all coal fired plants with dry particulate controls was about 30%. Hg removal efficiencies for a combined ESP and wet FGD systems are highly variable and gave poor correlation with the FGD design, coal composition, or measured Hg oxidation state.

Fahlke and Bursik⁸ (1995) studied the impact of flue gas cleaning on mercury species emissions from coal-fired steam generators in Germany. Results at two plants showed that 15% of the Hg was removed with the ash and ~30-40% was removed by the FGD system, for a net removal rate of between 45% and 55%. The residue is emitted in the form of gaseous Hg species. The results showed that the FGD system eliminates approximately 80% of the Hg⁺⁺ and that Hg⁰ increases by the factor 10.

Correlation Analysis of Utility Data - Data sets available for the present analysis are the HSTC data and the data collected by CONSOL Inc. The results of the selected correlation analysis conducted on these combined data are presented as follows.

CORRELATIONS BETWEEN FGD AND COAL QUALITY DATA WITH Hg REMOVALS

	Correlation with Percent Hg Removal				
	With Ash	Across FGD	Hg ⁺⁺	Hg ⁰	Hg ^{tot}
FGD Parameters:					
Slurry pH	0.457**	0.385*	0.424*	-0.415*	0.411*
L/G Ratio	0.025	0.182	0.179	-0.113	0.171
%SO ₂ Removal	0.462*	0.081	0.128	-0.186	0.133

	Correlation with Percent Hg Removal				
	With Ash	Across FGD	Hg ⁺⁺	Hg ⁰	Hg ^{tot}
Coal Quality:					
% Ash	0.277	0.363*	0.337	-0.111	0.3603*
% Nitrogen	0.129	0.359*	0.332	-0.110	0.341
% Oxygen	-0.726**	-0.461**	-0.509**	0.477**	-0.511**
% Sulfur	-0.033	0.048	0.041	-0.011	0.040
% Chlorine	-0.103	-0.038	-0.039	-0.029	-0.041
ppm Hg	0.016	-0.220	-0.199	0.117	-0.198

* Correlation is Significant at the 0.05 level (2-tailed).

** Correlation is Significant at the 0.01 level (2-tailed).

The results indicate a significant correlation between mercury removal and the pH of the FGD slurry. Higher pH values appear to increase the percentage of removal, except in the case of Hg⁰. Among the coal characteristics, oxygen content seems to have strong negative correlations with the mercury removal in all the cases, again with the exception of Hg⁰. The results show significant correlations between nitrogen and ash contents of coal, and the percentage of mercury removed across the FGD, and the total mercury removed. The results do not support the hypothesis of a strong correlation between chlorine content of coal and the percentage of mercury removed.

The results of selected correlation analysis between the coal ash composition and FGD inlet Hg concentrations on the measured Hg removals are shown in the following table.

**CORRELATIONS BETWEEN COAL ASH COMPOSITION AND
FGD INLET Hg DATA WITH Hg REMOVALS**

	Correlation with Percent Hg Removal				
	With Ash	Across FGD	Hg ⁺⁺	Hg ⁰	Hg ^{tot}
Ash Elements:					
CaO	0.449**	0.489**	0.470**	-0.188*	0.489**
SO ₃	0.500*	0.477*	0.458*	-0.145	0.481**
FGD Inlet Data:					
Gas Phase Hg ⁺⁺	-0.065	0.149	0.085	0.138	0.123
Gas Phase Hg ⁰	-0.079	-0.205	-0.191	0.159	-0.197
Gas Phase Hg ^{tot}	0.039	0.056	0.016	0.148	0.053

* Correlation is Significant at the 0.05 level (2-tailed).

** Correlation is Significant at the 0.01 level (2-tailed).

These data suggest that the higher the Ca and S in the coal ash, the greater the Hg removals (except for Hg⁰). These ash parameters also are strongly correlated to the amount of Hg⁺⁺ in the flue gas, suggesting that these elements could affect speciation. More work is necessary to confirm these observations.

Statistical Model for Mercury Removal - In order to predict the percentage removal of mercury across FGD systems, a linear model was developed. The variables used in this model included FGD slurry pH and L/G ratio, stack gas composition, and coal quality variables parameters. The results of the regression model are included in the full report. The overall explanatory power of the model was low, with an R-square of 0.334. In other words, the model could explain only 33.4% of the total variation in mercury removal across FGD. None of the regression coefficients were significant, and the overall explanatory power of the model is poor. Alternative specifications of the model with additional variables did not increase the overall explanatory power. These results indicate that, although FGD systems could be used to effectively reduce mercury emissions, removal efficiency could be influenced by a variety of factors which are not considered here. Further research needs to be done to better understand the mercury speciation in FGD systems and identify methods to increase removal efficiency.

HCl Emissions and Removal

The acid gas (HCl and HF) concentrations in the flue gas were measured at the ESP inlet and scrubber outlet (stack location) at both plants, and removal rates were calculated from these measurements. The HCl removal rates are shown in the following tables.

HCl EMISSIONS AND REMOVAL AT TEST SITE 3

	Test 1	Test 2	Test 3	Avg
% Cl in Coal	0.23	0.22	0.23	0.23
HCl Input, lb/hr*	69	67	60	65
Flue Gas Measurements:				
ESP Inlet ppmv	69	68	73	70
ESP Inlet lb/hr	38.9	38.3	38	38
FGD Outlet ppmv	1	0	1	1
lb/hr	0.7	0.1	0.6	0.6
% HCl Removal	98	>99	99	99

*Theoretical HCl input to boiler assuming all Cl in coal forms HCl upon combustion.

The HCl removal was ~99 for the three tests. Stack HCl emissions averaged 0.6 lb/hr. The estimated annual HCl emission rate, using 6000 hours of annual plant operation, is 1.8 tons per year.

HCl EMISSIONS AND REMOVAL AT TEST SITE 4

	Test 1	Test 2	Test 3	Avg
% Cl in Coal	0.15	0.14	0.14	0.14
HCl Input, lb/hr*	479	454	439	457
Flue Gas Measurements:				
ESP Inlet ppmv	72	61	65	66
ESP Inlet lb/hr	322	276	288	295
FGD Outlet ppmv	3	2	2	2
lb/hr	14	8	8	10
% HCl Removal	96	97	97	97

*Theoretical HCl input to boiler assuming all Cl in coal forms HCl upon combustion.

The HCl removal rate was 97%. Stack HCl emissions averaged 10 lb/hr. The estimated annual HCl emission rate is 30 tons per year.

HF Emissions and Removal

Hydrogen fluoride flue gas concentrations were measured at the FGD inlet and outlet at both plants. The HF removal data are shown in the following tables.

HF EMISSIONS AND REMOVAL AT TEST SITE 3

	Test 1	Test 2	Test 3	Avg
ppm F in Coal	115	106	120	114
HF Input, lb/hr *	3.6	3.3	3.2	3.4
Flue Gas Measurements:				
ESP Inlet ppmv	6	7	7	7
ESP Inlet lb/hr	1.8	2	1.9	1.9
FGD Outlet ppmv	<1	<0.5	<0.5	NA
lb/hr	<0.2	<0.1	<0.1	NA
% HF Removal	>90	>95	>95	NA

*Theoretical HF input to boiler assuming all F in coal forms HF upon combustion
NA denotes not applicable - below detection limit

The HF concentrations measured at the FGD outlet were below method detection limits of 0.1 to 0.2 lb/hr. Using the method detection limits, the minimum HF removal is 95%. Estimated annual HF emissions based on 6000 operating hours per year are <0.3 tpy.

HF EMISSIONS AND REMOVAL AT TEST SITE 4

	Test 1	Test 2	Test 3	Avg
ppm F in Coal	104	116	95	105
HF Input, lb/hr*	34	39	31	35
Flue Gas Measurements:				
ESP Inlet ppmv	9	15	8	11
ESP Inlet lb/hr	23	37	19	26
FGD Outlet ppmv	<0.4	<0.4	<0.4	<0.4
lb/hr	<1	<1	<1	<1
% HF Removal	>95	>97	>95	>96

*Theoretical HF input to boiler assuming all F in coal forms HF upon combustion

The HF concentrations measured at the FGD outlet were below method detection limits of 1 lb/hr. Using the method detection limits, the minimum HF removal rate is 96%. Estimated annual HF emissions based on 6000 operating hours per year are <3.0 tpy.

CONCLUSIONS AND RECOMMENDATIONS

In 1997, CONSOL measured the Hg emissions and removal at two Illinois coal-fired utilities equipped with limestone FGD systems. In the current study, CONSOL completed testing at two additional Illinois-based utilities. Working as a subcontractor to CONSOL, the Illinois State Geological Survey Society has completed a statistical analysis of the factors that influence Hg speciation and removal from these data sets, along with three additional data sets provided by CONSOL. The conclusions and recommendations reflect our findings from the Phase I and Phase II programs.

The ICCI test program demonstrated that wet FGD systems, installed and operated for SO₂ control, are capable of removing 45-60% of the flue gas Hg. In addition, another 7-35% of the coal Hg is collected on the ash, for a total system (ESP-FGD) Hg removal of 60-75%. This information will provide utilities with additional control options in the event that EPA proposes Hg emission reduction. If Hg regulations are enacted, demonstrating that existing wet scrubbers are effective in removing flue gas Hg will provide an incentive for using Illinois coal.

A statistical analysis of the available Hg emission data from scrubbed boilers showed a significant correlation between Hg removal and the scrubber slurry pH.

Specific conclusions are summarized below:

- Mercury emission measurement programs were completed at four Illinois utility FGD-equipped boilers burning Illinois coal during normal and routine plant and scrubber operation. The mercury emissions from the first plant (200 MWe) averaged $2.5 \mu\text{g}/\text{m}^3$ (0.005 lb/hr), which corresponds to ~30 lb/yr based on a 70% plant capacity. The mercury emissions from the second plant (180 MWe) averaged $2.9 \mu\text{g}/\text{m}^3$ (0.004 lb/hr), which corresponds to ~25 lb/yr. The mercury emissions from the third plant (40 MWe) averaged $1.9 \mu\text{g}/\text{m}^3$ (0.001 lb/hr), which corresponds to ~6 lb/yr. The mercury emissions from the fourth plant (400 MWe) averaged $2.8 \mu\text{g}/\text{m}^3$ (0.007 lb/hr), which corresponds to ~40 lb/yr.
- The mercury removal due to adsorption on the fly ash averaged 7% of the mercury in the feed coal for the first plant, 13% for the second plant, 48% for the third plant, and 11% for the fourth plant. Average carbon-in-the-ash values were 1%, 35%, 50%, and 3% respectively.
- The mercury removal across the flue gas desulfurization system was 48-56% for the first plant, 58-67% for the second plant, 46-50% for the third plant, and 57-64% for the fourth plant. The total system (ESP and FGD) removal was $55 \pm 8\%$ for the first plant, $72 \pm 9\%$ for the second plant, $75 \pm 6\%$ for the third plant, and $67 \pm 3\%$ for the fourth plant. The average Hg removal across the FGD scrubber for the four plants was 53%, while the average total Hg removal was 67%.
- The average Hg material balance closures for the four plants were 92%, 116%, 97%, and 104%. These closures were within the data quality objectives.
- The flue gas speciation data indicate the Hg fraction (Hg^{++}) collected in the KCl impinger of the Ontario Hydro sampling train is the Hg species that is removed across the FGD scrubber. The FGD outlet speciation showed little Hg in the KCl impingers indicating that almost all of the oxidized Hg species is being removed by the FGD.
- The Hg removal across the FGD systems and, to some extent, with the ash, is a function of the fraction of oxidized Hg in the flue gas. The data show that 80-90% of the oxidized Hg fraction is being removed with none of the elemental fraction being removed.
- A statistical analysis of the data collected during this program indicates that Hg removal across the FGD increases with increasing scrubber slurry pH. The coal quality data are correlated with Hg removal, but are of limited value because of similarities in the characteristics of the coals tested and in the Hg removal data for the plants evaluated.
- The HCl removal across the FGD systems of the first two plants averaged 82% and 83%. Upon further review of these data, it is believed that these removal rates are

biased low due to the sampling method used. A different sampling procedure was used for plants 3 and 4. The HCl removal rates for these plants were 99% and 97%. These are more reasonable values for HCl removal by FGD systems.

- The HF removal across the FGD system at the first site could not be determined due to insufficient detection limits. HF removal at the second test site averaged 70%. As in the case of the HCl emissions, we believe this value to be biased low due to the sampling procedure used. A different sampling method was used for plants 3 and 4. The HF removal for these plants was >95%.
- Testing conducted on a similar type of FGD material from an eastern utility firing eastern bituminous coal showed no Hg desorption or leaching under the conditions evaluated. An extrapolation of these data indicate that there is limited potential for Hg desorption and/or leaching in typical landfill applications.

DISCLAIMER STATEMENT

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TABLE 1
ANALYSIS OF TEST COALS FOR TEST SITE 3
(all values reported on a percent dry basis, unless otherwise noted)

Test ID	1	2 & 3	4	Avg	Standard Deviation	% Relative Standard Deviation
Date	6/23/98	6/24/98	6/25/98			
Analytical No.	983750	983751	983752			
Total Moisture	16.33	15.33	15.26	15.64	0.60	3.8%
Volatile Matter	42.33	42.66	42.46	42.48	0.17	0.4%
Ash	9.83	10.15	10.40	10.13	0.28	2.8%
Carbon	70.42	70.51	70.39	70.44	0.06	0.1%
Hydrogen	4.99	5.11	4.90	5.00	0.10	2.1%
Nitrogen	1.25	1.29	1.29	1.28	0.02	1.8%
Oxygen	9.14	8.48	8.54	8.72	0.36	4.2%
Sulfur	4.14	4.24	4.25	4.21	0.06	1.4%
Chlorine	0.23	0.22	0.23	0.23	0.01	2.5%
Fluorine, ppm	115	106	120	114	7	6.2%
Hg, ppm	0.08	0.09	0.09	0.09	0.01	11%
Heating Value, Btu/lb	12775	12754	12665	12731	58	0.5%
Major Ash Elements: (Ignited at 750 °C)						
SiO ₂	51.36	50.75	50.52	50.88	0.43	1%
Al ₂ O ₃	19.16	18.56	18.32	18.68	0.43	2%
TiO ₂	0.97	0.93	0.89	0.93	0.04	4%
Fe ₂ O ₃	18.98	20.19	19.66	19.61	0.60	3%
CaO	3.82	3.78	3.96	3.85	0.09	2%
MgO	0.93	0.88	0.88	0.90	0.03	3%
Na ₂ O	1.75	1.64	1.59	1.66	0.08	5%
K ₂ O	2.31	2.16	2.15	2.21	0.09	4%
P ₂ O ₅	0.20	0.09	0.18	0.16	0.06	37%
SO ₃	1.80	1.82	2.14	1.92	0.19	10%

Undetermined	-1.28	-0.80	-0.29	-0.79	-0.49	62%
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TABLE 2
ANALYSIS OF TEST COALS FOR TEST SITE 4
(all values reported on a percent dry basis, unless otherwise noted)

Test ID	1	2	3	Avg	Standard Deviation	% Relative Standard Deviation
Date	7/14/98	7/15/98	7/16/98			
Analytical No.	984110	984111	984112			
Total Moisture	17.40	17.09	16.77	17.09	0.31	1.8%
Volatile Matter	42.16	42.31	42.48	42.32	0.16	0.4%
Ash	10.08	10.02	9.82	9.97	0.14	1.4%
Carbon	70.64	70.85	70.76	70.75	0.10	0.1%
Hydrogen	4.85	4.77	4.68	4.77	0.08	1.8%
Nitrogen	1.37	1.35	1.33	1.35	0.02	1.5%
Oxygen	8.81	8.82	9.13	8.92	0.18	2.0%
Sulfur	4.09	4.05	4.14	4.09	0.04	1.1%
Chlorine	0.15	0.14	0.14	0.14	0.01	4.0%
Fluorine, ppm	104	116	95	105	10	10.0%
Hg, ppm	0.08	0.08	0.08	0.08	0.00	0.0%
Heating Value, Btu/lb	12748	12734	12777	12753	22	0.2%
Major Ash Elements: (Ignited at 750 °C)						
SiO ₂	48.07	48.87	48.58	48.51	0.40	1%
Al ₂ O ₃	17.75	17.79	17.35	17.63	0.24	1%
TiO ₂	0.87	0.89	0.88	0.88	0.01	1%
Fe ₂ O ₃	18.31	18.47	18.45	18.41	0.09	1%
CaO	4.77	4.95	4.43	4.72	0.26	6%
MgO	0.84	0.88	0.85	0.86	0.02	2%
Na ₂ O	1.23	1.24	1.17	1.21	0.04	3%
K ₂ O	2.18	2.08	2.06	2.11	0.06	3%

P ₂ O ₅	0.12	0.15	0.15	0.14	0.02	12%
SO ₃	3.58	3.63	3.69	3.63	0.05	2%
Undetermined	2.28	1.05	2.39	1.91	0.74	39%

TABLE 3
ANALYSIS OF BOTTOM ASH SAMPLES FOR TEST SITE 3
(all values reported on a percent dry basis, unless otherwise noted)

Test ID	1	2	3	Avg	Standard Deviation	% Relative Standard Deviation
Date	6/23/98	6/24/98	6/25/98			
Analytical No.	983753	983754	983755			
Total Moisture	0.17	0.15	0.18	0.17	0.02	9%
Ash	98.23	97.21	97.67	97.70	0.51	1%
Carbon	2.58	3.23	2.84	2.88	0.33	11%
Sulfur	0.31	0.31	0.28	0.30	0.02	6%
Hg, ppm	0.21	0.13	0.08	0.14	0.07	47%

TABLE 4
ANALYSIS OF BOTTOM ASH SAMPLES FOR TEST SITE 4
(all values reported on a percent dry basis, unless otherwise noted)

Test ID	1	2	3	Avg	Standard Deviation	% Relative Standard Deviation
Date	7/14/98	7/15/98	7/16/98			
Analytical No.	984107	984108	984109			
Total Moisture	2.15	1.18	1.74	1.69	0.49	29%
Ash	89.20	92.73	78.48	86.80	7.39	9%
Carbon	9.39	6.76	19.31	11.82	6.59	56%
Sulfur	0.58	0.31	0.85	0.58	0.27	46%
Hg, ppm	<0.01	0.05	0.05	0.04	0.03	75%

TABLE 5
ANALYSIS OF ECONOMIZER ASH SAMPLES FOR TEST SITE 4
(all values reported on a percent dry basis, unless otherwise noted)

Test ID	1	2	3	Avg	Standard Deviation	% Relative Standard Deviation
Date	7/14/98	7/15/98	7/16/98			
Analytical No.	984104	984105	984106			
Total Moisture	0.45	0.53	3.19	1.39	1.55	112%

Ash	73.45	70.74	45.14	63.11	15.56	25%
Carbon	25.80	27.89	51.50	35.06	14.22	41%
Sulfur	1.13	1.32	1.90	1.45	0.40	28%
Hg, ppm	0.03	0.06	0.04	0.04	0.02	35%

TABLE 6
ANALYSIS OF ESP ASH SAMPLES FOR TEST SITE 3
(all values reported on a percent dry basis, unless otherwise noted)

Unit #5 - Hopper #1 - Front

Test ID	1	2 & 3	3	Avg	Standard Deviation	% Relative Standard Deviation
Date	6/23/98	6/24/98	6/25/98			
Analytical No.	983758	983761	983755			
Total Moisture	10.94	6.48	4.87	7.43	3.13	42%
Ash	45.74	46.07	33.59	41.80	7.08	17%
Carbon	30.83	28.21	50.23	36.42	11.98	33%
Hg, ppm	1.86	0.58	0.87	1.10	0.67	61%

Unit #5 - Hopper #2 - Middle

Analytical No.	983757	983760	983763	Avg	SDEV	PRSD
Total Moisture	3.30	3.24	3.67	3.40	0.23	7%
Ash	59.82	57.38	49.10	55.43	5.60	10%
Carbon	23.09	21.37	35.00	26.49	7.39	28%
Hg, ppm	0.78	0.46	0.91	0.72	0.23	33%

Unit #5 - Hopper #3- Back

Analytical No.	983756	983759	983762	Avg	SDEV	PRSD
Total Moisture	2.17	1.21	1.60	1.66	0.48	29%
Ash	65.94	64.72	60.47	63.71	2.86	5%
Carbon	23.61	23.13	27.85	24.86	2.59	10%
Hg, ppm	0.33	0.38	0.87	0.53	0.30	56%

Unit #7 - Hopper #1- Front

Analytical No.	983767	983770	983773	Avg	SDEV	PRSD
Total Moisture	1.84	1.55	1.24	1.54	0.30	19%
Ash	48.01	48.61	50.74	49.12	1.43	3%
Carbon	42.40	41.86	44.55	42.94	1.42	3%
Hg, ppm	1.34	1.07	0.89	1.10	0.23	21%

Unit #7 - Hopper #2- Middle

Analytical No.	983765	983769	983772	Avg	SDEV	PRSD
Total Moisture	0.42	0.76	0.69	0.62	0.18	29%
Ash	54.89	55.72	55.76	55.46	0.49	1%
Carbon	43.75	40.21	41.18	41.71	1.82	4%
Hg, ppm	0.45	0.69	0.83	0.66	0.19	29%

TABLE 6 (Continued)
ANALYSIS OF ESP ASH SAMPLES FOR TEST SITE 3
(all values reported on a percent dry basis, unless otherwise noted)

Unit #7 - Hopper #3- Back

Analytical No.	983766	983768	983771	Avg	SDEV	PRSD
Total Moisture	0.75	0.56	0.47	0.59	0.14	24%
Ash	55.44	55.06	55.53	55.34	0.25	<1%
Carbon	39.54	43.84	44.29	42.56	2.61	6%
Hg, ppm	0.56	0.29	0.23	0.36	0.18	49%

Weighted Average Values for Composite ESP Hopper Ash

Test ID	1	2 & 3	3	Avg	Standard Deviation	PRSD
Date	6/23/98	6/24/98	6/25/98			
Ash	48.71	49.30	51.24	49.75	1.32	3%
Carbon	42.43	41.78	44.29	42.84	1.30	3%
Hg, ppm	1.25	1.02	0.87	1.05	0.19	18%

TABLE 7
ANALYSIS OF ESP ASH SAMPLES FOR TEST SITE 4
(all values reported on a percent dry basis, unless otherwise noted)

Hopper #1 - Front

Test ID	1	2	3	Avg	Standard Deviation	% Relative Standard Deviation
Date	7/14/98	7/15/98	7/16/98			
Analytical No.	984100	984097	984094			
Total Moisture	0.46	1.10	0.96	0.84	0.34	40%
Ash	94.91	97.11	96.43	96.15	1.12	1%
Carbon	3.61	0.87	1.11	1.86	1.51	81%
Hg, ppm	0.11	0.10	1.11	0.11	0.01	5%

Hopper #5 - Middle

Analytical No.	984101	984098	984095	Avg	SDEV	PRSD
Total Moisture	0.32	0.37	0.20	0.30	0.09	29%
Ash	93.46	96.20	96.76	95.47	1.76	2%
Carbon	4.66	3.04	2.57	3.42	1.09	32%
Hg, ppm	0.11	0.14	0.15	0.13	0.02	16%

Hopper #9 - Back

Analytical No.	984102	984099	984098	Avg	SDEV	PRSD
Total Moisture	0.29	0.26	0.22	0.26	0.03	14%
Ash	95.72	97.07	87.12	93.29	1.68	6%
Carbon	3.09	2.53	10.93	5.52	1.37	38%

Hg, ppm	0.08	0.10	0.07	0.08	0.02	18%
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TABLE 7 (Continued)
ANALYSIS OF ESP ASH SAMPLES FOR TEST SITE 4
(all values reported on a percent dry basis, unless otherwise noted)

Weighted Average Values for Composite ESP Hopper Ash

Test ID	1	2 & 3	3	Avg	SDEV	PRSD
Ash	94.70	96.78	93.44	94.97	1.68	2%
Carbon	3.79	2.15	4.87	3.60	1.37 0.01	38%
Hg, ppm	0.10	0.11	0.11	0.11		6%

TABLE 8
ANALYSIS OF FGD SOLIDS SAMPLES FOR TEST SITE 3
(all values reported on a percent dry basis, unless otherwise noted)

Test ID	1	2 & 3	4	Avg	Standard Deviation	% Relative Standard Deviation
Date	6/23/98	6/24/98	6/25/98			
Analytical No.	983774	983775	983776			
Total Moisture	16.48	16.13	16.20	16.27	0.18	1%
Ash	92.59	94.75	95.88	94.41	1.67	2%
Sulfur	16.16	18.12	17.66	17.31	1.02	6%
Hg, ppm	0.04	0.02	0.03	0.03	0.01	33%
Major Ash Elements: (whole sample basis)						
SiO ₂	2.37	1.96	1.48	1.94	0.44	23%
Al ₂ O ₃	0.48	0.40	0.31	0.40	0.08	21%
TiO ₂	0.02	0.02	0.02	0.02	0.00	0%
Fe ₂ O ₃	0.23	0.23	0.17	0.21	0.03	16%
CaO	40.09	40.15	39.82	40.02	0.18	<1%
MgO	0.18	0.18	0.16	0.17	0.01	7%
Na ₂ O	0.01	0.01	0.01	0.01	0.00	<1%
K ₂ O	0.11	0.08	0.06	0.08	0.03	30%
P ₂ O ₅	0.00	0.00	0.00	0.00	0.00	0%

SO ₃	49.11	51.69	53.31	51.37	2.11	4%
Undetermined	7.40	5.28	4.66	5.78	1.43	25%

TABLE 9
ANALYSIS OF FGD SOLIDS SAMPLES FOR TEST SITE 4
(all values reported on a percent dry basis, unless otherwise noted)

Test ID	1	2	3	Avg	Standard Deviation	% Relative Standard Deviation
Date	7/14/98	7/15/98	7/16/98			
Analytical No.	984091	984092	984093			
Total Moisture	0.42	0.31	0.21	0.31	0.10	33%
Ash	95.29	95.12	95.44	95.28	0.16	<1%
Sulfur	19.94	19.83	20.80	20.19	0.53	3%
Hg, ppm	0.97	0.66	0.50	0.71	0.24	34%
Major Ash Elements: (whole sample basis)						
SiO ₂	0.71	0.56	0.42	0.56	0.14	26%
Al ₂ O ₃	0.17	0.17	0.20	0.18	0.02	10%
TiO ₂	0.01	0.02	0.01	0.01	0.00	0%
Fe ₂ O ₃	0.23	0.23	0.21	0.22	0.01	5%
CaO	42.64	42.06	42.32	42.32	0.29	1%
MgO	0.44	0.33	0.19	0.32	0.12	39%
Na ₂ O	0.05	0.05	0.05	0.05	0.00	0%
K ₂ O	0.06	0.06	0.05	0.06	0.01	10%
P ₂ O ₅	0.03	0.03	0.02	0.03	0.01	33%
SO ₃	53.76	53.52	54.61	53.96	0.57	1%
Undetermined	1.90	2.97	1.82	2.26	0.61	27%

TABLE 10
ANALYSIS OF COMPOSITE LIMESTONE SAMPLES FOR TEST SITES 1 AND 2
(All values reported on a percent dry basis, unless otherwise noted)

Test Site	Site 1	Site 2
Date	6/23/98 to 6/25/98	7/14/98 to 7/16/98
Analytical No.	983777-983779	984103
Total Moisture	0.14	0.07
Ash	57.89	56.72
Carbon	11.31	11.68
Sulfur	0.03	0.04
Hg, ppm	<0.01	<0.03
Major Ash Elements: (whole sample basis)		
SiO ₂	2.88	0.72
Al ₂ O ₃	0.56	0.11
TiO ₂	0.03	0.01
Fe ₂ O ₃	0.31	<0.01
CaO	52.71	55.73
MgO	0.55	0.49
Na ₂ O	0.01	<0.01
K ₂ O	0.13	0.04
P ₂ O ₅	0.00	0.06
SO ₃	0.06	0.30
Undetermined	42.74	42.54

TABLE 11
ANALYSIS OF PRE-SCRUBBER BLOWDOWN SAMPLES FOR TEST SITE 3
(concentration units are mg/L)

Test ID	1	2 & 3	4	Avg	SDEV	PRSD
Date	6/23/98	6/24/98	6/25/98			
Analytical No.	983783	983784	983785			
pH	1.57	1.54	1.42	1.51	0.08	5%
Total Susp. Solids	1410	2570	7840	4000	3379	84%
Aluminum	129	122	150	134	15	11%
Calcium	1330	1450	1280	1353	87	6%
Iron	158	150	261	190	62	33%
Magnesium	750	706	649	705	50	7%
Manganese	10.2	9.8	11.6	11.0	1.0	9%
Potassium	87.9	90.8	187	122	56	46%
Sodium	201	203	317	240	66	28%
Bromide	<5	<5	<5	<5	NA	NA
Chloride	4350	4480	4300	4377	93	2%
Fluoride	180	180	177	179	2	1%
Sulfate	9080	10800	8980	9620	1019	11%
Hg	0.06	0.04	0.04	0.05	0.01	25%

TABLE 12
ANALYSIS OF WASTE WATER DISCHARGE SAMPLES FOR TEST SITE 3
(concentration units are mg/L)

Test ID	1	2 & 3	4	Avg	SDEV	PRSD
Date	6/23/98	6/24/98	6/25/98			
Analytical No.	983787	983788	983789			
pH	2.17	3.36	2.38	2.64	0.63	24%
Total Susp. Solids	26	31	27	28	3	9%
Chloride	3950	4080	3100	3710	530	14%

Fluoride	17	44	55	39	19	50%
Hg	<0.01	<0.01	<0.01	<0.01	NA	NA

TABLE 13
ANALYSIS OF WASTE WATER SOLIDS SAMPLES FOR TEST SITE 3
(all values reported on a percent dry basis, unless otherwise noted)

Test ID	1	2 & 3	4	Avg	Standard Deviation	% Relative Standard Deviation
Date	6/23/98	6/24/98	6/25/98			
Analytical No.	983780	983781	983782			
Total Moisture	9.06	13.91	4.55	9.17	4.66	51%
Ash	85.99	90.48	76.03	84.17	7.37	9%
Carbon	5.20	1.77	17.59	8.19	8.29	101%
Sulfur	4.04	6.06	6.08	5.39	1.17	22%
Hg, ppm	1518	1044	1105	1222	2571	21%
Major Ash Elements:						
SiO ₂	30.33	27.48	26.60	28.14	1.94	7%
Al ₂ O ₃	11.89	10.74	9.99	10.88	0.95	9%
TiO ₂	0.50	0.43	0.47	0.47	0.03	7%
Fe ₂ O ₃	4.94	4.29	4.32	4.51	0.37	8%
CaO	9.34	13.92	11.67	11.64	2.28	20%
MgO	10.35	8.89	3.72	7.65	3.47	45%
Na ₂ O	1.77	1.85	1.08	1.57	0.42	27%
K ₂ O	2.32	2.14	1.95	2.14	0.19	9%
P ₂ O ₅	0.23	0.20	0.28	0.24	0.04	18%
SO ₃	9.99	17.21	15.14	14.11	3.71	26%
Undetermined	18.34	12.86	24.78	18.66	5.94	32%

TABLE 14
Hg CONCENTRATION OF ONTARIO HYDRO SAMPLING TRAIN FILTER SOLIDS
FOR TEST SITE 3

Test ID	1	2	3	4	Avg	SDEV	PRSD
Date	6/23/98	6/24/98	6/24/98	6/25/98			
ESP Inlet Filter, ppm	0.70	1.5	1.1	0.68	0.99	0.39	39%
ESP Outlet Filter, ppm	10.8	11.0	13.2	6.6	10.4	2.75	26%
FGD Outlet Filter, ppm	2.0	1.6	9.3	<0.5	3.4	4.0	118%

TABLE 15
Hg CONCENTRATION OF ONTARIO HYDRO SAMPLING TRAIN FILTER SOLIDS
FOR TEST SITE 4

Test ID	1	2	3	Avg	SDEV	PRSD
Date	7/14/986/	7/15/986/	7/16/986/			
ESP Inlet Filter, ppm	0.22	0.21	0.23	0.22	0.01	5%
FGD Outlet Filter, ppm	1.8	5.5	1.7	3.0	2.2	72%

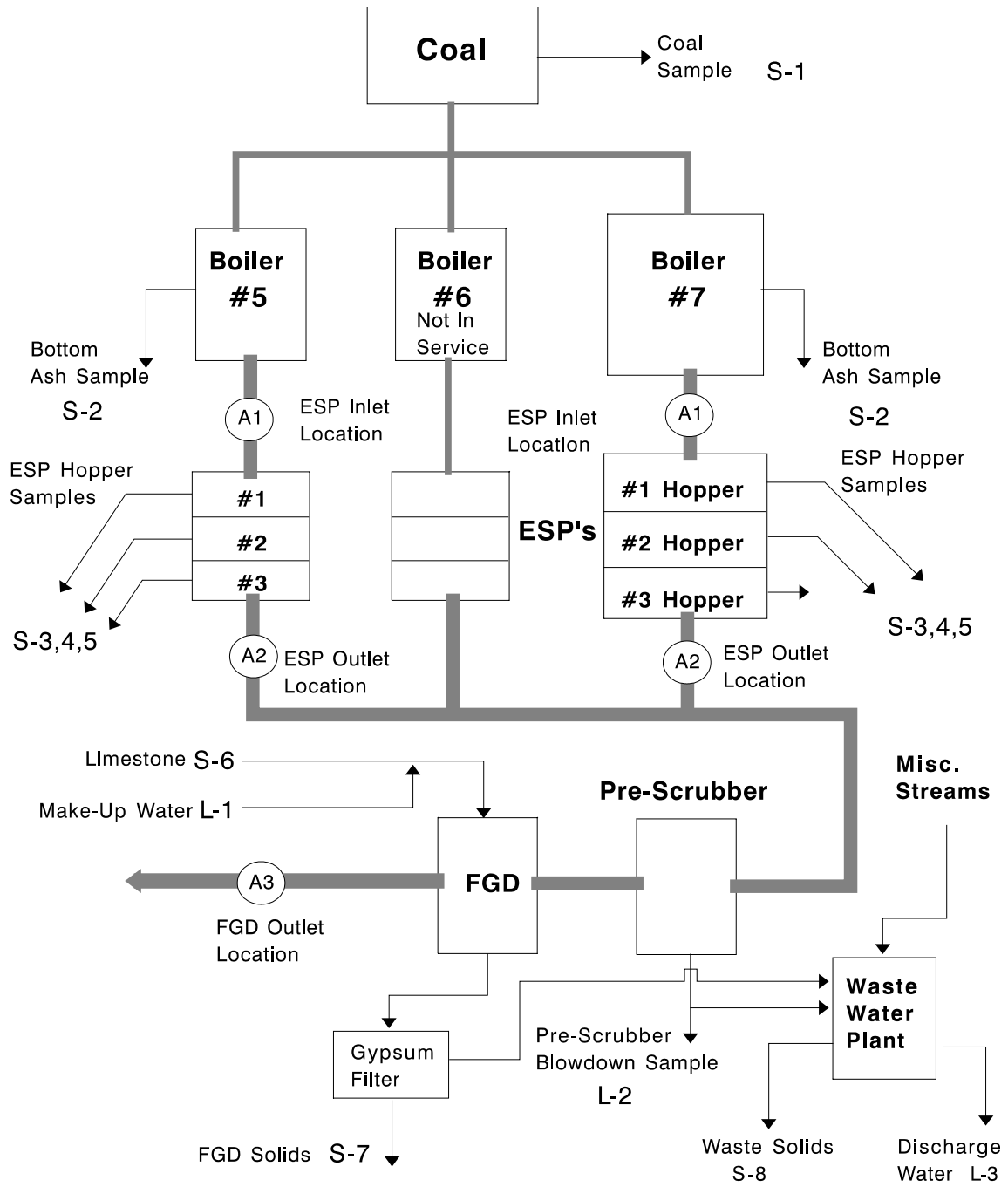


Figure 1. Schematic of Sampling Locations for Test Site 3.

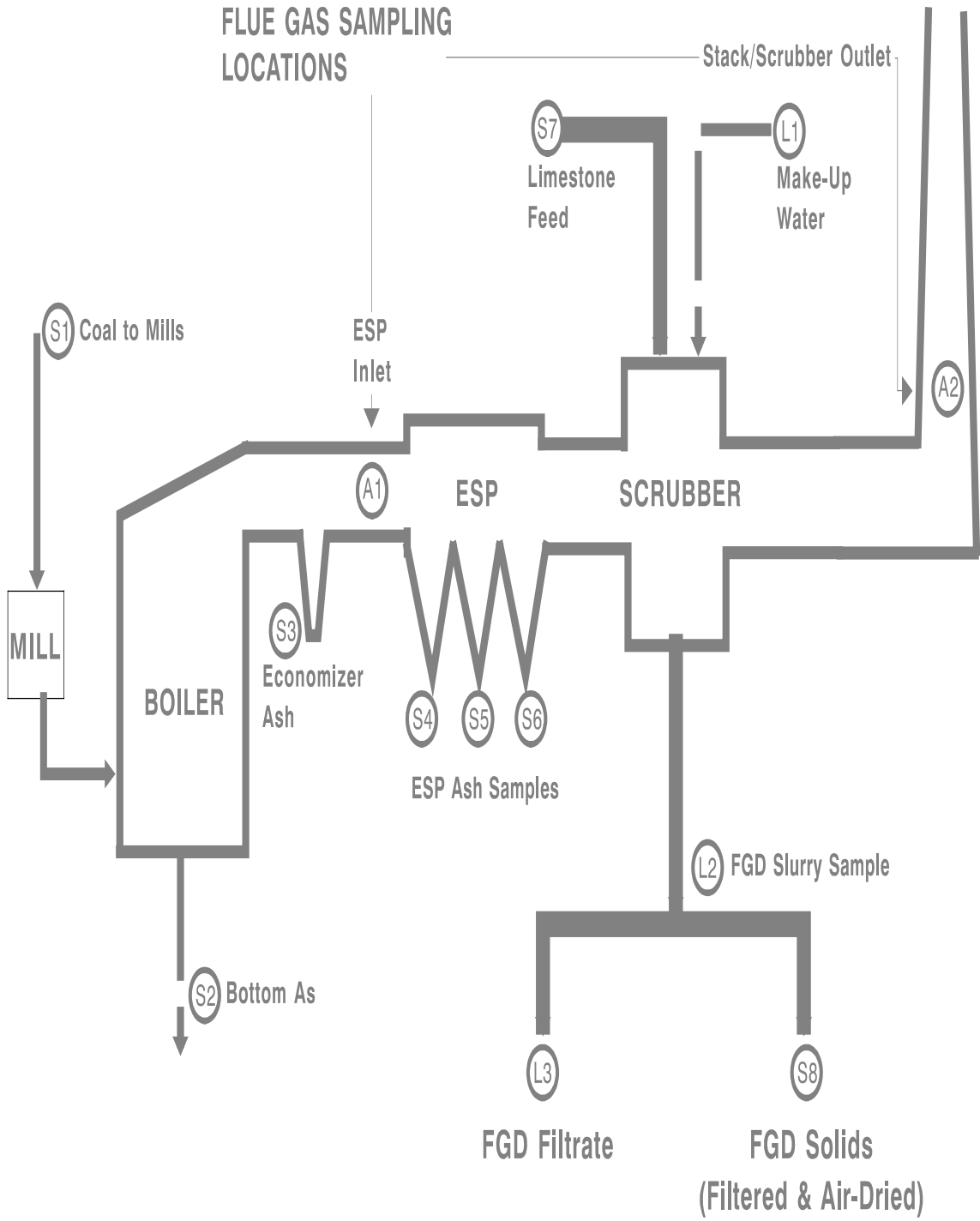
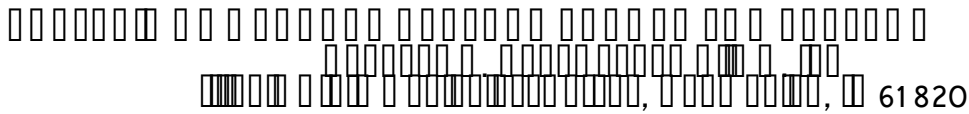


Figure 2. Schematic of Sampling Locations for Test Site 4.

ANALYSIS OF MERCURY CAPTURE ACROSS FGD SYSTEMS

Mercury capture efficiency (MCE) is a critical performance metric for FGD systems, particularly in the context of mercury emissions from coal-fired power plants. This analysis examines the factors influencing MCE across various FGD configurations, including wet, dry, and semi-dry systems. The study highlights the importance of maintaining optimal pH levels and ensuring sufficient residence time within the scrubber to maximize mercury removal. Additionally, the impact of inlet gas composition and the presence of other pollutants on MCE is discussed. The findings suggest that while wet FGD systems generally achieve higher MCE, they also face challenges related to corrosion and wastewater management. Dry and semi-dry systems offer advantages in terms of water consumption and waste generation but may require more precise control of operating conditions to maintain high MCE. Overall, the analysis underscores the need for a holistic approach to FGD design and operation to optimize mercury capture while minimizing environmental and operational impacts.



1 Review of literature on mercury capture across FGD systems

Flue gas desulfurization (FGD) systems are installed in power plants primarily to remove sulfur dioxide. But during this process other flue gas components including mercury could also be removed. The literature presented below summarizes the results of the past works on the possibility of mercury removal by the FGD systems.

Before the passage of the Clean Air Act Amendments of 1990, The Electric Power Research Institute (EPRI) began a study of chemical emissions from electric power plants entitled Power plant Integrated Systems: Chemical Emissions Studies (PISCES). The PISCES data show that mercury is removed by both wet and dry FGD systems which are commonly used to reduce sulfur dioxide emissions. The above data show that mercury removal efficiencies range from about 10% to 90%. The PISCES data showed a large variability in mercury removal efficiency, which may be explained by the differences in the ratio of elemental to oxidized mercury in the different flue gases. In 1991, preliminary tests conducted at EPRI's High Sulfur Test Center (HSTC) in New York showed that the wet limestone FGD system removed about 90% of the inlet mercury, while spray dryer removed only about 45%. In 1992, EPRI performed a more exhaustive study to determine the variability in the inlet flue gas mercury concentrations, to correlate the wet FGD scrubber operating conditions with mercury removal efficiency. The results showed that wet limestone FGD system removed about 96% of the inlet mercury. The removal efficiency was found to be independent of the changes made in the operating conditions. About 98% of the mercury at the wet scrubber inlet was in the oxidized form. In 1993 EPRI conducted 3-month test program to assess the feasibility of FGD technologies for hazardous air pollutants like mercury. The specific objectives were to confirm some of the previous results, to determine if oxidized mercury removal is limited by gas-film mass transfer, determine the

removal efficiency for elemental mercury, and to determine the flue gas conditions that affect the ratio of oxidized to elemental mercury. The results showed good agreement between the two test programs. As in some of the 1992 tests, elemental mercury concentrations were generally higher in the outlet gas compared to the inlet gas. This could be because some of the absorbed oxidized mercury is reduced to elemental mercury by the scrubber liquor and then stripped from the liquor to the outlet gas stream. The results of the 1992 tests showed that the removal of oxidized mercury was independent of the FGD slurry chemistry conditions. However, later results suggest that the oxidized mercury removal efficiency may be controlled by other mechanisms. The results of the 1993 study seems to indicate that the removal efficiency for oxidized mercury seems to be limited only by gas-film mass transfer for the flue gas. The oxidized mercury removal efficiency was greatly reduced when mercury was injected into the flue gas. The results suggest that a different form of oxidized mercury was present in the flue gas when mercury spiking apparatus was in service. The speciation of mercury in the flue gas is not affected by changes in the HCl concentration in the flue gas at scrubber inlet temperatures of 275-325⁰F. The results further showed that the mercury balance closures for the pilot system are all within the range of 70% to 130% closure, with the exception of two short-term tests.

In order to evaluate the potential of wet FGD systems to remove mercury, tests were conducted at EPRI's Environmental Control Technology Center (ECTC) formerly called HSTC. The results showed that wet scrubbers removed only oxidized mercury. The inlet mercury concentrations averaged 9 $\mu\text{g}/\text{m}^3$, with approximately 98% in the oxidized form. Total outlet mercury averaged 0.5 $\mu\text{g}/\text{m}^3$, with about 70-75% in the elemental form. Overall mercury removal efficiency averaged 96% because of high concentrations of oxidized mercury. Changing the pH of the reaction tank, concentration of chloride, adipic acid, and formic acid in the scrubbing slurry did not affect the mercury removal. The results further confirm that elemental mercury is not easily removed across a scrubber and that the removal effectiveness for oxidized mercury may be dependent on the oxidized species present.

There have been some early works in Netherlands to test efficiency of FGD systems in mercury removal. Meij and Alderliesten (1989) studied the effectiveness of wet FGD in removing Hg in coal fired electric utilities in Netherlands. The results showed that though most of the inorganic gases are removed in a wet FGD, the average Hg removal is somewhat lower, on average 60%. The results further showed that removals depend on the behavior and operating conditions of the demisters.

Meij (1991) investigated the fate of mercury and the influence of wet flue-gas desulfurization including the removal in the FGD in coal-fired power plants in Netherlands. Test with 37 coal samples showed that the gaseous Hg concentration in the flue gases ranges from 0.3 to 35 $\mu\text{g m}_0^{-3}$, with a mean value of $4.1 \pm 5.8 \mu\text{g m}_0^{-3}$. This means an annual emission of 50 Kg Hg at a 600 MW coal fired power plant without FGD unit and at 5700 hours a year full load. Tests with FGD's based on wet lime/limestone - gypsum showed mercury removal between 8% and 72%, with an average of 52%. Gutberlet (1984) and KHM (1983) also got similar results in their tests in West Germany (60% removal) and Sweden (75% removal) respectively. The results showed that Hg emission by a 600 MW power plant is reduced from 50 kg to less than 25 kg by introducing FGD. The results further showed that 50 to 70% of the Hg in the flue gases will be removed by wet FGD leaving a residual concentration of 1 to 2 $\mu\text{g m}_0^{-3}$. Twenty five percent of Hg leaves the FGD plant via flue gases, 60% via gypsum, 10% via the sludge and the rest 5% via the effluent of the wastewater treatment plant.

Gleiser and Felsvang (1994) analyzed the efficiency of using activated carbons in FGD systems in united states and Europe. The results of the tests at eight dry scrubbing installations showed that uncontrolled mercury concentration is in the range of 3-11 $\mu\text{g}/\text{Nm}^3$ and the inherent mercury removal efficiency ranges from a low of 6% to a high of 96%. The mercury removal efficiency is found to be enhanced by injection of activated carbon upstream of the spray dryer absorber which increased the removal efficiency to more than 99%. The results further indicated a strong influence of the coal chlorine content on mercury

removal. Tests with iodine impregnated and sulfur impregnated activated carbons showed significant improvement in mercury removal, with 100% removal when iodine impregnated carbon was used. Thus the above results showed that if the chlorine content of coal is high dry scrubbing system can achieve a high mercury removal efficiency. For coals with low chlorine content mercury removal efficiency could be enhanced by injection of normal activated carbons or enhancing the coal chlorine content. The more expensive iodine or sulfur impregnation could be considered when additional sodium or chlorine cannot be introduced into the boiler.

Chu and Porcella (1994) tested the mercury removal efficiency of ESPs and FGD systems in coal fired electric utility plants. The results revealed Hg removals up to 60% in ESP systems. The mean removal efficiency for all coal fired plants with dry particulate controls was about 30%. Hg removal efficiencies for a combined ESP and wet FGD systems are highly variable and gave poor correlation with the FGD design, coal composition, or measured Hg oxidation state. The Hg removal efficiencies for ESP/FGD systems ranged from as low as 0% to as high as 90%. The mean Hg removal efficiency for the combined ESP/FGD system was 45%. Although previous studies (Peterson *et al.*, 1994) have shown that oxidized mercury is removed to a greater degree than elemental mercury, Chu and Prcella did not find evidence to support this.

Fahlke and Bursik (1995) studied the impact of flue gas cleaning on mercury species emissions from coal-fired steam generators in Germany. Two coal fired power plants- one with slag tap boilers and one with a dry bottom boiler were compared. Both the units were provided with electrostatic precipitators, nitrogen oxide removals and FGD systems. The results showed that only 15% of the Hg introduced by coal leaves the unit with the bottom or fly ash. About 30 to 40% of the Hg is separated in the FGD systems. The overall separation rate for the total system ranges between 45 to 55%, the residue is emitted in the form of gaseous Hg species. At full load, the Hg concentration in the cleaned gas is found to be less

that $6 \mu\text{g m}^3$. The results showed that the FGD system eliminates approximately 80% of the Hg^{2++} . However, the results show an increase of Hg^0 by the factor 10.

Flesvang and Brown (1994) studied the effectiveness of spray dryer absorbers on mercury removal. The results show that mercury collection efficiency ranges from 7 to 15% when Western U.S. coal is used. When the coal type is Eastern U.S. coal, the mercury collection efficiency ranges from 96.5 to 99.4%. For the Polish coal, the efficiency was 89%. The particulate type in all the plants was either baghouse or precipitator. The results showed that under certain circumstances the spray dryer absorbers can be extremely effective in mercury removal.

Mendelsohn, Wu, Huang and Livengood (1994) conducted preliminary experiments using a laboratory-scale wet scrubbing system to improve the capture of Hg^0 . The above system is characterized in previous work on combined sulfur dioxide/nitrogen oxides control (Mendelsohn and Harkness, 1991). The feed gas stream consisted of nitrogen containing about $40 \mu\text{g/m}^3$ of Hg^0 . The scrubber was initially operated as a partially flooded column with water, a calcium hydroxide solution, or a calcium hydroxide plus potassium polysulfide solution as the scrubbing liquor. No significant mercury removal was found in any of those cases. Removals up to 40% were obtained when stainless steel packing was added to the scrubber with polysulfide in FGD liquor. The studies however showed that use of polysulfide in FGD systems could be precluded as a very high pH is required to maintain its stability. In order to increase efficiency Mendelsohn and Harkness also tried techniques for changing the chemical form of mercury in order to produce more soluble species. These techniques included additives that combine strong oxidizing properties with relatively high vapor pressures. Tests with the addition of sulfur dioxide to the gas stream showed the additives to be very reactive, which could result in excessively high additive consumption in order to realize effective mercury removal. Tests with a chloric acid based chemical, NOXSORBTM (a product of the Olin Corporation) yielded an outlet reading of zero for Hg^0 for approximately 24 minutes. The nitric oxide outlet concentration also decreased rapidly to

near zero and then rose gradually to where it was almost equal to inlet value. The typical feed-gas compositions included 1,000 ppm sulfur dioxide, 200 ppm nitric oxide, 15% carbon dioxide, and 33 of $\mu\text{g}/\text{m}^3$ of Hg^0 . Tests with and without nitric oxide in the flue gas suggested that nitric oxide promoted Hg^0 removal by NOXSORBTM. These results showed that a combined process that removed Hg^0 and nitric oxide could be more effective and feasible. Studies along this direction were pursued by Livengood and Mendelsohn (1997). In order to explore in more detail the interactions among Hg^0 , oxidizing additives, and the various flue-gas species, a simulated flue gas was passed through a series of bubblers for 30 minutes. A solution of the reactive chemical was placed in the first bubbler, while the second and third bubblers usually contained distilled water. The results from the bubbler tests indicated that iodine solutions could be effective in oxidizing Hg^0 even at very low concentrations (< 1 ppm). When bromine was used, substantial conversion of Hg^0 was obtained when only oxygen and nitrogen were in the gas stream, but the addition of nitric oxide and sulfur dioxide again diminished that conversion significantly. The above results showed that neither iodine nor bromine is likely to be cost-effective in a commercial system. Different results were obtained for solutions containing chlorine or chlorine compounds. While chlorine solutions alone did not increase Hg^0 removals, addition of nitric oxide to the gas stream greatly increased the amount of mercury removed, possibly due to the formation of an intermediate compound such as nitrosyl chloride which could happen rapidly with Hg^0 . The tests further showed that sulfur dioxide depressed Hg^0 removal. Mercury removal with chloric-acid solutions also appeared to increase with increasing chloric acid concentration regardless of gas composition. Similarly, the presence of nitric oxide greatly increased Hg^0 removal. This could be because of the gas-phase reaction of nitric oxide and chloric acid forming nitric acid. The presence of sulfur dioxide decreased Hg^0 removal but it remained intermediate to that of with and without nitric oxide.

Livengood, Huang, Mendelsohn, and Wu (1995) evaluated the effectiveness of activated carbons and sorbents based upon chemical pretreatment of low cost mineral

substrates in mercury removal by FGD systems. They report that lime hydrates, either regular or high-surface area, are not effective in removing elemental mercury. Mercury removals with activated carbons were found to decrease with increasing temperature, larger particle size, and decreasing mercury concentration in the gas. Chemical pretreatment was found to greatly increase the removal capacity of activated carbon and inert substrates. Sorbents treated with different chemicals were found to respond in significantly different ways to changes in flue-gas temperature.

Huang, Wu and Livengood (1996) evaluated efficiencies of different sorbents in the removal of elemental mercury using a fixed-bed adsorption system. Results showed that conventional flue-gas cleanup technologies are moderately effective in controlling HgCl_2 but are very poor at controlling elemental mercury. Various sorbents and chemical additives like activated carbon impregnated with different chemicals, modified zeolites, and glass fibers coated with special chemicals have been reported in for mercury removal. Of these potential additives, the activated-carbon-based chemicals and alkali-sulfide compounds were investigated. The results showed that either elemental mercury or its chloride form can be the predominant form in coal-combustion flue gas. Very little of the elemental mercury is removed by conventional FGD systems. When lime hydrates are not effective in removing elemental mercury the results showed that removals are enhanced by addition of activated carbon. Mercury removals with activated carbon increase with decreasing temperature, smaller particle size, increasing sorbent loading, and increasing mercury concentration in the gas. The results further showed that chemical pretreatment with sulfur and CaCl_2 can greatly increase the removal capacity of activated carbon. Sorbents treated with different chemicals respond in significantly different ways to changes in flue-gas temperature.

Livengood and Mendelsohn (1997) investigated the possibilities of improved mercury control in wet scrubbing through conversion of Hg^0 to more soluble mercury compounds. The results of initial bench-scale experiments conducted at Argonne National Laboratory, show that a change in speciation enhances the capture of mercury in wet scrubbing. In some

cases nitric oxide has been found to have a strong beneficial effect on Hg^0 conversion. The results indicate the possibilities of combined control process for sulfur dioxide, nitric oxide, and mercury. The above results showed that higher removals could be obtained if more of the reagent was made available for reaction in the gas phase. In the light of the above findings, Livengood and Mendelsohn (1998) initiated a series of tests in which an ultrasonic atomizer (to simulate a more *real-world* duct injection process) was used to inject small droplets of the oxidizing solutions into a flowing gas stream containing Hg^0 vapors and other typical flue-gas components. The initial tests involving the atomization of chlorine or chloric-acid solutions into a flowing stream of simulated flue gas have confirmed the potential for enhanced Hg^0 removal that was identified in the earlier bubbler scrubber tests. At the highest NOXSORBTM concentration (40%) studied, approximately 100% of the gaseous Hg^0 was transferred to the liquid phase. Addition of nitric oxide appeared to significantly enhance Hg^0 removal and simultaneous removal of nitric oxide (up to about 80%). The presence of sulfur dioxide in the flue gas did seem to have a negative effect on Hg^0 and nitric oxide removals with NOXSORBTM.

When chlorine solutions are used, up to 75% of the Hg^0 was transferred to the liquid phase. Addition of sulfur dioxide had a large negative effect on Hg^0 removal for chlorine solutions. The authors argue that though chlorine did not perform as well as NOXSORBTM, under the conditions studied, the process economics may be favorably influenced by the considerably lower cost of chlorine.

2 Statistical analysis of the data

The statistical analysis of the data was performed using the statistical software package Minitab. The data were analyzed using the following statistical tests: (1) the t-test to determine if the mean values of the two groups were significantly different; (2) the F-test to determine if the variances of the two groups were significantly different; (3) the chi-square test to determine if the observed frequencies were significantly different from the expected frequencies; (4) the ANOVA test to determine if the means of the three groups were significantly different; (5) the regression analysis to determine the relationship between the independent and dependent variables.

2.1 Correlation analysis

Table 1. Comparison of the results of the sensitivity analysis for the different parameters, showing the percentage change in the results for a 1% change in the parameter value.

	% Change in CO ₂ emissions per unit of output	% Change in CO ₂ emissions per unit of output per unit of input	% Change in CO ₂ emissions per unit of output per unit of input ⁺⁺	% Change in CO ₂ emissions per unit of output per unit of input	% Change in CO ₂ emissions per unit of output per unit of input
FGD data					
FGD efficiency	0.4570**	0.3852*	0.4239*	-0.4152*	0.4105*
FGD investment	0.0250	0.1819	0.1788	-0.1113	0.1705
% SO ₂ abated	0.4620*	0.0814	0.1278	-0.1855	0.1327
Stack flue gas data					
SO ₂ emissions	-0.1835	-0.2152	-0.2185	0.1598	-0.2191
SO ₂ abatement	-0.1917	-0.2185	-0.2229	0.1672	-0.2233
% SO ₂	0.0102	0.0962	0.1005	-0.1365	0.0915
% SO ₂ ²	-0.1442	-0.2046	-0.2204	0.2650	-0.2079
% SO ₂ ³	-0.1881	-0.0923	-0.0986	0.2705	-0.1124
Coal quality data					
Coal quality	-0.3932*	-0.0912	-0.1247	0.1550	-0.1319
Coal quality ²	-0.3235	-0.3142	-0.2854	0.0013	-0.3139
Coal quality ³	0.2770	0.3625*	0.3373	-0.1111	0.3603*
Coal quality ⁴	0.1651	-0.0972	-0.0440	-0.1594	-0.0633
Coal quality ⁵	-0.0899	-0.1693	-0.1320	-0.0792	-0.1607
Coal quality ⁶	0.1292	0.3593*	0.3323	-0.1102	0.3413
Coal quality ⁷	-0.7255**	-0.4605**	-0.5085**	0.4767**	-0.5110**
Coal quality ⁸	-0.0325	0.0481	0.0406	-0.0112	0.0400
Coal quality ⁹	-0.1028	-0.0384	-0.0387	-0.0291	-0.0413
Coal quality ¹⁰	0.1060	-0.1457	-0.0915	-0.1308	-0.1144
Coal quality ¹¹	0.0156	-0.2196	-0.1987	0.1165	-0.1976

** Significant at the 0.01 level (2-tailed test).
* Significant at the 0.05 level (2-tailed test).

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