Flue gas Hg measurements from coal-fired boilers equipped with wet scrubbers

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Abstract: The U.S. EPA has indicated they are considering additional SO_2 and NO_x emission reductions, and EPA is under a consent agreement to propose mercury reduction regulations by 2004 for the utility industry. The boiler manufacturers and the utility industry have developed improved combustion modification techniques to reduce NO_x emissions. These advanced combustion modification techniques, plus selective catalytic reduction (SCR), offer the potential to reduce NO_x emissions at reduced cost. Wet and dry FGD systems have been shown to reduce SO_2 emissions by up to 95%. CONSOL has shown that conventional wet FGD and ESP systems can remove an average of $67 \pm 6\%$ of the inlet mercury. These data show that utility boilers equipped with ESP-scrubber combinations are removing two-thirds of the mercury in the as-fired coal at no added cost. The mercury speciation data show that 80 to 95% of the oxidized mercury, as determined by the Ontario Hydro method, is removed by the scrubber. The average mercury material balance closure at the six plants was $103 \pm 8\%$. The mercury removed from the scrubber reported to the scrubber by-product. Standard leachate testing conducted on fixated and unfixated scrubber by-product from one test showed no mercury leaching. Mercury volatility was evaluated by heating the scrubber by-product $140°F$ for eleven weeks. After eleven weeks, no loss of mercury was reported.

Based on these findings, there may be combinations of environmental control systems that can achieve significant SO_2, NO_x, and mercury reductions at lower cost than the conventional approach of three add-on processes: FGD for SO_2 control, selective catalytic reduction for NO_x control, and carbon injection for mercury control.

Keywords: mercury control, coal-fired boilers, SO_2, and NO_x control.

1   Introduction

The U.S. Environmental Protection Agency (EPA) is considering a three-pollutant environmental control strategy to reduce SO_2 and NO_x emissions below those required by the Clean Air Act Amendments of 1990 and to establish emission limits for mercury. In the past, utilities and steam-electric boiler owners have responded to environmental requirements by adding control technology – FGD for SO_2 and SCR, SNCR or combustion modifications for NO_x. Advances in combustion modifica-

tions and the results of this research indicated that it is possible to reduce SO_2, NO_x, and mercury using only FGD systems and combustion modifications or a combination of modifications and a low space velocity SCR.

The U.S. EPA, the U.S. Department of Energy (DOE), the Electric Power Research Institute (EPRI) [1], and their contractors have studied extensively the partitioning of hazardous air pollutants (HAPs) at coal-fired utility plants. The majority of the HAPs listed in Title IV of the Clean Air Act Amendments of 1990 are captured in existing particulate collection devices (ESPs, fabric filters). The exceptions are the elements or compounds denoted as Class III (mercury (Hg), selenium (Se), hydrofluoric acid (HF), and hydrochloric acid (HCl), which, because of their volatility, remain as a vapour at the ESP or fabric filter exit.

In its report to Congress [2], EPA identified ongoing concerns with mercury (Hg) emission from coal-fired utilities. EPA identified this source category as the largest single source contributor of U.S. anthropogenic Hg emissions. In 1999, EPA instituted an 'information collection request' (ICR) with the objective of gathering more data concerning Hg emissions from coal-fired utilities [3]. The ICR required periodic coal sampling and Hg analysis for over 1000 boilers. In addition, ~ 100 plants will be required to determine the total and speciated Hg emission rates. This programme was completed in 1999, and these data are being used to evaluate the need for Hg controls.

Currently, there is no proven control technology to remove Hg from the flue gas for the coal-fired utility boiler source category. Hg removal by carbon injection has been tested at the pilot scale, and it is estimated that Hg-removal costs for full-scale applications will range from $10 million to $40 million per ton of Hg removed. Clearly, Hg reductions based on present technology are uncertain and costly.

Studies [4] of coal-fired utility boilers have shown that conventional wet scrubbers (flue gas desulphurization – FGD technology) remove mercury. However, the studies show a wide variation in removal (0–100%), indicating the need for additional data to identify the reason for the reported variation. The primary goal of this study was to develop a more precise data set to determine the mercury removal achieved by wet FGD systems. These data, along with EPA and DOE emission assessment results, will provide the U.S. utility industry with information to evaluate the removal achieved by ESP-wet FGD systems for Hg.

Advancements in the design and application of low-NO_x burners (LNB) and overfired air (OFA) have achieved significant reductions of NO_x emissions [5]. For example, the combination of micronized coal reburning and the Low-NO_x Concentric Firing System can reduce NO_x emissions to 0.25 lb of NO_x per million Btu [6]. For wall-fired boilers equipped with advanced LNB and OFA, NO_x emissions were reduced by 68% [7]. Combining these low-NO_x firing systems and the selective catalytic reduction process could yield a lower cost control system capable of achieving less than 0.15 lb NO_x per million Btu. For example, an SCR design to lower NO_x emissions from 0.25 to 0.15 lb NO_x per million Btu would remove only 40% of the NO_x. This would significantly reduce the SCR space velocity, reducing retrofit, catalyst replacement, and ammonia costs. The combination system has not been demonstrated in the United States.

The U.S. Department of Energy has demonstrated that wet and dry FGD systems can remove up to 95% of the sulphur in the as-fired coal. Wet and dry FGD systems are operating in the United States, Europe, and Asian countries. Further discussion of FGD technology performance and reliability is not warranted.

CONSOL Inc. completed flue gas Hg measurements at five coal-fired boilers and one industrial boiler equipped with conventional wet scrubbers for SO_2 control. The goals of this project are to determine the mercury (Hg) removal achieved by wet FGD systems and by combined ESP-wet FGD systems at coal-fired utility plants, and to correlate Hg removal with coal properties and boiler/scrubber operating parameters. The correlation analysis was conducted by the Illinois State Geological Survey (ISGS). The data from this study will help to determine the effectiveness of Hg removal in wet FGD systems.

2   Experimental procedures

2.1   Sampling methods

Five utility boilers and one industrial boiler equipped with ESP-wet scrubber combinations agreed to participate in the FGD mercury removal programme. Site visits were conducted at each station by the CONSOL sampling team. During the site visits, programme requirements were discussed with plant operating personnel, sampling locations were identified, and arrangements were made with plant personnel to provide assistance during the sampling programme.

A minimum of three mercury material balance tests were conducted at each site. Each test period included simultaneous flue gas sampling at the ESP inlet, the ESP exit (FGD inlet), and at the stack (FGD outlet). When this programme was initiated, there was no validated speciated mercury sampling method for coal-fired boilers. The Hg measurements at the first site were determined using the EPA Method 29 sampling train. Flue gas Hg speciation was estimated by assuming that the first two nitric acid/peroxide impingers collect the oxidized fraction and the $KMnO_4$ impingers collect elemental Hg fraction. Subsequent to this first programme, DOE and EPRI funded a programme to evaluate the Ontario Hydro Hg Speciation method for both total and speciated measurements of Hg in coal combustion flue gas. This work resulted in the validation of this method for these measurements [8]. The gas phase mercury concentrations at the next five sites were determined using the Ontario Hydro Hg Speciation method [9]. The Ontario Hydro method uses three KCl-filled impingers to collect the oxidized Hg. The KCl impingers are followed by H_2O_2 impingers to remove SO_2. The H_2O_2 impingers are followed by acidified $KMnO_4$ impingers that collect elemental Hg.

In addition to flue gas samples, representative process stream samples were obtained during the test period (from the boiler and scrubber). Process stream samples included: coal, coal-mill rejects, ash (bottom, economizer, ESP-hoppers), limestone or lime reagent, scrubber make-up water, scrubber by-product (gypsum, sludge), and scrubber discharge water. The chemical analyses of these samples and the mass flow rate of each stream were used to calculate mercury material balances.

Process stream samples collected at the stations were analysed to determine the fate of Hg. These samples also were analysed for major ash elements (Fe, Si, Al, etc.) to evaluate the material balances. Standard analytical procedures were used to analyse the flue gas and process stream samples.

2.2 Stability of captured Hg in FGD sludge

FGD sludge often is mixed with fly ash and lime prior to disposal; this practice is known as 'fixation'. The fixated and unfixated FGD sludge from Plant 6 was evaluated to determine if the Hg removed and collected with the FGD sludge was stable. Two FGD materials were evaluated: the unfixated FGD sludge, and FGD sludge that was blended with fly ash and lime for disposal (fixated). The standard EPA TCLP (toxicity characterization leaching procedure – U.S. EPA Method 1311) was used to determine if Hg could be leached from the solids. In this procedure, 100 g of sample is combined with 2 L of an extraction solution and then mechanically agitated for 18–20 hours. At the completion of the mix period, the sample is filtered and the filtrate is analysed for Hg and other species of interest. In this programme, Hg analyses were conducted on the solids before and after the leaching procedure. Three solutions were used: acetic acid buffered to a pH of 2.8, acetic acid buffered with NaOH to a pH of 4.9, and deionized water. In another series of tests, samples of the unfixated and fixated FGD sludge were placed in drying ovens and held at constant temperatures between 75°F and 140°F for 11 weeks. Hg analyses were conducted on these samples before and after heating to determine whether Hg was volatilized.

2.3 Utility operating conditions

One objective of the test programme was to determine the accuracy and reliability of existing mercury-in-flue-gas sampling methods. This required repetitive measurements conducted under similar conditions. The operating staff at each utility was asked to maintain similar boiler and scrubber operating conditions for each test period. The operating parameters maintained at each facility during the sampling programmes are presented in Table 1.

Table 1 Boiler/scrubber operating parameters.

	Plant 1	Plant 2	Plant 3	Plant 4	Plant 5	Plant 6
Boiler configuration	PC	PC	Cyclone	Stoker	PC	PC
% O_2 @ Economizer	3.0	3.5	2.3	7.7	2.4	2.5
Flue gas parameter						
% CO_2	12.6	11.1	13.3	11.1	13.5	14.0
% O_2	6.5	7.5	4.9	7.7	4.9	6.0
SO_2 lb/MM Btu	0.18	1.05	0.74	0.85	1.15	0.20

Scrubber parameters

Scrubber type	Mg-lime	Limestone forced oxidation	Limestone natural oxidation	Chiyoda limestone	Limestone natural oxidation	Mg-lime
Scrubber slurry % solids	31.6	ND	32.5	ND	ND	11.0
FGD slurry density, g/cc	ND	1.08	ND	1.15	ND	1.09
FGD slurry pH	6.5	6.1	5.8	5.0	5.8	6.5
L/G ratio	60–75	94	73	NA	50	28–32
SO_2 removal, %	97	82	87	87	82	96

ND = Not determined.

Three boiler configurations were represented: four pulverized coal-fired (PC), one stoker-fired, and one cyclone-fired. A variety of scrubber types was evaluated, including two magnesium-enhanced lime systems, two natural-oxidation limestone scrubbers, one conventional forced-oxidation limestone scrubber, and one Chiyoda forced-oxidation limestone scrubber. The scrubber slurry pH range was between 5.8 and 6.5 for five of the systems, and 5.0 for the Chiyoda scrubber. The SO_2 removal efficiency ranged from 82 to 97%.

2.4   Coal analyses

The literature [10] suggests that coal composition can influence Hg speciation in the flue gas. Comprehensive coal analyses were conducted on daily coal samples from each plant. Little variability was observed in these samples. The average coal analyses from samples collected at the six test sites are presented in Table 2. All of the plants were firing bituminous coal. Plant 1 fired a Pittsburgh seam high-volatile bituminous coal. Plants 2, 3, 4, and 5 fired Illinois Basin bituminous coals. Plant 6 fired a blend of coals from southern Ohio. The Hg content of the coals ranged between 0.09 and 0.19 p.p.m., dry basis ($\mu g/g$). This range is typical for U.S. coals. The chlorine content varied between 0.11 and 0.23%, dry basis (1100–2300 p.p.m.). Again these are fairly typical values for eastern bituminous coals. Correlations between Hg removal and speciation with these coal quality parameters will be discussed later in this report.

3   Results and Discussion

3.1   Mercury removal by fly ash

Measurable concentrations of Hg were found in the process stream ash samples (bottom, economizer, and ESP ash). Mercury removal by the fly ash was calculated

Table 2   Analysis of coal feed samples (units are % dry basis unless noted).

	Plant 1	Plant 2	Plant 3	Plant 4	Plant 5	Plant 6
Volatile matter	36.72	41.24	32.49	42.48	42.32	40.37
Ash	13.89	10.93	18.51	10.13	9.97	13.61
Carbon	73.60	73.60	66.31	70.44	70.75	68.34
Hydrogen	4.81	5.05	4.13	5.00	4.77	4.57
Nitrogen	1.41	1.45	1.47	1.28	1.35	1.26
Oxygen	2.84	8.20	6.05	8.72	8.92	8.81
Total sulphur	3.52	3.78	3.54	4.21	4.09	3.45
Pyritic sulphur	2.01	2.06	2.13	ND	ND	ND
Sulphate sulphur	0.03	0.05	0.22	ND	ND	ND
Organic sulphur	1.48	1.67	1.19	ND	ND	ND
Chlorine	0.11	0.16	0.11	0.23	0.14	0.13
Mercury, p.p.m.	0.12	0.09	0.09	0.09	0.08	0.19
Fluorine, p.p.m.	ND	62	161	114	105	169
Heating value, Btu/lb	13130	12737	11729	12731	12753	12332

using the following equation:

$$\text{fly ash removal} = \frac{\left(\text{AR} \times \text{Hg}^{\text{ash}}\right)}{\left(\text{CFR} \times \text{Hg}^{\text{coal}}\right)} \times 100\%$$

where CFR = coal firing rate, lb/h; Hg^{coal} = mercury concentration of coal, p.p.m. wt; AR = ash rate, lb/h; Hg^{Ash} = mercury concentration of ash, p.p.m. wt.

The calculated Hg removed in the ash streams at each plant is shown in Table 3. These data indicate that between 7% and 48% of the Hg originally contained in the coal and released into the combustion gas is collected on the ash samples. Only a small amount of Hg is collected in the bottom ash samples for the PC-fired plants, while the stoker unit showed a 13% removal rate. An insignificant amount of Hg is collected with the economizer ash. The majority of the Hg removal occurs with the ESP ash. Hg removal for these samples in the PC-fired systems ranged from 7 to 24% and averaged 12%. The cyclone-fired system showed 13% Hg removal with the ash. The stoker-fired unit demonstrated the highest Hg removal with the ESP ash, which was 35%. This most likely is attributable to the high carbon content of the ash ($\sim$ 50%).

3.2 Mercury removal across the FGD system

The Hg removal across the FGD system was determined from the simultaneous gas phase Hg measurements at the FGD inlet and outlet. The Hg removal data are presented in Table 4. The Hg removal across the FGD systems for the six plants ranged from 45 to 67%, with an average value of 54 $\pm$ 7%. The standard deviation among repeat measurements was $\sim$ 10%. The data show that slightly more than half of the flue gas Hg entering the FGD is removed.

3.3 Hg removal across the ESP-FGD system and emission rates

This test programme showed that Hg is removed by the fly ash particles (and, in some cases, bottom ash) and by the FGD system. The combined Hg removal across the ESP and FGD is the total system Hg removal. The total Hg removal is defined as the difference between the Hg input (based on the coal firing rate and coal Hg concentration) and the Hg emissions measured at the stack. Total Hg removals for the six plants tested are shown in Table 5. Total Hg removal ranged from 59 to 75%, and the overall average was 67 $\pm$ 6%. At Plants 3 and 4, the total Hg removals were 72 and 75%, respectively. The measured relative standard deviation ranged from 5 to

Table 3 Fly ash Hg removal – % of total Hg input.

% Hg removed in ash	Plant 1	Plant 2	Plant 3	Plant 4	Plant 5	Plant 6
Number of tests	4	4	3	4	3	3
Bottom ash	0	0	0	13	2	2
Economizer ash	0	0	0	NA	0	0
Hg in ESP ash	24	7	13	35	9	8
Total in all ash samples	24	7	13	48	11	10
% Carbon in ESP ash	3–5	0.8–1.2	32–38	41–44	2–5	0.10

Table 4 Hg removal across FGD system as % of total Hg input to FGD.

	Plant 1	Plant 2	Plant 3	Plant 4	Plant 5	Plant 6
Test 1	63	—	68	48	64	57
Test 2	59	65	77	45	54	53
Test 3	48	53	57	45	53	63
Test 4	54	50	—	45	—	—
Average	56	56	67	45	57	58
Std. dev.	6	8	10	1	6	5
PRSD	11%	14%	15%	3%	10%	9%

13%. The data indicate that about two-thirds of the Hg in the coal is removed across the ESP-FGD system. These measurements were obtained during normal and routine operations, and no adjustments were made to optimize Hg removal. The estimated average Hg input into the system, the measured Hg emission rates, and Hg removal for each of the six plants are as follows:

Plant no.	Hg input	Hg emissions	Reduction, %
	(Units are mg Hg/MM Btu heat input)		
1	5.74	1.97	66
2	3.08	1.36	56
3	2.42	0.69	72
4	3.25	0.79	75
5	2.85	0.95	67
6	7.01	2.59	63

3.4 Fate of Hg in utility system and material balance data

In addition to determining the Hg removal by FGD processes, two further objectives were to determine the fate of the removed Hg and to calculate Hg material balances to assess the quality of the measurements. Representative process stream samples were obtained and analysed. The average mercury mass flow rate for each process stream in each plant is shown in Table 6. The average material balance closures at all of the plants were between 92 and 116%. The only significant mercury input was due

Table 5 Hg removal across utility system as % of total Hg input to system.

	Plant 1	Plant 2	Plant 3	Plant 4	Plant 5	Plant 6
Test 1	70	60	73	69	67	63
Test 2	65	58	80	74	63	60
Test 3	67	56	62	76	70	67
Test 4	64	53	—	82	—	—
Average	66	56	72	75	67	63
Std. dev.	3	6	9	6	3	4
PRSD	5%	11%	13%	8%	5%	9%

Table 6   Fate of Hg and material balance data (Hg mass flow, mg/sec).

	Plant 1	Plant 2	Plant 3	Plant 4	Plant 5	Plant 6
Input Streams						
Coal	3.09	1.51	1.72	0.33	3.13	25.68
Limestone	0	0	0	0	0	0
Make-up water	0	0	0	0	0	0
Total Hg Input	3.09	1.51	1.72	0.33	3.13	25.68
Output Streams						
Mill reject	0	0	NA	NA	0	0
Bottom ash	0	0	0	0.04	0.06	0.29
Economizer ash	0	0	0	NA	0.01	0.03
ESP ash	0.74	0.11	0.24	0.12	0.26	2.93
Chiyoda pre-scrubber*				0.06		
FGD solids	1.38	0.61	1.27	0.02	1.86	14.00
FGD filtrate	0	0	0	0	0	0
Stack emissions	1.06	0.67	0.49	0.08	1.05	9.48
Total outlet	3.18	1.39	2.00	0.32	3.24	27.05
% Hg closure	103%	92%	116%	97%	104%	104%

* Pre-scrubber blowdown slurry specific to chiyoda scrubber.

to the coal. A small amount of the mercury was removed in the coal mill rejects (for the PC-fired units), but the level was insignificant. Very little Hg is removed (0 to 2%) in the ash prior to the air preheater (bottom and economizer ash samples). The output streams containing significant fractions of Hg are the ESP hopper ash, the FGD solids, the stack emissions, and, in the case of the Chiyoda scrubber, the pre-scrubber blowdown. With the exception of the Chiyoda system, 40 to 70% of the Hg removed by the FGD reports to the FGD solids. No mercury was detected in the FGD filtrate water. The Chiyoda scrubber is equipped with a pre-scrubber, and the blowdown stream removed ~35% of the flue gas Hg prior to the FGD scrubber. It is speculated that this pre-scrubber removal is attributed to the solubility of the oxidized Hg fraction in the spray water.

Hg material balance closures were calculated for each test. The individual closures are presented in Table 7. The grand average material balance closure for the 21 tests was 103%. For this type of testing, the data quality objective was an average material balance closure of ± 20%, with no test greater than ± 30%. With the exception of one test (131% material balance closure), these objectives were met. The Hg material balance closure validates the gas phase measurements and the determined removals.

Table 7   Hg balance closures, %.

	Plant 1	Plant 2	Plant 3	Plant 4	Plant 5	Plant 6
Hg balance closures	90	75	117	118	99	106
	95	104	108	97	108	103
	97	88	125	94	102	103
	131	102		79		
Average	103	92	116	97	104	104
Grand average ± std. dev.						103 +8

3.5   Stability testing of FGD solids

The unfixated and fixated FGD solids from Plant 6 were subjected to TCLP leaching procedures and were heated to determine whether the captured mercury would be re-emitted. The Hg concentrations of the unfixated and fixated FGD samples were 0.70 ± 0.03 p.p.m. and 0.39 ± 0.03 p.p.m., respectively. The concentration of Hg found in the leachate samples for all three extraction solutions (acetic acid buffered to 2.8, acetic acid buffered to 4.9, and DI water) was below the detection limit of 0.01 mg/L. The Resource Conservation and Recovery Act (RCRA) limit for Hg in the leachate is 0.20 mg/L. Based on this criterion, both FGD materials would be classified as non-hazardous. Mercury analysis conducted on the filtered unfixated solids after extraction ranged from 0.68 ± 0.03 p.p.m. to 0.73 ± 0.03, which is statistically the same as the unextracted material. The mercury concentration determined on the filtered fixated solids after extraction was 0.39 ± 0.03 p.p.m., which is the same as the unextracted material. Based on the EPA TCLP method, it was concluded that the Hg contained with the solids is in a non-leachable form. Work reported by others (e.g. Rice *et al.* [11]) suggests that the TCLP procedure might not provide an adequate representation of the environment in an ash or FGD disposal site because the leaching time typically used (18–24 hr) may not recognize the rapid leaching and sequestration of trace elements by secondary phases (such as aluminium and iron hydroxides), or may not be long enough to represent the leaching behaviour of some elements (such as arsenic and vanadium). While this means that more research into leaching test methods are warranted, the TCLP method was used in this study because it is the accepted EPA procedure for landfills.

Both of the FGD wastes were exposed to elevated temperatures for 11 weeks. The highest temperature was 140°F. Analyses conducted at the end of the exposure period showed no loss of Hg. It was concluded from these tests that Hg did not re-volatilize when exposed to temperatures up to 140°F.

3.6   Mercury speciation and removal across the ESP and FGD system

Hg speciation results can provide insight into the removal mechanism. Total Hg and speciated Hg at the ESP inlet and at the stack are presented in Figures 1–6. In these figures, the concentration of the Hg species measured is shown in a stacked bar graph. The Hg material balance closure at the ESP inlet is given above the bar labelled 'In'. With the exception of Plant 1, these measurements were made with the Ontario Hydro method.

Plant 1 – The speciation data for each test completed at Plant 1 are shown in Figure 1. The Hg material balance closure at the ESP inlet was excellent. The equivalent gas phase Hg concentration reporting to the ESP ash varied from 1.5 to $4.0 \, \mu g/m^3$. This fraction represents the Hg removed from the flue gas by the ESP. The Hg emissions were consistent, ranging from 3.0 to 3.8 $\mu g/m^3$. At the site, the gas phase values were obtained using the EPA Method 29 sampling train. In Method 29, it is assumed that the Hg collected in the nitric acid/peroxide impingers is oxidized and the Hg collected in the permanganate impingers is elemental. Comparison of the inlet and outlet oxidized Hg concentration shows almost total oxidized Hg removal. No Hg was found on the particulate filter at the FGD outlet. The mass of the elemental Hg fraction slightly increased across the FGD.
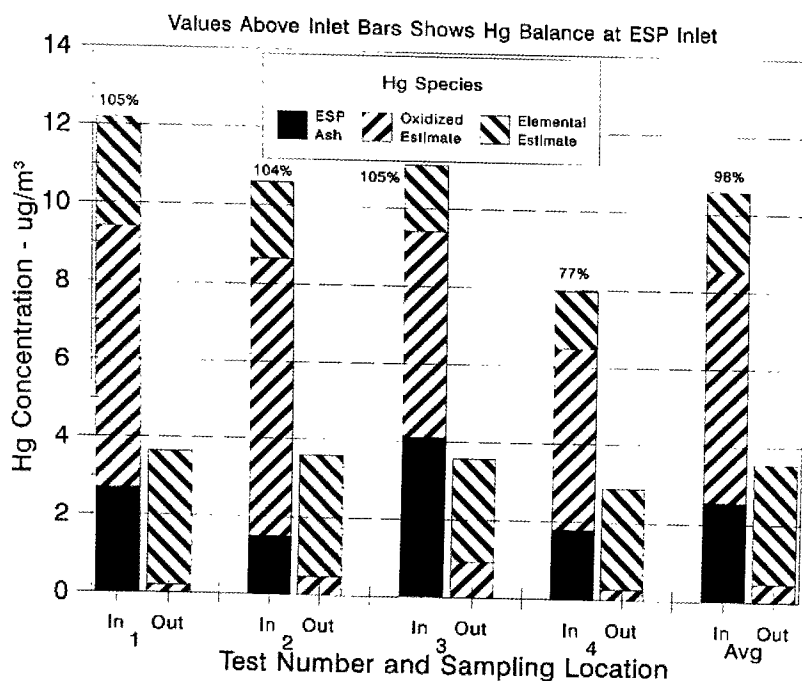
Figure 1   Flue gas Hg speciation at the ESP inlet and FGD outlet of Plant 1. (Speciation determined using Method 29.).

Plant 2 – The material balance closure at the ESP inlet for the first test at Plant 2 was high, but excellent closures were obtained for the next three tests (Figure 2). At the ESP inlet, oxidized mercury was the dominant species. At Plant 2, the inlet gas phase Hg concentrations were obtained using the Ontario Hydro Method. In this method, it is assumed that the Hg collected in the KCl impingers is oxidized and the Hg collected in the permanganate impingers is elemental. The scrubber outlet mercury samples were obtained using a modified Method 29 train with DI water in the first two impingers, nitric acid/peroxide in the next two impingers, and permanganate in the final two impingers. The Hg collected in the impingers upstream of the permanganate is assumed to be oxidized, and the Hg collected in the permanganate impingers is assumed to be elemental. The Hg emissions at the stack were between 1.9 and 2.8 $\mu g/m^3$. The majority of the Hg emissions were elemental mercury. However, some Hg was observed on the particulate filter. Based on the results of subsequent programmes, it is believed that the Hg collected on the filter is a result of gas phase absorption caused by insufficient sample probe and/or filter temperature. These data suggest that the mercury species collected in the KCl impingers, or the oxidized estimate, is the species removed across the scrubber. A slight increase in elemental mercury across the scrubber again was observed.

Plant 3 – Three tests were conducted, with excellent mercury closures at the ESP inlet (Figure 3). As in the previous cases, the estimated oxidized mercury species was the dominant form at the ESP inlet. The ESP inlet Hg concentration ranged between 11.6 and 12.2 $\mu g/m^3$. The outlet measurements indicate significant particulate and
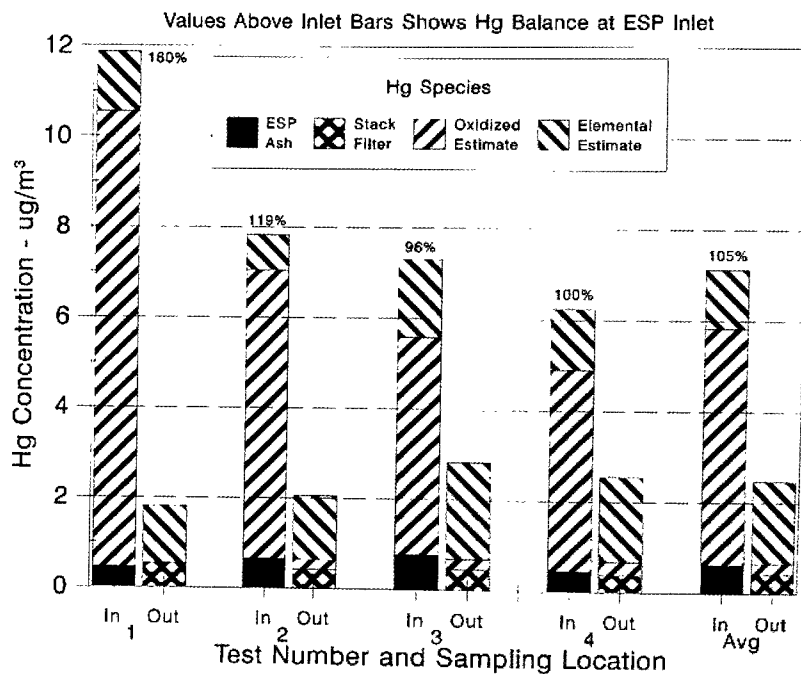
Values Above Inlet Bars Shows Hg Balance at ESP Inlet

Figure 2   Flue gas Hg speciation at the ESP inlet and FGD outlet of Plant 2.

Values Above Inlet Bars Show Hg Material Balance ESP Inlet
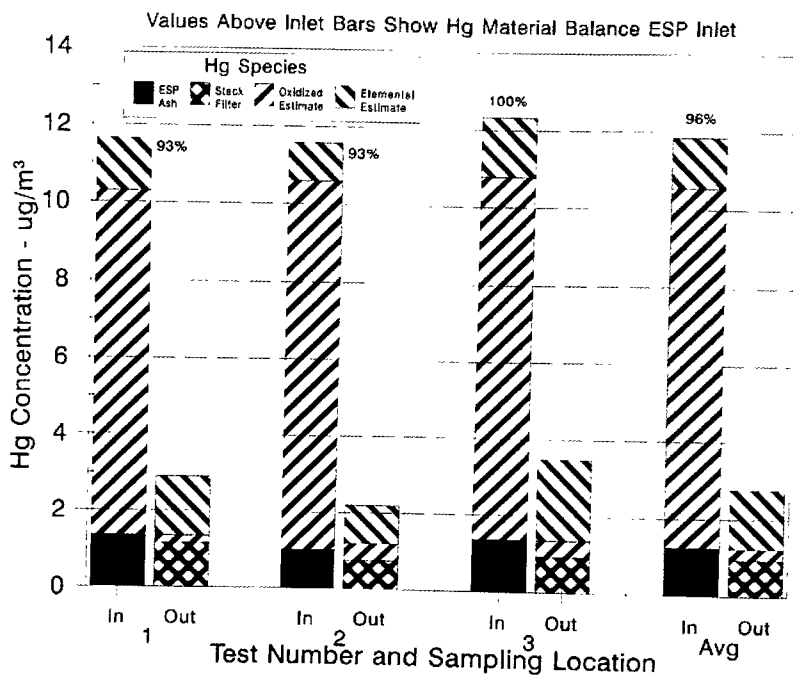

Figure 3   Flue gas Hg speciation at the ESP inlet and FGD outlet of Plant 3.

elemental Hg fractions and a very small oxidized Hg concentration. The outlet Hg concentrations were between 2.5 and 3.8 $\mu g/m^3$. As at the previous plant, some Hg was measured on the filter. After this programme, modifications were made to the sampling train to allow for higher temperatures. In the later test programmes, insignificant Hg was found on the filter.

Plant 4 – Four tests were conducted at the ESP inlet, scrubber inlet, and the scrubber outlet (Figure 4). At the ESP inlet, 42% (3.40 $\mu g/m^3$) of the Hg was in the particulate fraction, 34% (2.10 $\mu g/m^3$) in the flue gas as oxidized, and 24% (1.47 $\mu g/m^3$) in the flue gas as elemental. If we assume that the Hg collected with the ash solids was originally in the oxidized fraction of the flue gas, then the Hg speciation from combustion is ~80% oxidized and ~20% elemental. The Hg material balance closures at the inlet were between 79 and 106%. There was very little Hg in the particulate matter at the scrubber inlet. The scrubber inlet Hg concentrations were 2.45 $\mu g/m^3$ oxidized and 1.07 $\mu g/m^3$ elemental. Although not shown in the figure, these values are similar to the ESP inlet concentrations. The scrubber outlet contained no Hg in the particulate phase and 0.70 $\mu g/m^3$ oxidized and 1.19 $\mu g/m^3$ elemental. Most of the oxidized Hg is removed by the combined action of the pre-scrubber and FGD scrubber. The elemental Hg is unchanged.

Plant 5 – Three tests were conducted at the ESP inlet and the scrubber outlet, with excellent mercury closures at the ESP inlet (Figure 5). The total ESP inlet Hg concentration was between 6.50 and 8.87 $\mu g/m^3$. Of this total, 20% (1.50 $\mu g/m^3$) was found on the particulate, 61% (4.73 $\mu g/m^3$) was oxidized, and 19% (1.55 $\mu g/m^3$) was
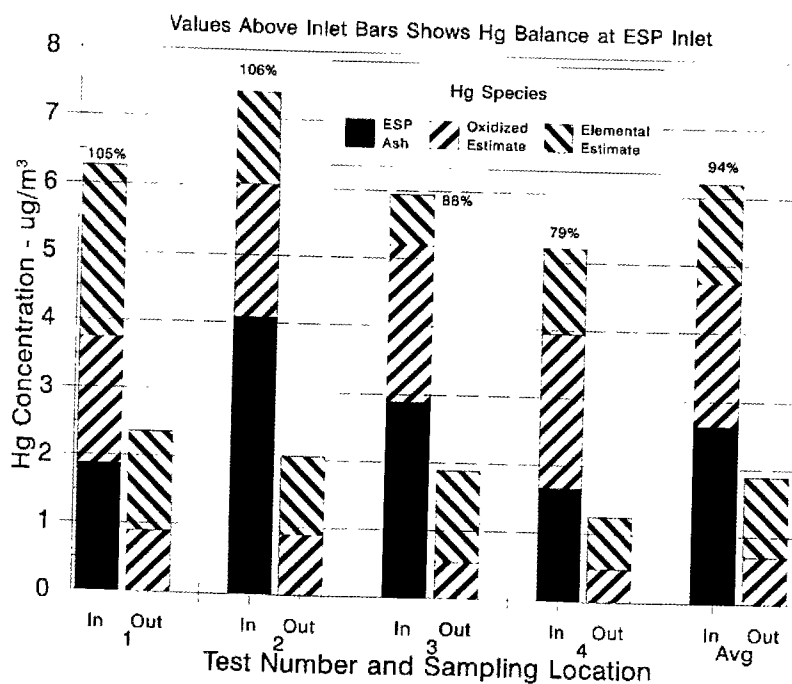

Figure 4 Flue gas Hg speciation at the ESP inlet and FGD outlet of Plant 4.
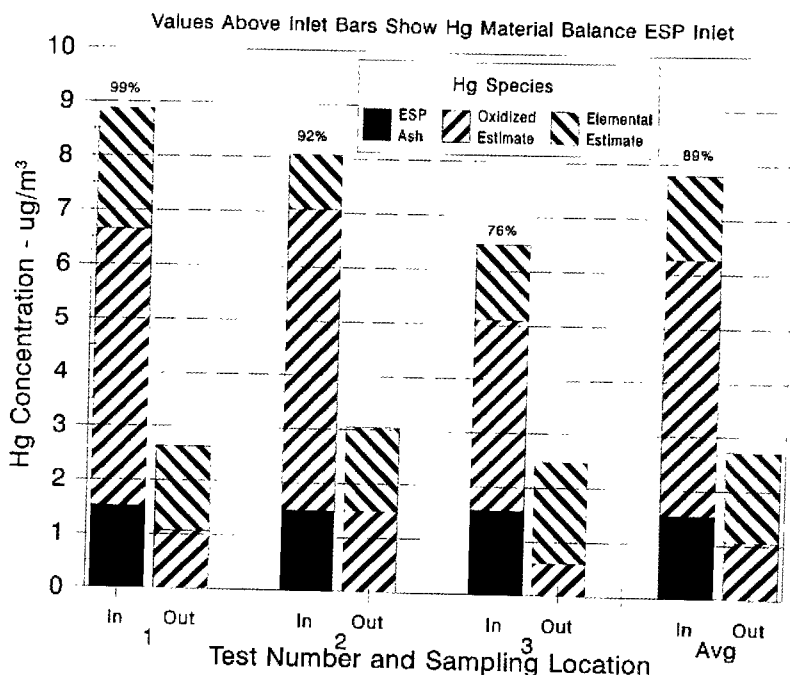
Figure 5   Flue gas Hg speciation at the ESP inlet and FGD outlet of Plant 5.

elemental. Assuming that the Hg collected by the fly ash is oxidized Hg, the Hg speciation is 80% oxidized and 20% elemental. The FGD outlet Hg concentrations ranged between 2.50 and 3.07 μg/m^3. No Hg was found in the particulate phase, 1.06 μg/m^3 was oxidized, and 1.66 μg/m^3 was elemental. The flue gas oxidized Hg fraction at the scrubber inlet is removed at a rate of $\sim$80% by the scrubber; however, a slight increase in the elemental fraction was observed.

Plant 6 – Three tests were conducted with excellent mercury closures at the FGD inlet (Figure 6). The total FGD inlet Hg concentration ranged between 16.72 and 18.82 μg/m^3. Of this total, 71% was oxidized and 29% was elemental. The FGD outlet Hg concentrations ranged between 6.92 and 7.81 μg/m^3. Of this total, 17% was oxidized and 83% was elemental. A 20% increase was observed in the measured elemental fraction at the FGD outlet. There was no measurable Hg associated with the particulate.

If it is assumed that the Hg removed with the fly ash and the Hg collected in the KCl impingers is oxidized Hg, the ratio of oxidized to elemental Hg at the ESP inlet for the six plants is $\sim$8:1. Very low concentrations of oxidized Hg (estimated from the sampling train impinger solutions) were measured at the stack. The majority of the oxidized mercury is removed by the ESP/FGD combination. There was no decrease and, in some cases, there was an increase in the elemental Hg concentration across the FGD. These data indicate that the Hg species collected in the nitric acid/peroxide impingers of Method 29 and the KCl impingers of the Ontario Hydro Method is the
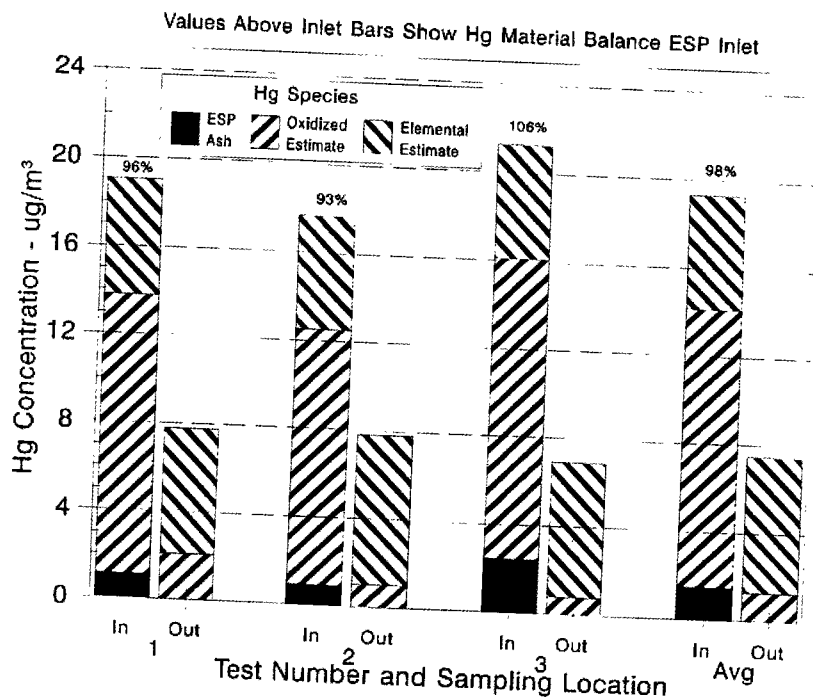
Figure 6   Flue gas Hg speciation at the ESP inlet and FGD outlet of Plant 6.

species that is being removed by the FGD system. The cause of the increase in the elemental Hg fraction at the FGD outlet is unknown. This increase could be due either to artifact formation in the sampling trains or chemical reduction of some fraction of the oxidized Hg to elemental Hg in the FGD system.

3.7   Statistical analysis of parameters influencing Hg removal

A statistical analysis of the data from these six plants and one additional set of plant data (PC-fired boiler with a forced oxidation limestone scrubber firing Pittsburgh Seam coal data, supplied by the U.S. DOE), was conducted by the Illinois State Geological Survey. The correlations of Hg removal with the FGD data, stack flue gas data, and coal quality are presented in Table 8. Their results show a significant correlation between the oxidized mercury removal and the pH of the scrubber slurry, with higher pH resulting in increased Hg removal. Among the coal quality parameters, the coal oxygen concentration showed a strong negative correlation with oxidized Hg removal. A weaker correlation was identified between the nitrogen and ash content and total Hg removal. No correlation was evident between the chlorine concentration in the coal and either the observed speciation or the Hg removal. However, all the coals included in this programme would be considered mid-chlorine coals.

Table 8   Correlations between Hg removal and FGD data, stack flue gas data and coal quality data.

	% Hg removal with ash	% Hg removal across FGD	% removal of Hg^{++}	% removal of HgO	% total Hg removal
FGD Data					
pH	0.4570*	0.3852†	0.4239†	−0.4152†	0.4105†
L/G ratio	0.0250	0.1819	0.1788	−0.1113	0.1705
% SO_2 removal	0.4620†	0.0814	0.1278	−0.1855	0.1327
Stack Flue Gas Data					
Stack gas flow, acfm	−0.1835	−0.2152	−0.2185	0.1598	−0.2191
Stack gas flow, dscfm	−0.1917	−0.2185	−0.2229	0.1672	−0.2233
% O_2	0.0102	0.0962	0.1005	−0.1365	0.0915
% CO_2	−0.1442	−0.2046	−0.2204	0.2650	−0.2079
% H_2O	−0.1881	−0.0923	−0.0986	0.2705	−0.1124
Coal Quality Data					
Total moisture	−0.3932†	−0.0912	−0.1247	0.1550	−0.1319
Volatile matter	−0.3235	−0.3142	−0.2854	0.0013	−0.3139
Ash	0.2770	0.3625†	0.3373	−0.1111	0.3603†
Carbon	0.1651	−0.0972	−0.0440	−0.1594	−0.0633
Hydrogen	−0.0899	−0.1693	−0.1320	−0.0792	−0.1607
Nitrogen	0.1292	0.3593*	0.3323	−0.1102	0.3413
Oxygen	−0.7255*	−0.4605*	−0.5085*	0.4767*	−0.5110*
Total sulphur	−0.0325	0.0481	0.0406	−0.0112	0.0400
Chlorine	−0.1028	−0.0384	−0.0387	−0.0291	−0.0413
Heating value	0.1060	−0.1457	−0.0915	−0.1308	−0.1144
Hg, p.p.m.	0.0156	−0.2196	−0.1987	0.1165	−0.1976

* Correlation is significant at the 0.01 level (2-tailed).
† Correlation is significant at the 0.05 level (2-tailed).

4   Application

The U.S. EPA has prepared a report to Congress that analyses U.S. mercury emissions and health effects. Coal-fired electric utilities have been identified as the largest anthropogenic Hg source. In 1999, EPA will collect additional information regarding Hg emissions from coal-fired utilities to determine if Hg controls are necessary. Initial control cost estimates, based on carbon injection, for the removal of Hg from coal-fired utilities range from $10 to $40 million per ton of Hg removed. For comparison purposes, the cost effectiveness of SO_2 and NO_x removal is between $70 and $300 per ton of SO_2 removed, and between $150 and $3000 per ton of NO_x removed. Clearly, Hg control costs are very high. Controlling Hg emissions with existing FGD systems would not increase FGD or plant operating costs; the cost effectiveness of FGD Hg control in an existing system is $0 per ton of Hg removed. Information documenting the level of Hg control achieved by ESP/FGD systems and identifying the process parameters that influence Hg removal will provide utilities and regulators with information to assess control options if Hg regulations are deemed necessary.

5 Summary

A mercury measurement programme was conducted on six full-scale, coal-fired boilers equipped with lime and limestone FGD scrubbers. The goals were to determine mercury removal achieved by wet FGD systems and by combined ESP-wet FGD systems at coal-fired utility plants, and to correlate mercury removal with coal properties and boiler scrubber operating parameters. The mercury removal due to the ash was between 7 and 48%. The 48% removal was at a stoker-fired industrial boiler and is a result of significant Hg removal in both the fly ash (35%) and the bottom ash (13%).

The average Hg removal across the FGD systems was 54 ± 7% and ranged from 45 to 67%.

The average total Hg removal across the boiler system (ESP and FGD) was 67 ± 6% and ranged from 56 to 75%.

The Hg material balance closures were between 75 and 131% for the 21 tests. The grand average closure was 102%. The average balances for each site were within data quality objectives.

The Hg in the FGD waste is stable and is not susceptible to leaching or revolatilization under the conditions evaluated.

The ESP inlet and stack flue gas speciation data indicate that 80 to 95% of the oxidized Hg fraction is removed across the ESP and FGD scrubber. The FGD outlet samples showed a slight increase in the elemental Hg fraction.

The statistical analysis of the Hg emission data from seven scrubbed utilities showed a significant correlation between Hg removal and FGD slurry pH.

Acknowledgement

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