

March 22, 1999

Mr. William H. Maxwell
Office of Air Quality Plans & Standards (MD-13)
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Subject: Electric Utility Steam Generating Unit
Mercury Test Program -
Milton R. Young Station

Dear Mr. Maxwell:

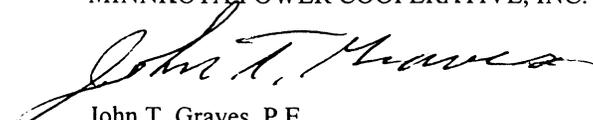
This letter is response to our telephone conversation of March 17, 1999. As you are aware, Milton R. Young Station Unit 2 was selected for testing under the above subject program. Unit 2 was previously tested in the spring of 1998 as part of the DOE's utility mercury speciation characterization studies conducted by FETC. The report of this testing is entitled **MERCURY SPECIATION SAMPLING AT MINNKOTA POWER COOPERATIVE'S MILTON R. YOUNG STATION**. It is our understanding that this testing meets the requirements of the subject test program. As this information has been previously forwarded to the EPA by DOE, we ask that this test report be accepted as fulfilling our obligations for testing of Unit 2 under the program, without being resubmitted.

The previously submitted report not only gives the required test data on the last emissions control device, the FGD unit in the case of Unit 2, but also across the ESP. This provides data similar to what would be obtained by testing Unit 1. Unit 1 meets the same classification for testing as Unit 2, except that it isn't equipped with an FGD unit. Because this data is in the previously submitted report, we request that it be utilized to fulfill the testing and reporting requirements for Milton R. Young Unit 1.

Due to the June 1, 1999 date for submittal of a site-specific test plan and QAPP, an expeditious response to our request would be greatly appreciated. Should you have any questions concerning this matter, please contact me at 701-795-4221.

Yours truly,

MINNKOTA POWER COOPERATIVE, INC.



John T. Graves, P.E.
Environmental Manager

c: Luther Kvernem
Stuart Libby
Kevin Thomas
✓ William Grimley, U.S. EPA

Minnkota Power

COOPERATIVE, INC.

34, 35

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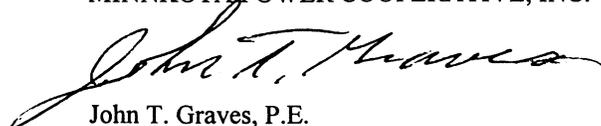
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MERCURY SPECIATION SAMPLING AT MINNKOTA POWER COOPERATIVE'S MILTON R. YOUNG STATION

Final Report

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ABBREVIATIONS

Al_2O_3	alumina (aluminum oxide)
ANSI	American National Standards Institute
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
Btu	British thermal unit
$^{\circ}\text{C}$	degrees Celsius
CAAAAs	Clean Air Act Amendments
CaO	calcium oxide
CEM	continuous emission monitor
Cl_2	chlorine gas
CO_2	carbon dioxide
CVAA	cold-vapor atomic adsorption
DOE	U.S. Department of Energy
EERC	Energy & Environmental Research Center
EPA	U.S. Environmental Protection Agency
ESP	electrostatic precipitator
$^{\circ}\text{F}$	degrees Fahrenheit
Fe_2O_3	iron(III) oxide
FGD	flue gas desulfurization
g	gram
H_2O_2	hydrogen peroxide
H_2SO_4	sulfuric acid
HCl	hydrogen chloride
HF	hydrofluoric acid
Hg	mercury
Hg^0	elemental mercury
Hg^{2+}	oxidized mercury
HNO_3	nitric acid
hr	hour
ICR	information collection request
K_2O	potassium oxide
KCl	potassium chloride
klb	kilopound
L	liter
lb	pound
MMBtu	million (10^6) British thermal units
mg	milligrams
MgO	magnesium oxide
min	minute
MW	megawatt
NA	not acceptable
Na_2O	sodium oxide

ABBREVIATIONS (continued)

NaOH	sodium hydroxide
ND	not detected
NIST	National Institute of Standards and Technology
nm	nanometer
Nm ³	normal cubic meter (20°C and 1 atmosphere)
NO _x	nitrogen oxides (nitric oxide and nitrogen dioxide)
O ₂	oxygen
P ₂ O ₅	phosphorus pentoxide
ppb	parts per billion
ppm	parts per million
psig	pounds per square inch gauge
QA	quality assurance
QC	quality control
scf	standard cubic feet
scfm	standard cubic feet per minute
SiO ₂	silica (silicon dioxide)
SO ₂	sulfur dioxide
SO ₃	sulfur trioxide
Std. Dev.	standard deviation
TiO ₂	titanium oxide
µg	micrograms
% ^{v/v}	percentage by volume
% ^{w/v}	percentage by weight

MERCURY SPECIATION SAMPLING AT MINNKOTA POWER COOPERATIVE'S MILTON R. YOUNG STATION

EXECUTIVE SUMMARY

1.0 INTRODUCTION

The 1990 Clean Air Act Amendments (CAAAAs) required the U.S. Environmental Protection Agency (EPA) to determine whether the presence of mercury in the stack emissions from fossil fuel-fired electric utility power plants poses an unacceptable public health risk. Two mercury reports to Congress were issued (1). Given the current state of the art, these reports did not state that mercury controls on coal-fired electric power stations should be required. However, they did indicate that EPA views mercury as a potential threat to human health and additional research/information was necessary. To address the issue of mercury emissions and their impact on the Devils Lake area, a consortium was set up, which contracted with the Energy & Environmental Research Center (EERC).

The consortium consisted of the following groups:

- Minnkota Power Cooperative, Inc., the owner and operator of the Milton R. Young Station, located near Center, North Dakota
- Cooperative Power Association, the owner and operator of the Coal Creek Station located near Underwood, North Dakota
- North Dakota Industrial Commission
- U.S. Department of Energy (DOE) through the Jointly Sponsored Research Program with the EERC
- EPRI

The project is divided into two tasks. Task 1 is focused on determining the abundance and forms of mercury emitted. Task 2 addresses discrepancies noted in the literature regarding the

source of mercury in lakes. This report gives the results from the mercury sampling that was completed at the Milton R. Young Station during the week of May 18, 1998.

2.0 OBJECTIVES

The four primary objectives of the Milton R. Young Mercury Speciation Test Program (Task 1) are as follows:

- Determine the mercury emissions and speciation of the mercury emissions from the station
- Use a continuous emissions monitor (CEM) to measure total mercury at the stack
- Provide electrostatic precipitator (ESP) and flue gas desulfurization (FGD) removal efficiencies for each the mercury species
- Calculate mercury material balances

3.0 APPROACH

Flue gas sampling at the Milton R. Young Station's Unit 2 was completed to determine the mercury speciation at five different points in the system: at the air preheater inlet, inlet to one of the ESPs, outlet of the ESP/inlet to the FGD unit, outlet of the FGD unit, and the stack. All mercury speciation measurements were made using the Ontario Hydro method, which has been validated in pilot-scale tests at the EERC. During the testing, the FGD system was operated in two different modes. The first (Condition A) was with fly ash as the scrubbing medium, and the second (Condition B) was with lime as the SO₂ sorbent.

3.1 Results

Figures ES-1, ES-2, and ES-3 present graphically the results of the mercury sampling. Figures ES-1 and ES-2 show the mercury removal across the ESP and FGD system, respectively. Figure ES-3 shows the mercury speciation at the stack. A summary of the speciated mercury emission factors for Unit 2 at the Milton R. Young Station is given in Table ES-1.

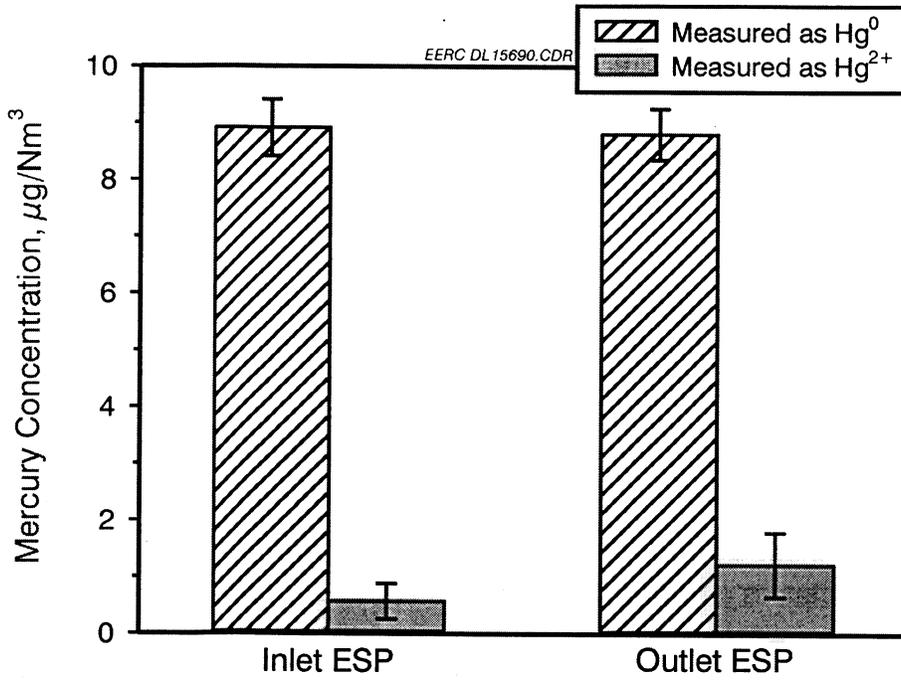


Figure ES-1. The change in vapor-phase speciated mercury across the ESP.

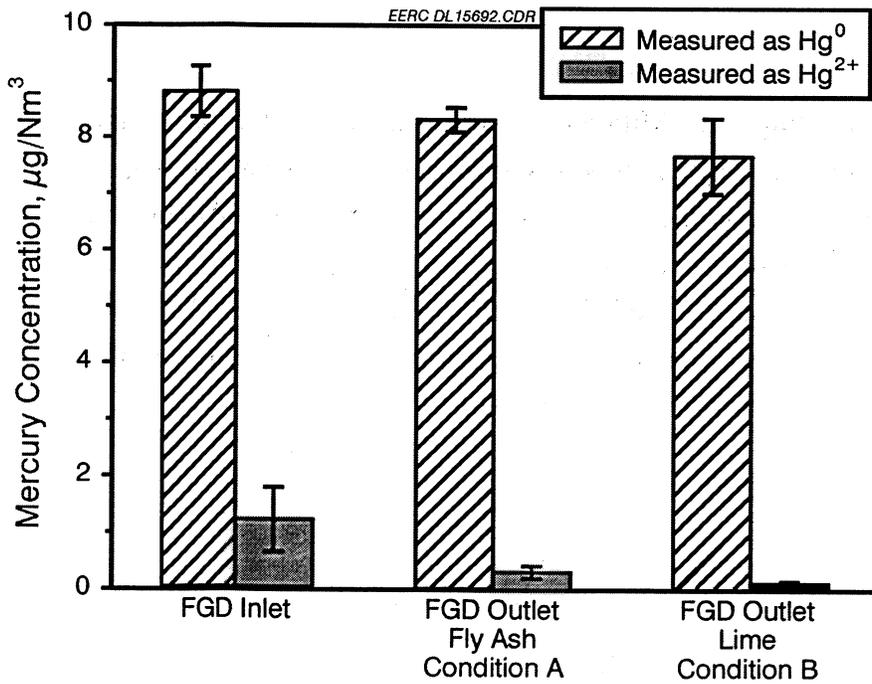


Figure ES-2. The change in vapor-phase speciated mercury across the FGD system at two conditions.

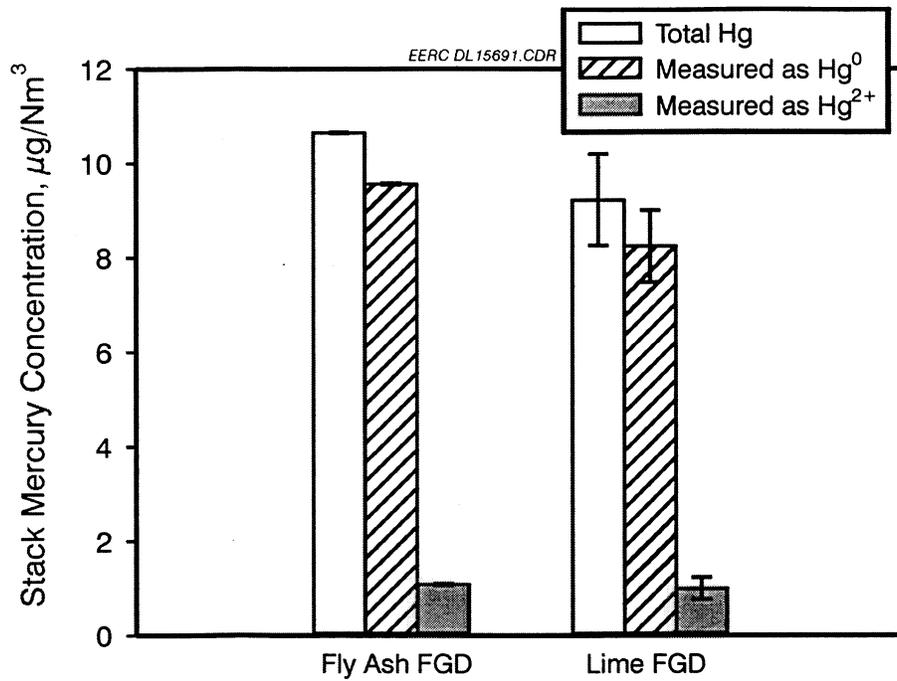


Figure ES-3. Mercury speciation emission measurements at the stack of Unit 2.

TABLE ES-1
Emission Factors for Mercury at Unit 2 Stack

Condition	Hg ²⁺ , lb/10 ¹² Btu	Hg ⁰ , lb/10 ¹² Btu	Total Hg, lb/10 ¹² Btu
A	0.88	8.42	9.31
A	0.93	8.41	9.34
B	0.67	6.78	7.44
B	1.08	8.06	9.14
B	0.87	7.59	8.45

3.2 Conclusions

The following conclusions were drawn from the results of the testing at the Milton R. Young Station:

- The mercury emitted at stack was about 10% oxidized mercury (Hg^{2+}) and 90% elemental mercury (Hg^0).
- The FGD system, whether utilizing fly ash or lime as the sorbent, removes almost all the Hg^{2+} but little if any Hg^0 .
- It appears that about 5% of the mercury was removed by the ESP and another 5% of the Hg^0 was converted to Hg^{2+} across the ESP.
- The Semtech Hg 2000 CEM gave total mercury results very comparable to those given by the Ontario Hydro mercury speciation sampling method.
- The mercury emission factor for Unit 2 of the Milton R. Young Station was $8.74 \pm 0.81 \text{ lb}/10^{12} \text{ Btu}$.
- Good mercury balances were obtained around Unit 2, the ESP, and FGD systems.
- Mercury captured on the fly ash tended to stay there, even when mixed in highly basic or acidic solutions.

MERCURY SPECIATION SAMPLING AT MINNKOTA POWER COOPERATIVE'S MILTON R. YOUNG STATION

1.0 INTRODUCTION

1.1 Test Program Background

The 1990 Clean Air Act Amendments (CAAAAs) required the U.S. Environmental Protection Agency (EPA) to determine whether the presence of mercury in the stack emissions from fossil fuel-fired electric utility power plants poses an unacceptable public health risk. EPA's conclusions and recommendations were presented in the *Mercury Study Report to Congress* (1) and *Utility Air Toxics Report to Congress* (1). The first report addressed both the human health and environmental effects of anthropogenic mercury emissions, while the second addressed the risk to public health posed by the emission of mercury and other hazardous air pollutants from steam-electric generating units. Although these reports did not state that mercury controls on coal-fired electric power stations would be required given the current state of the art, they did indicate that the EPA views mercury as a potential threat to human health. Therefore, it was concluded that mercury controls at some point may be necessary. EPA also indicated that additional research/information was necessary before any definitive statement could be made. This has led to the issuance of a controversial information collection request (ICR) by EPA.

A consortium was set up to determine the speciation and levels of mercury emissions from North Dakota power plants and if these emissions impact the Devils Lake area. The Energy & Environmental Research Center (EERC) was contracted to measure mercury emissions from two North Dakota power plants and to determine the level of mercury in sediments in Devils Lake. The consortium consisted of the following groups.

- Minnkota Power Cooperative, Inc., the owner and operator of the Milton R. Young Station, located near Center, North Dakota
- Cooperative Power Association, the owner and operator of the Coal Creek Station located near Underwood, North Dakota
- North Dakota Industrial Commission

- U.S. Department of Energy (DOE) through the Jointly Sponsored Research Program with the EERC
- EPRI

The project is divided into two tasks. Task 1 is focused on determining the abundance and forms of mercury emitted at two North Dakota utilities. Task 2 addresses discrepancies noted in the literature regarding the source of mercury in lakes. This report presents the results from the mercury sampling that was completed at the Milton R. Young Station during the week of May 18, 1998.

1.2 Test Program Objectives for Task 1

The following objectives of the Milton R. Young Mercury Speciation Test Program (Task 1) were accomplished:

- Determine the mercury emissions and speciation of the mercury emissions from the station
- Use a continuous emissions monitor (CEM) to measure total mercury at the stack
- Provide electrostatic precipitator (ESP) and flue gas desulfurization (FGD) removal efficiencies for each the mercury species
- Calculate mercury material balances

1.3 Sampling Approach

Table 1-1 identifies the mercury-sampling test program matrix. Representative samples were collected and analyzed for mercury from each the targeted flue gas streams, two solid streams, and five FGD liquid/sludge streams.

2.0 TEST DESCRIPTION

This section describes the Milton R. Young Station and the various sample locations that were used for the test program. The process operation during testing is also described.

TABLE 1-1
Mercury Speciation Test Program Matrix at Milton R. Young Power Station

Process Stream	Target Mercury Species		
	Hg ⁰ (elemental)	Hg ²⁺ (oxidized)	Total Hg
Flue Gas Sample Streams			
Air Preheater Inlet	X	X	X
ESP Inlet	X	X	X
ESP Outlet/ FGD Inlet	X	X	X
FGD Outlet	X	X	X
Stack	X	X	X
Solid Samples			
Fuel Conditioner Outlet			X
ESP Hoppers (1-4)			X
Liquid Samples			
Fly Ash Slurry (Condition A)			X
FGD Slurry (Condition A)			X
Lime Slurry (Condition B)			X
FGD Slurry (Condition B)			X
Ash Sluice Water			X
FGD Pond Return Water			X

2.1 Unit Description

The Milton R. Young Station is a minemouth electrical generating plant located near Center, North Dakota. The plant is operated by Minnkota Power Cooperative and is its primary source of power generation. The plant supplies electricity for people in eastern North Dakota and northwestern Minnesota through 12 associated distribution cooperatives. The Milton R. Young Station consists of two units. Unit 1, which began operating in 1970, has a capacity of 234.5 megawatts (MW) and is owned and operated by Minnkota Power. Unit 2, with a generating capacity of 438 MW, began operating in 1977 and is owned by Square Butte Electric Cooperative. Unit 2 supplies power to Minnkota Power and Minnesota Power in Duluth, Minnesota. Both units are cyclone-fired boilers manufactured by Babcock & Wilcox. The mercury sampling completed for this project was done on Unit 2. Unit 2's cyclone-fired boiler has a 2400-psig rating and consumes 8150 tons of lignite daily.

The fuel fired at the Milton R. Young station is a North Dakota lignite provided by BNI Coal, Ltd. Once the lignite has been hauled to the plant from the nearby BNI mines, it is dumped into the primary crusher, which produces a fuel size of about 1¼ in. When the fuel is needed, it is conveyed to secondary crushers, which take it down to ¼ in. The lignite is then carried by heated air to the cyclone burners, and combustion occurs, resulting in a temperature of up to 3000° F. In a cyclone boiler, approximately 50% of the ash from combustion is removed as a molten slag. The slag is sluiced out to the bottom ash solids sedimentation basin where the solids are dewatered and the water is recycled to the ash-handling system.

Both Units 1 and 2 are equipped with ESPs for removal of fly ash from the boiler exhaust gases. However, the ESPs for the two units are of different designs. Unit 1 has hanging wire ESPs, while those on Unit 2 are rigid frame. The two rigid frame ESPs installed on Unit 2 were manufactured by Wheelabrator-Frye, with each having a specific collection area of 188, two chambers, and eight hoppers. The ESPs have always exceeded 99.4% collection efficiency for particulate matter. The actual particulate collection efficiency during the testing is shown in Table 2-1. As this table shows, the measured particulate collection efficiency during the testing period was >99.8%. This allows the Milton R. Young station to meet the Federal Environmental Emission Standard of 0.1 lb of particulate matter per million Btu input. Because of its high alkali content, the ash from the ESP hoppers is used to remove sulfur in the scrubber system.

To comply with environmental regulations for sulfur dioxide (SO₂) emissions, Unit 2 has installed two scrubber modules that have the capacity to remove up to 90% of the SO₂. The scrubber towers are each designed to handle a total of 85% of the flue gas at full load. A minimum of 15% of the inlet flue gas bypasses each absorber tower and is used for gas reheat. Each module contains a reaction tank, spray nozzles, liquid-gas contactors, and demisters. These scrubber modules were designed to use of the inherent calcium content of the North Dakota lignite fly ash to capture SO₂. Additional lime can also be added to ensure the plant is in compliance with the SO₂ emission standards (1.2 lb of SO₂ /MMBtu). The scrubber modules use all the fly ash collected by the ESPs from both Units 1 and 2. The fly ash goes from the ESP hoppers to a storage silo before going to the reaction tank where water is added from the sluice tank. The scrubbers typically operate at a slurry pH of 4 to 6. At this pH, the state of oxidation of the sulfur species is essentially 100% sulfate. The scrubber blowdown is controlled by the suspended solids. Therefore, the blowdown is done on a periodic basis rather than continuously. On a mass balance basis, the only mercury leaving the scrubber is either in the blowdown or the exiting gas. Makeup water for the scrubber modules comes from the ash pond.

TABLE 2-1

ESP Particulate Collection Efficiency During the Week of Mercury Sampling

Day	ESP Inlet Dust Loading, grains/scf	ESP Outlet Dust Loading, grains/scf	ESP Particulate Collection Efficiency, %
2	1.3423	0.0017	99.87
2	2.0673	0.0013	99.94
4	2.3089	0.0003	99.99
5	1.5002	0.0012	99.92
5	1.6209	0.0016	99.90

2.2 Sampling Test Plan, Locations, and Collection Procedures

Figure 2-1 is a simplified process flow diagram for Unit 2 depicting the boiler-ESP-FGD system. Solid circles represent sampling locations for the flue gas sample streams. Although not shown, the flow is split immediately after exiting from the boiler. The original sampling scheme

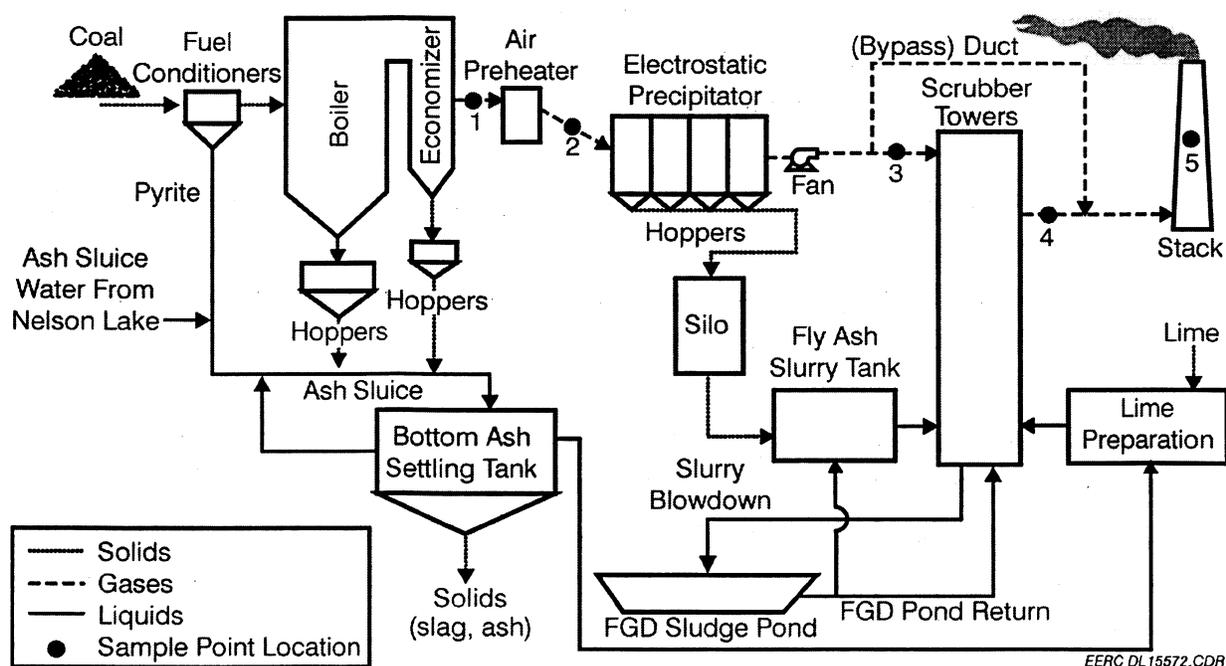


Figure 2-1. Process flow diagram for Unit 2 of the Milton R. Young Power Station.

was to do all sampling along one of the gas streams. Two sampling conditions were to be tested. The first test (Condition A) was to have the scrubber tower use only fly ash as the SO₂ scrubbing media. The second test (Condition B) was to have the scrubber use a lime slurry. Testing for both conditions was to be done utilizing Scrubber Module A; however, because of problems at the plant with the stirring mechanism of the Scrubber Module A, the original plan could not be followed. It was necessary to move the sampling rails and sampling systems to Scrubber Module B to complete the Condition B test.

2.2.1 Flue Gas Sample Streams

The original flue gas sampling test plan is shown in Table 2-2. Although the test plan was not followed because problems occurred with the stirring mechanism of Scrubber Module A, good data were still obtained. In addition, during Day 4, two additional ESP inlet samples were taken because a probe broke and therefore the data could not be used. Table 2-3 shows the actual mercury sampling that was completed.

The primary flue gas sample streams of interest were the flue gas streams entering and exiting the ESP and FGD systems and the stack. The first four points determine the effectiveness of these air pollution control devices at removing targeted species of mercury released during coal combustion. Although these data are important to understanding the effects of air pollution control devices on mercury speciation, it is the mercury measurements at the stack that are of prime significance. Not only is it important to measure total mercury at the stack, but also the mercury speciation, because the rate of deposition of mercury in the environment is highly dependent on the type of mercury being emitted (2).

Mercury speciation measurements were also made at the inlets to the preheater and the stack. The purpose of sampling at the air preheater was to prove that at temperatures above about 800°F the mercury is all in the elemental (Hg⁰) form. In addition to mercury measurements, chlorides were also determined at the FGD inlet.

Although the original test plan included using an EPA Method 1 full-traverse sampling procedure, the availability of ports at some of the sampling locations made this impossible. Therefore a one-dimensional traverse was made (one port, three locations) at the ESP outlet/FGD inlet, and FGD outlet. A 12-point traverse grid, however, was completed at the ESP inlet and the

TABLE 2-2
Original Mercury Speciation Sampling Test Plan

Day	Condition	Air				
		Preheater Inlet	ESP Inlet	ESP Outlet/ FGD Inlet	FGD Outlet	Stack*
1	A	1	1	1	1	1
2	A	1	2	2	2	2
3		Changing scrubber conditions from all fly ash to all lime				
4	B	1	1	1	1	1
5	B	1	2	2	2	2

* The Semtech Hg 2000 CEM was to be used to measure total mercury at the stack.

TABLE 2-3
Actual Mercury Speciation Sampling Completed

Day	Condition	Air				
		Preheater Inlet	ESP Inlet	ESP Outlet/ FGD Inlet	FGD Outlet	Stack*
1		Setup of equipment				
2	A	1	NA**	2	2	2
3		Changing scrubber conditions from all fly ash to all lime				
4			2	Changing scrubber modules		
5	B	1	3	3	3	3

* The Semtech Hg 2000 CEM was also used to measure total mercury at the stack.

** Data not acceptable because sampling probe broke.

stack. Table 2-4 shows the traverse setup that was completed at each sampling location. As shown in the table, a single-point sample was taken at the air preheater inlet, as well as for the chloride measurement. All sample locations were such that the sampling ports meet the EPA minimum requirements for upstream and downstream distance from the nearest flow disturbances. At the stack, four ports were sampled located 90 degrees from each other. At the ESP inlet, only three ports were available for sampling.

TABLE 2-6
Analysis of the BNI North Dakota Lignite on a Dry Basis

Proximate Analysis, wt%	
Moisture Content	37.30
Volatile Matter	46.36
Fixed Carbon	41.81
Ash	11.83
Ultimate Analysis, wt%	
Hydrogen	4.00
Carbon	58.02
Nitrogen	1.04
Sulfur	1.01
Oxygen, by difference	24.10
Ash	11.83
Heating Value, Btu/lb	10,304
Coal Ash Analysis, % conc. as oxides	
SiO ₂	11.2
Al ₂ O ₃	8.6
Fe ₂ O ₃	13.2
TiO ₂	0.2
P ₂ O ₅	0.1
CaO	21.3
MgO	7.3
Na ₂ O	11.7
K ₂ O	0.2
SO ₃	26.2

cases the amount of mercury was below the detection limits of the cold-vapor atomic adsorption (CVAA) instrument. Therefore these amounts are considered insignificant in determining the mass balance for mercury.

2.2.3 *Liquid Sample Stream*

The liquid samples collected during the test program are shown in Table 2-7. Each of the slurry feeds (fly or lime) was collected from the reaction tank. The FGD slurries were collected from the slurry recycle. Assuming the system has reached a steady state, the concentration of mercury in the recycle will be the same as in the blowdown.

TABLE 2-7
Liquid Samples Collected at the Milton R. Young Station

Sample No.	Date	Time	Type of Sample
1 – Lime Slurry Feed	5-18-98	1538	Lime + ash sluice water
2 – Lime Slurry Feed	5-19-98	935	Lime + ash sluice water
4 – Lime Slurry Feed	5-21-98	935	Lime + ash sluice water
5 – Lime Slurry Feed	5-22-98	848/1630	Lime + ash sluice water
1 – Fly Ash Slurry Feed	5-18-98	1530	Fly ash + FGD pond return water
2 – Fly Ash Slurry Feed	5-19-98	825/1515	Fly ash + FGD pond return water
4 – Fly Ash Slurry Feed	5-21-98	813	Fly ash + FGD pond return water
5 – Fly Ash Slurry Feed	5-22-98	835/1640	Fly ash + FGD pond return water
1 – FGD Pond Return Water	5-18-98	1540	FGD Sludge pond water
2 – FGD Pond Return Water	5-19-98	940/1540	FGD Sludge pond water
3 – FGD Pond Return Water	5-21-98	930	FGD Sludge pond water
4 – FGD Pond Return Water	5-22-98	845/1649	FGD Sludge pond water
1 – FGD Slurry B	5-18-98	1401	Reacted FGD slurry
2 – FGD Slurry B	5-19-98	1104/1635	Reacted FGD slurry
5 – FGD Slurry A	5-22-98	1030/1336	Reacted FGD slurry

2.3 Process Operation During Testing

Tables 2-8 and 2-9 summarize the process operating conditions and gas emissions during the mercury speciation test program. As in Table 2-7 shows, operation of Unit 2 during this test program was representative of normal daily operation at or near full load and there was little variation in the 5 days of the test program. SO₂ and particulate emissions were in compliance, with no ESP operating problems identified.

TABLE 2-8
Average Milton R. Young Unit 2 Operating Conditions Summary

Date	Total Gross Load, MW	Total Coal Flow, klb/hr	Total Gas Flow at the Stack, scfm	Main Steam Flow, klb/hr	Superheat Outlet Temp., °F	Reheat Outlet Temp., °F	Boiler Drum Pressure, psig	Air		Stack Temp., °F
								Heater Inlet Temp., °F	Boiler Exit Gas Temp., °F	
5-18-98	453.6	705.5	1,567,656	3037.9	1001.0	997.2	2662.4	822.5	355.0	204.0
5-19-98	448.3	702.5	1,582,153	3005.6	994.1	988.3	2629.5	825.4	357.5	226.1
5-20-98	461.2	705.2	1,542,167	3069.7	995.0	992.8	2670.9	841.3	360.4	210.9
5-21-98	448.3	663.6	1,493,445	2992.7	1001.1	995.8	2620.9	838.8	361.3	242.1
5-22-98	447.5	658.4	1,524,750	2994.5	999.9	992.3	2621.2	841.3	364.0	254.7

TABLE 2-9
Average Milton R. Young Unit 2 Flue Gas Emissions

Date	Boiler	Stack	Stack	Scrubber A	Scrubber B	Stack SO ₂	SO ₂	SO ₂ *
	O ₂ , %	CO ₂ , %	NO _x , ppm	Inlet SO ₂ , ppm	Inlet SO ₂ , ppm	Emissions, ppm	Collection Efficiency, %	Emission Rate, lb/MMBtu
5-18-98	4.3	11.1	496.2	626.5	----	303.8	51.5	0.83
5-19-98	4.2	11.2	455.6	612.7	----	346.6	43.4	0.94
5-20-98	4.1	11.2	485.7	608.2	----	303.5	50.1	0.83
5-21-98	4.1	11.3	481.7	----	581.6	348.2	40.1	0.94
5-22-98	4.2	11.4	499.2	----	555.4	388.9	29.8	1.04

* The plant is required to meet a SO₂ emission rate of 1.2 lb/MMBtu.

The target excess O₂ at the boiler exit was to be 4.1% ± 0.5%. As Table 2-8 shows, the unit easily fell within this range. The average excess O₂ for the entire 5-day sampling period was 4.2% ± 0.1%. The average O₂ levels and moisture content at each of the flue gas sampling points are shown in Table 2-10. It should be noted that because of the confusion of changing scrubber modules, the excess O₂ concentrations at all points other than the boiler were taken several days after the test was completed. However, on the basis of the excess O₂ at the boiler exit, which was still 4.2%, the O₂ measurement should be representative of the O₂ during actual sampling. On the basis of the O₂ data, the most substantial leak is across the air preheater.

TABLE 2-10
Average Excess Oxygen and Moisture Content at Mercury Speciation Sampling Points

Sample Location	Excess O ₂ (on a dry basis), %	Moisture Content, %
Boiler	4.2	13.8
Air Preheater Inlet	4.8	14.0
ESP Inlet	6.1	13.9
ESP Outlet/FGD Inlet	6.4	14.3
FGD Outlet	6.1	18.9
Stack	6.2	17.3

3.0 FLUE GAS SAMPLING AND ANALYTICAL METHODS

This section describes the methods and analytical procedures that were used for this test program to determine the mercury speciation and chlorides in the flue gas, as well as the total mercury in the solid and liquid streams of the plant. The details of all the EPA sampling procedures discussed in the section (EPA Methods 1–4, 5, 17, 29, and 26A) can be found on the EPA's Emission Measurement Center Web Site at the address <http://www.epa.gov/tnn/emc>.

One issue that has been extensively discussed with respect to mercury speciation methods is the temperature at which the particulate filter should be maintained. On the basis of current procedures, the requirement is that the filter and sample probe be maintained at the flue gas temperature. For most of the flue gas sampling points, the exception being the inlet to the air preheater, an EPA Method 17 in-stack borosilicate glass filter was used. This ensured that the filter and probe were maintained at the flue gas temperature. An out-of-state filter was used for the air preheater inlet sample.

All components of the sample train were composed of either glass or Teflon. The length of the probes at each of the flue gas sample points is shown in Table 3-1.

3.1 Ontario Hydro Mercury Speciation Method

The Ontario Hydro method was developed by Keith Curtis and other researchers at Ontario Hydro Technologies in late 1994. Since testing with EPA Method 29 appeared to show that some of the Hg^0 was captured in the nitric acid–hydrogen peroxide ($\text{HNO}_3\text{--H}_2\text{O}_2$) impingers, an attempt was made to more selectively capture the oxidized mercury (Hg^{2+}) by substituting three aqueous 1N potassium chloride (KCl) impinger solutions for one of the $\text{HNO}_3\text{--H}_2\text{O}_2$ solutions. A schematic of the impinger train is shown in Figure 3-1. The Ontario Hydro method has been

TABLE 3-1
Probe Length at Each Sample Point

Sample Point	Probe Length, ft
Air Preheater	6
ESP Inlet	13
ESP Outlet	9
FGD Outlet	9
Stack*	11

* Stack diameter at the sampling point was 24.1 ft.

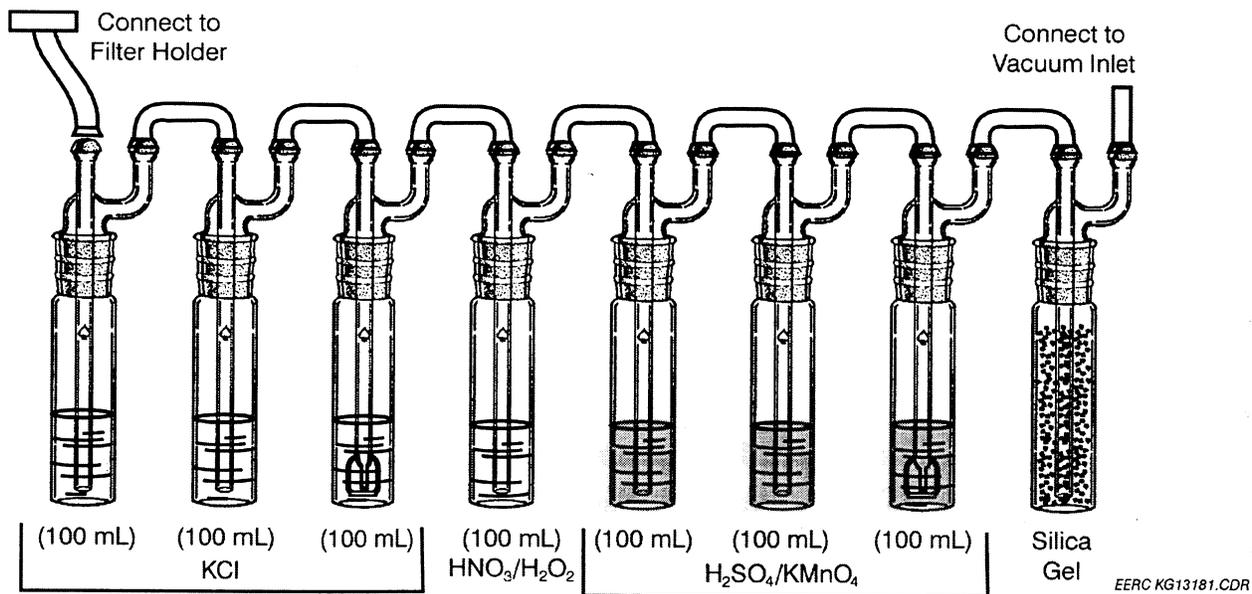


Figure 3-1. A schematic of the Ontario Hydro impinger train.

extensively tested at the EERC and has been shown to provide the best mercury speciation data for coal-fired boilers (3, 4). The method is currently being evaluated by the American Society for Testing and Materials (ASTM) Subcommittee D22.03.01.

All glassware for the sample trains was precleaned with using a 4-hr soak in a 10% HNO_3 solution, with no impinger glassware used more than once in the field test. Samples collected using the Ontario Hydro method were recovered into the following fractions:

- Probe ash and particulate filter and ash – Container No. 1
- Probe rinse with 0.1 N HNO_3 solution – Container No. 2A
- Back half of the filter holder and connecting U-tubes 0.1 N HNO_3 rinses plus the three KCl impinger solution and their 0.1 N HNO_3 rinses – Container No. 2B
- The HNO_3 - H_2O_2 solution and its 0.1 N HNO_3 rinse and the rinse of the U-tube between the last KCl impinger and H_2O_2 – Container No. 3
- H_2SO_4 - KMnO_4 impinger and rinses (0.1 N HNO_3 rinses and 8 N HCl rinses) and the rinse of the U-tubes rinses – Container No. 4

Figure 3-2 shows a schematic of the impinger train teardown procedures.

The solutions were analyzed on-site using a Leeman CVAA instrument. The particulate fraction was taken back to the EERC. After an HCl/HF microwave digestion procedure was used, the filter samples analysed were then analysed using a CVAA.

For the liquid samples, the preparation steps prior to analyses using CVAA is different for each of the three types of solutions. The preparation steps for each solution are described below:

KCl Solution. The KCl sample fractions are immediately preserved with acidified KmnO_4 after sampling. This solution is then digested using a potassium persulfate digest procedure.

$\text{HNO}_3\text{-H}_2\text{O}_2$ Solution. The solution is first preserved with 10% HCl, then combined with $\text{H}_2\text{SO}_4\text{-KMnO}_4$ solution until a purple color persists. At this point, hydroxylamine sulfate is added until the solution becomes clear.

$\text{H}_2\text{SO}_4\text{-KMnO}_4$ Solution. Hydroxylamine sulfate is added to the $\text{KMnO}_4\text{-H}_2\text{SO}_4$ sample until the solution turns clear.

1. Rinse filter holder and connector with 0.1N HNO_3 .
2. Add $\text{H}_2\text{SO}_4/\text{KMnO}_4$ to each impinger bottle until purple color remains.
3. Rinse with 0.1N HNO_3 .
4. Rinse with 8N HCl if brown residue remains.
5. Final rinse with 0.1N HNO_3 .

Rinse Bottles Sparingly with

- 0.1N HNO_3
- 8N HCl
- 0.1N HNO_3

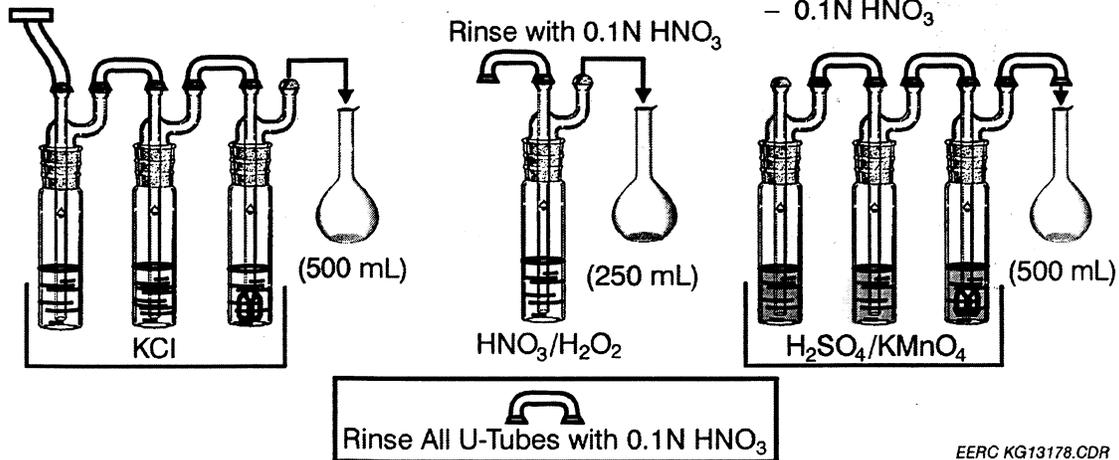


Figure 3-2. A schematic of the impinger train teardown procedures.

For the Ontario Hydro method, the KCl fraction results are reported as Hg^{2+} , and the sum of the mercury measured in the $\text{HNO}_3\text{-H}_2\text{O}_2$ solution and $\text{H}_2\text{SO}_4\text{-KMnO}_4$ solution is reported as Hg^0 . The mercury measured on the filter ash is defined as particulate-bound mercury. The exact form of the mercury on the particulate matter is still unknown. For these tests, since EPA Method 17 was followed (filter holder is placed in the duct) the mercury found in the probe rinse was insignificant.

3.2 EPA Method 26A

To measure concentration of chlorides in the flue gas, EPA Method 26A was used. A schematic of the train is shown in Figure 3-3. This method was designed to measure both the HCl and Cl_2 concentrations in the flue gas. During the sampling, the separation of the halides (HCl) from the halogens (Cl_2) is accomplished physically within the impinger matrices. Cl_2 exhibits a low solubility in acid solutions (0.1 N H_2SO_4), but is collected effectively in basic solutions (0.1 N NaOH). The HCl, on the other hand, is captured effectively by the 0.1 N H_2SO_4 solution. The impinger train is operated similarly to other sampling procedures such as EPA Method 5 or EPA Method 29.

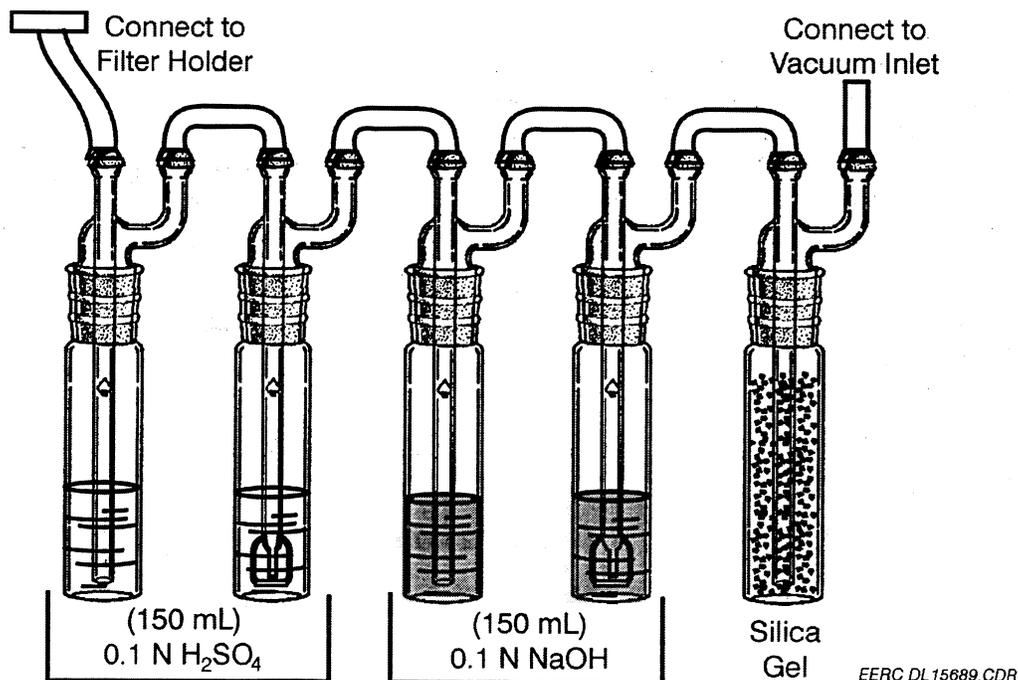


Figure 3-3. A schematic of the EPA Method 26A impinger train that was used for chloride measurement.

Once the chlorides were collected in the solutions, they were analyzed using ion chromatography techniques. Prior to analysis, the 0.1 N H₂SO₄ solution was passed through an ion-exchange resin to convert any chloride salts back to the acid and also to remove any calcium or iron that might have been captured in the solution, as these may cause scaling in the chromatography column. Preparation of the 0.1 N NaOH solution was done by adding sodium thiosulfate to the solution to reduce any hypohaleous acid that might form.

3.3 Semtech Hg 2000 Analyzer

A Semtech Hg 2000 mercury CEM manufactured by Semtech Metallurgy AB, Lund, Sweden, was used at the stack location. The instrument measures Hg⁰ on a real-time basis using a Zeeman-shifted ultraviolet sensor. The Zeeman shift detection technology eliminates interference from SO₂ absorption. Because the instrument is designed to measure only Hg⁰, to get total mercury the other forms of mercury (Hg²⁺) must be converted to Hg⁰. This is done by passing the flue gas through a stannous chloride solution prior to its entering the CEM. The operating range of the instrument is 0.3 µg/Nm³ to 20 mg/Nm³. The Semtech Hg 2000 has been certified by TUEV Rheinland for determining compliance with the German legal limit of 50 µg/Nm³ for total mercury from waste incinerators.

3.4 Oxygen Concentration, Flue Gas Velocity, and Moisture

To determine the O₂ levels at each sample location, a Teledyne portable O₂ analyzer using a paramagnetic cell was used. This portable O₂ analyzer's linearity was verified prior to us using EPA Protocol 1 certified gas standards. In addition, the plant has O₂ CEMs that give the O₂ concentration at the outlet of the boiler. Therefore, any leaks into the ducts at each of the sample points could be determined. For the purposes of this report, the mercury concentrations are reported on a constant-O₂ basis (3% O₂).

Flue gas velocity, moisture, and flow rate determinations were performed according to EPA Methods 2 and 4 in conjunction with the Ontario Hydro method.

3.5 Quality Assurance/Quality Control

An overall QA/QC program in place at the EERC is designed to maintain overall data integrity. However, additional procedures were instituted specifically for this project.

3.5.1 Instrument Setup and Calibration

The instrument used in the field for mercury determination was a Leeman Labs PS200 CVAA. To measure mercury, the instrument was set up for absorption at 253.7 nm with a carrier gas of nitrogen and 10% ^{w/v} stannous chloride in 10% ^{v/v} HCl as the reductant. Each day the drying tube and acetate trap were replaced and the tubing checked. The rinse container was cleaned and filled with fresh solution of 10% ^{v/v} HCl. After the pump and lamp were turned on and warmed up for 45 minutes, the aperture was set to the manufacturer specifications. A four-point calibration curve was then completed using matrix-matched standards. The detector response for a given standard was logged and compared to specifications to ensure the instrument had been properly set up. A quality control standard of a known analyte concentration was analyzed immediately after the instrument was standardized in order to verify the calibration. This quality control standard was prepared from a different stock than the calibration standards. It was required the values obtained read within 5% of the true value before the instrument was used. After the initial QC standardizations were completed, standards were run every five samples to check the slope of the calibration curve. All samples were run in duplicate, and one in every ten samples was spiked to verify analyte recovery. A QC chart is maintained at the EERC to monitor the long-term precision of the instrument.

Prior to the testing, all gas-sampling equipment was calibrated according to the *Quality Assurance Handbook for Air Pollution Measurement Systems: Volume III. Stationary Source Specific Methods*. The uncertainty of the individual measurements was determined using the performance test codes in ANSI/ASME PTC 19.1-1985, Part 1, Measurement Uncertainty, as a guideline.

3.5.2 Presampling Preparation

All data sheets, volumetric flasks, and petri dishes used for sample recovery were marked with preprinted labels. The liquid samples were recovered into premarked volumetric flasks and logged, then analyzed on-site. The filter samples were placed in premarked petri dishes and taken back to the EERC, where they were analyzed using mixed acid digestion techniques. The labels contained identifying data, including date, time, run number, sample port location, and the name of the sampler.

3.5.3 Glassware and Plasticware Cleaning and Storage

All glass volumetric flasks and transfer pipets used in the preparation of analytical reagents and calibration standards were designated Class A to meet federal specifications. Prior to being used for the sampling, all glassware was washed with hot, soapy water, then rinsed with deionized water three times, soaked in 10% V/V nitric acid for a minimum of 4 hours, rinsed an additional three times with deionized water, and dried. The glassware was then stored in closed containers until it was used at the plant.

3.5.4 Analytical Reagents

All acids that were used for the analysis of mercury were trace-metal-grade. Other chemicals that were used in the preparation of analytical reagents were analytical-reagent-grade. The calibration standards used for instrument calibration and the QC standards used for calibration verification were purchased commercially and certified to be accurate within $\pm 0.5\%$ and were traceable to NIST Standard Reference Materials.

3.5.5 Blanks

As part of the QA/QC procedures, a field blank was associated with sampling. A field blank is defined as a complete impinger train including all glassware and solutions that is taken out to the field during sampling and exposed to ambient conditions. These sample trains are then taken apart and the solutions recovered and analyzed in the same manner as those sample trains used for sampling activities. If the field blank shows contamination above instrument background, steps must be taken to eliminate or reduce the contamination to below background levels. However, in all cases the fields blanks taken during the sampling activities at the Milton R. Young Station were shown to be insignificant, as shown in Table 3-2.

TABLE 3-2
Results of Mercury Speciation Field Blanks

Day	KCl Solution, $\mu\text{g/L}$	H_2O_2 Solution, $\mu\text{g/L}$	KMnO_4 Solution, $\mu\text{g/L}$
2	<0.1	<0.1	<0.1
5	<0.1	<0.1	<0.1

All acids, chemical reagents, and deionized water used for mercury determination were analyzed for background levels of mercury. Each time a new batch of reagents was prepared an aliquot was immediately taken and analyzed for mercury. Again, no mercury contamination was found.

3.5.6 Spiked Samples

In order to ensure that adequate levels of accuracy were maintained, spiked samples were also submitted for analysis. These samples were made up independently of the chemist doing the analyses. The spikes were required to be within 20% of the true value. The spiking solutions were from a stock separate from the calibration standard stock. The analytical results for the spiked samples are shown in Table 3-3. Often the H₂O₂ solution has a spike recovery that is

TABLE 3-3
Results of Mercury Speciation Field Spikes

Date	<u>KCl Solution</u>			<u>H₂O₂ Solution</u>			<u>KMnO₄ Solution</u>		
	Measured Value, ppb	Spike, ppb	Spike Recovery, %	Measured Value, ppb	Spike, ppb	Spike Recovery, %	Measured Value, ppb	Spike, ppb	Spike Recovery, %
5-18-98	5.34	5	106.8	8.16	10	81.6	5.58	5	111.6
5-18-98	10.05	10	100.5						
5-19-98	19.47	20	97.4	8.30	10	83.0	4.59	5	91.8
5-21-98	5.55	5	111.0	4.25	5	85.0	4.42	5	88.4
5-21-98	10.68	10	106.8	4.22	5	84.4	19.00	20	95.0
5-21-98	20.02	20	100.1	15.23	20	76.2			
5-22-98	5.28	5	105.6	8.74	10	87.4	5.08	5	101.6
5-22-98	10.21	10	102.1	16.1	20	80.5	15.9	20	79.5
5-22-98				8.2	10	82.0			
5-22-98				15.22	20	76.1			
5-23-98	5.95	5	119.0	8.54	10	85.4	3.9	5	78.0
5-23-98	10.44	10	104.4	8.61	10	86.1	8.47	10	84.7
5-23-98	10.54	10	105.4	8.70	10	87.0			
5-23-98				17.15	20	85.8			
Average			105.4			83.1			91.3
Std. dev.			5.9			3.7			11.3

somewhat low. However, the H₂O₂ solution impinger is only used to protect the KMnO₄ from the SO₂ in the flue gas steam. The mercury capture in the H₂O₂ solution is very low and therefore, as long as the spike recovery is reasonable (within 30%), it is considered acceptable. As can be seen, the analyses of these spikes are within the tolerance specified.

4.0 MERCURY RESULTS

The mercury concentration for the solid and liquid samples collected during testing are shown in Tables 4-1 through 4-3.

Coal Mercury. The mercury analysis of the coal is shown in Table 4-1. The mercury averaged 91 ppb for the two coal samples taken during Condition A testing, but only 66 ppb for Condition B. Based on the flue gas mercury analysis discussed in Section 4.1 and mercury balances discussed in Section 4.4, the mercury concentration in the coal should have been about the same for Condition A and Condition B. Why this is not the case is unknown. Most likely this difference was because the coal samples taken during Condition B were not representative of the coal being fed that day.

The mercury concentration was also measured in the pyrite catch. Although the concentration of mercury in this material was more than an order of magnitude higher than in the coal, 2.7 µg/g compared to less than 0.1 µg/g for the coal, the amount of material collected as pyrite is very low. Therefore, the total amount of mercury removed in the pyrite catch is insignificant.

TABLE 4-1
Mercury in the BNI Coal

Condition	Coal Hg Concentration,
	ppb
A	96
A	86
B	74
B	57

ESP Ash and Sample Filter Mercury. The mercury collected on the filter of the sample trains at the ESP inlet is shown in Table 4-2. The average mercury concentration on the ash collected from the ESP hopper at Condition A and Condition B is 96 ppb and 101 ppb, respectively (based on four samples at each condition). These results compare very well, given that the collection processes are very different and there has been no attempt made to apportion the mercury based on the percentage ash collected at each field. It should be noted that the mercury on the filters was negligible at all other sampling locations because the particulate removal efficiency of the ESP was very high, > 99.5%.

FGD Slurry Mercury. An FGD slurry can either be a reacted or unreacted slurry. The unreacted slurry is made up of the fresh sorbent, fly ash for Condition A and lime for Condition B, and water that comes from the FGD pond return or bottom ash sluice system. The reacted slurry is the sorbent and water after being in contact with the SO₂-containing flue gas. At the Milton R. Young Station, the reacted slurry is recycled to the FGD system, with periodic blowdown to maintain the suspended solids level. The mercury concentration in the slurry was determined by the concentration of mercury in solids and the mercury concentration in the water. The mercury concentration of the blowdown was assumed to be the same as the mercury concentration in the recycled reacted slurry. The concentration of mercury in each fraction of the FGD slurries is shown in Table 4-3.

TABLE 4-2
Mercury Collected on the Filters of the
Ontario Hydro Train at the Inlet to the ESP

Condition	Hg Concentration on Sample Filter, ppb
A	84
A	73
B	84
B	88
B	109

TABLE 4-3
Mercury Concentrations in the FGD Slurries

Condition	Unreacted Slurry		Reacted Slurry	
	Solid, µg/g	Liquid, µg/L	Solid, µg/g	Liquid, µg/L
A	0.131	<0.01	0.134	0.10
A	0.135	<0.01	0.124	0.16
B	<0.01	<0.01	0.087	3.89
B	<0.01	<0.01	0.154	4.50

The mercury concentration was also determined in the FGD sludge pond and the bottom ash sluice system water because these are the two sources of water that make up the unreacted slurries. The fly ash slurry used the bottom ash sluice water, and the lime slurry used FGD pond return water. The mercury concentration for the bottom ash sluice water was <0.1 µg/L and the average of four samples for the FGD pond return water was 0.11 µg/L.

4.1 Mercury Speciation Results

This section presents the flue gas mercury speciation results across the ESP and FGD systems. The mercury speciation results are shown in Table 4-4. The table only shows the particulate-bound mercury for the ESP inlet results because it was less than the detection limit at all the other sample points. All data are based on 68°F, dry conditions and are adjusted to 3% oxygen. Figures 4-1 and 4-2 show the mercury removal across the ESP and FGD systems. The original data sheets for the flue gas mercury are presented in Appendix A. Examples of the calculations used in this report are shown in Appendix B. All the mercury data were averaged, and a standard deviation was calculated at the ESP inlet and ESP outlet/FGD inlet. As can be seen from the tables, there was less than 10% variability in the data at these two locations. Therefore, process conditions of the plant were relatively constant and had little effect on mercury measurements. At the FDG outlet, tests were made at two different conditions, as a fly-ash-only scrubber (Condition A) or as a lime-only scrubber (Condition B). The results shown in the tables and figures for the FDG outlet and stack are presented as a function of the test condition.

Comparing the ESP inlet and outlet mercury concentrations (shown in Table 4-4 and Figure 4-1) it appears that little, if any, mercury is removed across the ESP. However, based on

TABLE 4-4
Mercury Speciation Results Across the ESP and FGD Systems

	ESP Inlet				ESP Outlet		
	Total Hg, $\mu\text{g}/\text{Nm}^3$	Particulate- Bound Hg, $\mu\text{g}/\text{Nm}^3$	Hg^0 , $\mu\text{g}/\text{Nm}^3$	Hg^{2+} , $\mu\text{g}/\text{Nm}^3$	Total Hg, $\mu\text{g}/\text{Nm}^3$	Hg^0 , $\mu\text{g}/\text{Nm}^3$	Hg^{2+} , $\mu\text{g}/\text{Nm}^3$
	9.72	0.43	8.76	0.52	10.08	9.39	0.68
	10.13	0.40	9.20	0.53	10.88	8.73	2.15
	8.82	0.43	8.18	0.19	9.83	8.95	0.87
	10.50	0.52	8.92	1.06	9.26	8.15	1.11
	10.69	0.68	9.50	0.51	10.17	8.84	1.33
Average	9.97	0.49	8.91	0.56	10.04	8.81	1.23
Std. Dev.	0.75	0.11	0.50	0.31	0.59	0.45	0.57

	FGD Inlet			FGD Outlet			Stack		
	Total Hg, $\mu\text{g}/\text{Nm}^3$	Hg^0 , $\mu\text{g}/\text{Nm}^3$	Hg^{2+} , $\mu\text{g}/\text{Nm}^3$	Total Hg, $\mu\text{g}/\text{Nm}^3$	Hg^0 , $\mu\text{g}/\text{Nm}^3$	Hg^{2+} , $\mu\text{g}/\text{Nm}^3$	Total Hg, $\mu\text{g}/\text{Nm}^3$	Hg^0 , $\mu\text{g}/\text{Nm}^3$	Hg^{2+} , $\mu\text{g}/\text{Nm}^3$
Condition A	10.08	9.39	0.68	8.41	8.16	0.24	10.65	9.56	1.07
	10.88	8.73	2.15	8.86	8.48	0.39	10.64	9.55	1.08
Average	10.48	9.06	1.42	8.64	8.32	0.31	10.64	9.56	1.08
Std. Dev.	0.57	0.47	1.04	0.32	0.22	0.11	0.01	0.01	0.01
Condition B	9.83	8.95	0.87	7.05	6.91	0.12	8.22	7.45	0.76
	9.26	8.15	1.11	8.08	8.01	0.08	10.16	8.97	1.22
	10.17	8.84	1.33	8.29	8.12	0.16	9.29	8.30	0.98
Average	9.75	8.65	1.10	7.81	7.68	0.12	9.22	8.24	0.99
Std. Dev.	0.46	0.44	0.23	0.67	0.67	0.04	0.97	0.76	0.23

the mercury measured in the fly ash collected in the ESP hoppers, about 5% of the total mercury was removed by the ESP. As discussed later in this report, the mercury balance across the ESP is still >80%. In addition, there may be some conversion of Hg^0 to Hg^{2+} across the ESP. (Note, however, statistically it may be insignificant). Although the concentration of Hg^{2+} is low at both locations, there is approximately twice as much Hg^{2+} at the outlet compared to the inlet ($0.56 \mu\text{g}/\text{Nm}^3$ compared to $1.23 \mu\text{g}/\text{Nm}^3$). Evidence has been presented in the literature showing some conversion of mercury species can occur across an ESP (5).

The effects of the two different FGD conditions on mercury removal across the FGD are shown in Figure 4-2. The FGD is shown to effectively remove the Hg^{2+} , but little if any Hg^0 . This is in agreement with all the mercury data that have been collected in the last several years across wet FGD systems. Because the Hg^{2+} concentration in the flue gas stream is so low, it is very difficult to determine if any real difference exists between the two conditions under which

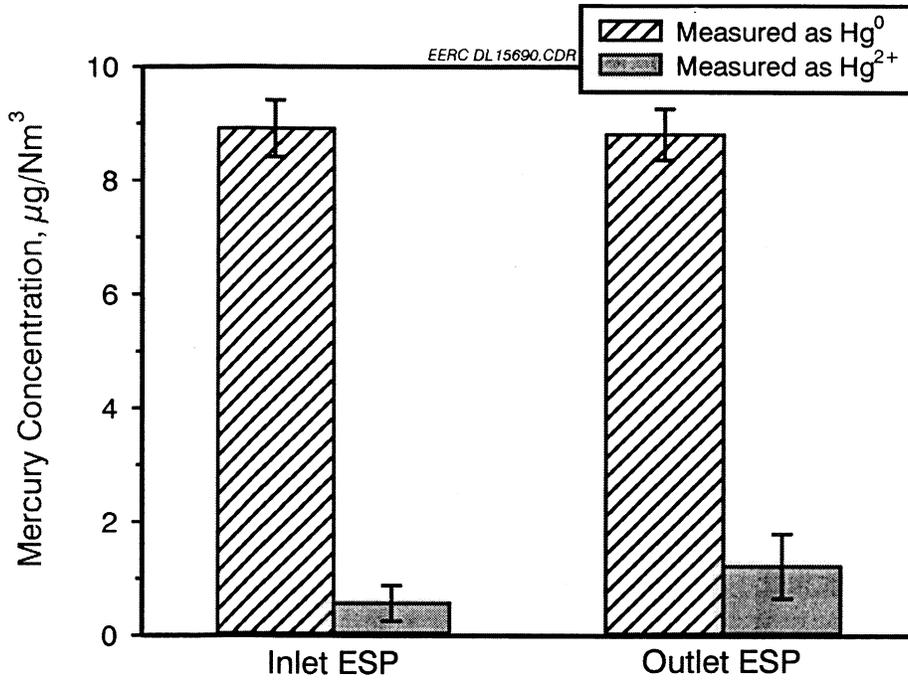


Figure 4-1. The change in vapor-phase speciated mercury removal across the ESP.

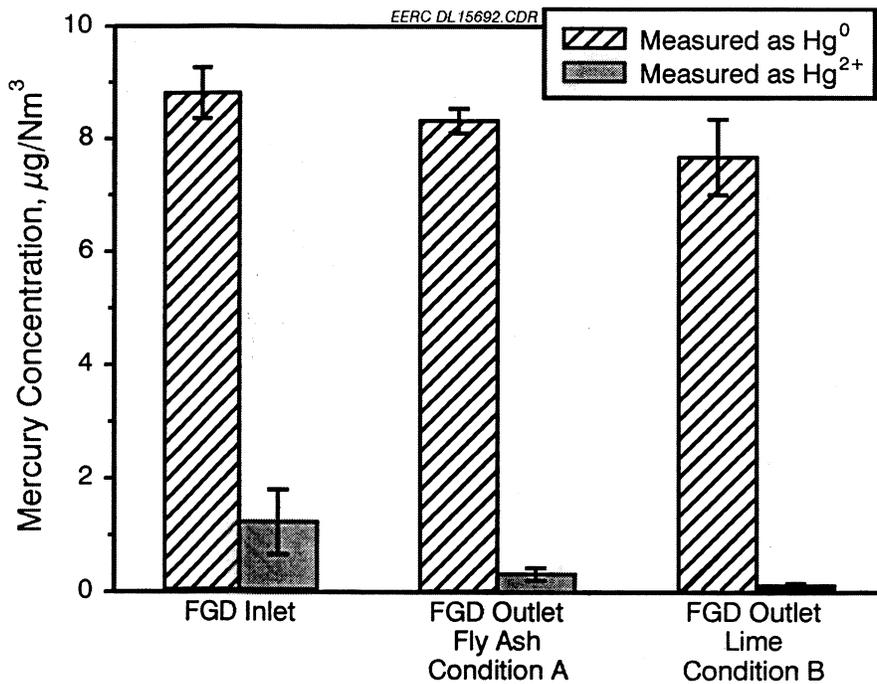


Figure 4-2. The change in vapor-phase speciated mercury across the FGD system at two conditions.

the FGD system was operated. The Hg^{2+} concentrations were slightly lower following the FGD when lime was used as a scrubbing medium compared to fly ash. However, the difference may also be explained by variability in the data.

The speciation of the mercury emission at the stack of Unit 2 is shown in Figure 4-3. Within the variability of the data (as shown by the error bars) there is no difference between data collected for Condition A (fly ash FGD) and Condition B (lime FGD). Because a high percentage of the flue gas bypassed the FGD system, it would take a very substantial difference between the two conditions to express itself at the stack.

Two Ontario Hydro method samples were completed at the inlet to the air preheater. The temperature at this location was about 800°F . The purpose of these samples was to determine if the Hg^{2+} was present in the flue gas these temperatures. As expected, 99% of the mercury captured at this location was measured as Hg^0 . The data are shown in Appendix A.

Because it is thought the level of chlorides in the flue gas stream may influence mercury speciation, four EPA Method 26A sample trains were completed at the inlet to the FGD system. This sample method was designed to measure both the HCl concentration in the gas stream and the Cl_2 . In practice, the method does not work very well as a chloride speciation measurement

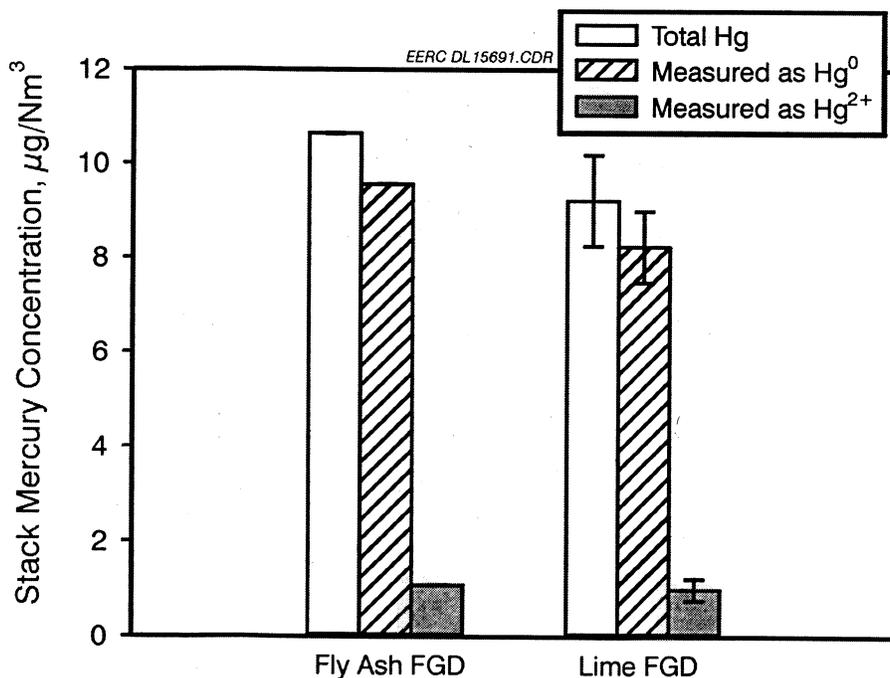


Figure 4-3. Mercury speciation emission measurements at the stack of Unit 2.

method, but does provide a good measurement of the total chloride concentration in the flue gas. The EPA Method 26A results are shown in Table 4-5. As shown, the chloride concentration is very low. This is typical of all western fuels (both lignites and subbituminous). For these fuels, the chloride concentration is usually less than 5 ppm.

4.2 Semtech Hg 2000 CEM Results

The Semtech CEM was used only at the stack. Although the instrument was developed to only measure Hg^0 , using a conversion system designed at the EERC the instrument was able to measure total mercury. For this project, it was originally intended that the Semtech CEM would provide mercury speciation data. This was to be accomplished by bypassing the conversion system periodically to measure Hg^0 and by difference determining the concentration of Hg^{2+} in the flue gas. However, because of the high moisture content of the flue gas, the instrument would not operate properly without first passing through the conversion system where a chiller removed the moisture. All the results from the Semtech are shown graphically in Figure 4-4. As shown, it took some time before the total concentration at the stack leveled out after we were forced to move to the other scrubber module.

A direct comparison between the CEM data and the Ontario Hydro method data was made during the last day of testing (Condition B). These data are shown in Figure 4-5. The results are shown to be reasonably comparable.

TABLE 4-5
Chloride Concentrations in the Flue Gas at the FGD Inlet

Condition	HCl Concentration, ppm	Cl ₂ Concentration, ppm
A	1.15	ND*
A	1.26	ND
B	1.74	ND
B	1.45	ND

* Not detected or below detection limits.

4.3 Emission Factors

The emission factors at the stack of Unit 2 are shown in Table 4-6. The emission factors for both test conditions averaged $8.7 \text{ lb Hg}/10^{12} \text{ Btu}$ with a standard deviation of $0.81 \text{ lb Hg}/10^{12} \text{ Btu}$. About 90% of the total mercury emissions at the stack was Hg^0 , and 10% was Hg^{2+} . The particulate-bound mercury was insignificant (less than the detection limits). It is possible that there were slightly lower mercury emissions when the lime scrubber was used (Condition B). However, the results are within the data variability. Based on the results reported for in the *Comprehensive Assessment of Toxic Emissions from Coal-Fired Power Plants* (6) these emission factors are fairly typical for coal-fired boilers. The results from this study showed that the emission factors for mercury ranged from 2 to $22 \text{ lb Hg}/10^{12} \text{ Btu}$. The one plant tested that fired a North Dakota lignite averaged about $9 \text{ lb Hg}/10^{12} \text{ Btu}$ (Coal Creek).

4.4 Mercury Balance

The mercury balance is determined by comparing the rate of mercury entering plant to the rate of mercury leaving the plant. The various sources resulting in mercury entering Unit 2 and

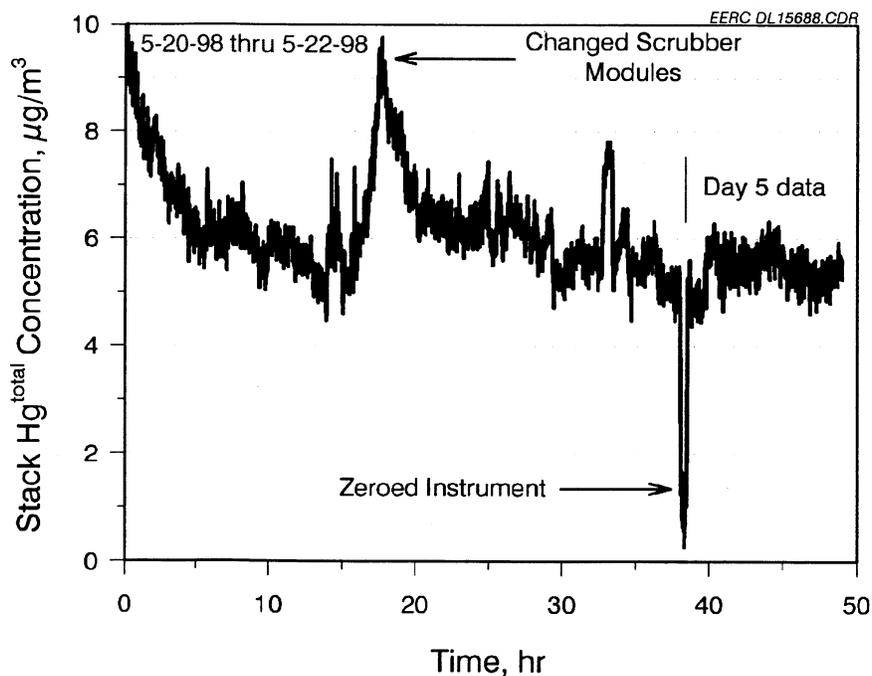


Figure 4-4. Total mercury measurements at the stack using the Semtech Hg 2000 CEM (data are shown as measured in the stack)

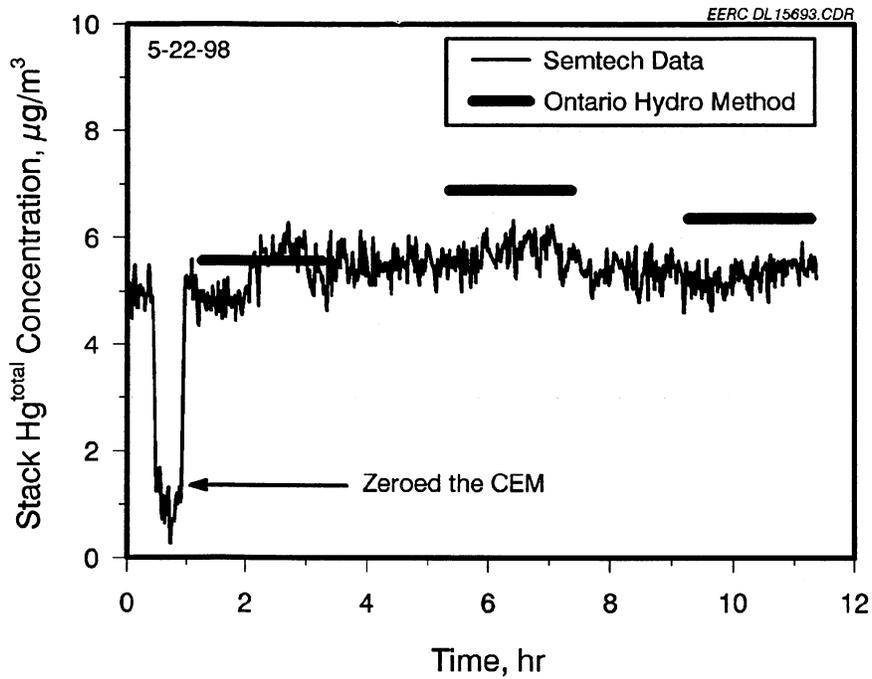


Figure 4-5. Direct comparison between Semtech mercury CEM and the Ontario Hydro method for Day 5 (data are shown as measured in the stack).

TABLE 4-6
 Emission Factors for Mercury at Unit 2 Stack

Coal Feed Rate, klb/hr	Coal Heating Value,* Btu/lb	Stack Gas Flow Rate, scfm	Emission Factors		
			Hg ²⁺ , lb/10 ¹² Btu	Hg ⁰ , lb/10 ¹² Btu	Total Hg, lb/10 ¹² Btu
Condition A					
700.4	6460	1,593,517	0.88	8.42	9.31
701.7	6460	1,586,133	0.93	8.41	9.34
Condition B					
661.1	6460	1,522,067	0.67	6.78	7.44
662.9	6460	1,522,900	1.08	8.06	9.14
660.9	6460	1,521,317	0.87	7.59	8.45

* Based on as-received value.

those resulting in mercury leaving Unit 2 are shown in Table 4-7. In general, the plant recycles 100% of the fly ash from both Units 1 and 2. Because it is being recycled, the fly ash was not considered a source of mercury for purposes of the mercury balance for Condition A. However, during Condition B testing, Unit 2 was operating using only lime. Therefore, the rate of mercury leaving the ESP with the fly ash had to be considered in calculating a mercury balance. All the mercury balance data are expressed in units of lb/min. To express the data on the same basis, all flue gas flow rates were calculated on a moisture-free and 3% oxygen basis. The fuel feed rate was calculated on a dry basis.

The rate of mercury entering the plant with the coal is shown in Table 4-8. As stated earlier in the report, the mercury concentration for the two coal samples taken during Condition B testing were considerably lower than those obtained earlier, which as explained later in the report, skews the mercury balance.

To calculate the rate of mercury leaving with the ESP ash, the ash removal rate had to first be measured. The ESP inlet and outlet dust loading are shown in Table 2-1. Knowing the flue gas flow rate, the ash removal rate for the ESP was 358.1 lb/min for Condition A and 325.9 lb/min for Condition B. As stated earlier, the mercury concentration in the fly ash was 96 ppb and 101 ppb for Condition A and B, respectively. This results in mercury removal rate of 0.34×10^{-4} lb/min mercury for Condition A and 0.33 lb/min mercury for Condition B.

Knowing the flow rates of the slurries and the mercury concentration in each of the solutions (shown in Table 4-3) allowed the rate of mercury removal from the flue gas stream by the FGD system to be calculated. The rate of mercury leaving with the scrubber blowdown was difficult to accurately calculate. The blowdown is controlled by suspended solids. The actual flow rate was not directly measured because it was not continuous and occurred several times during a day. Therefore, several assumptions were made to estimate the rate of scrubber blowdown. These included the average volume of FGD liquor expelled and the number of times during the day in which this occurred. On the basis of discussion with plant personnel, it was calculated that the scrubber blowdown was 260 gal/min during Condition A and 150 gal/min during Condition B. Also, the flow rate of the unreacted slurries was assumed to be at steady state and therefore these flow rates were the same as the blowdown rate. The flow rate of mercury in the FGD slurries is shown in Table 4-9.

TABLE 4-7
Sources of Mercury for Determining the Mercury Balance

Source of Mercury to the Plant	Source of Mercury Exiting the Plant
Coal	Stack Gas
Lime (Condition B only)	Fly Ash (Condition B only)
Makeup Water	Scrubber Blowdown

TABLE 4-8
Coal Mercury

Condition	Coal Feed Rate*, lb/min	Coal Hg Concentration, ppb	Mercury Generated by the Coal, lb/min
A	7319	96	7.0×10^{-4}
A	7333	86	6.3×10^{-4}
B	6908	74	5.1×10^{-4}
B	6927	57	4.0×10^{-4}

* Calculated on a dry basis (37.3% water).

TABLE 4-9
Mercury Flow Rate in FGD Slurries

Condition	<u>Unreacted Slurry</u>		<u>Reacted Slurry</u>	
	Solid, lb/min	Liquid, lb/min	Solid, lb/min	Liquid, lb/min
A	0.95×10^{-4}	$<0.002 \times 10^{-4}$	0.60×10^{-4}	0.002×10^{-4}
A	0.94×10^{-4}	$<0.002 \times 10^{-4}$	0.71×10^{-4}	0.003×10^{-4}
B	$<0.06 \times 10^{-4}$	$<0.002 \times 10^{-4}$	0.21×10^{-4}	0.049×10^{-4}
B	$<0.06 \times 10^{-4}$	$<0.002 \times 10^{-4}$	0.21×10^{-4}	0.056×10^{-4}

The mercury flow rates in the flue gas were determined using the measured mercury flue gas concentration shown in Table 4-10. The mercury flow rates at the ESP inlet, ESP outlet/FGD inlet, and at the stack were calculated directly from the measured mercury concentration. Because the only sampling ports at the FGD outlet were located prior to the bypassed flue gas being reintroduced to the system, it was necessary to know the percentage of the flue gas bypassing the FGD. Unfortunately, this was not directly measured at the plant. The bypass flow rate is a function of the need for flue gas reheat and the outlet SO₂ concentration required to be in compliance with EPA requirements. The bypass flow rate, however, can be calculated using an energy balance. Using this method, the calculated bypass was approximately 60% for Condition A and for Condition B 90%. It should be noted, however, that the enthalpy balance was very sensitive to the gas temperature and flue gas moisture content.

The inlet sources of mercury to the plant for Condition A were the coal and makeup water for the scrubber and ash sluice system. The mercury flow rate from the coal was 6.65×10^{-4} lb/min, and the total amount of mercury in the water used for makeup purposes was $<0.0004 \times 10^{-4}$. The mercury leaving the plant in the flue gas was 6.48×10^{-4} lb/min and in the FGD blowdown, 0.66×10^{-4} lb/min. Therefore, the total inlet mercury flow rate was 6.65×10^{-4} lb/min and the total outlet mercury rate was 6.85×10^{-4} lb/min, giving a total outlet/inlet mercury balance of 103.0%. Unfortunately, the balance was not nearly as good for Condition B because of the very low mercury value in the coal. The inlet mercury flow rate from the coal was measured as 4.55×10^{-4} lb/min. The added lime and makeup water together are less than 0.006×10^{-4} lb/min, giving a total of 4.61×10^{-4} .

TABLE 4-10
Mercury Flow Rate in Flue Gas Streams

Sample Location	Condition A Hg Flow Rate, lb/min	Condition B Hg Flow Rate, lb/min
ESP Inlet	6.63×10^{-4}	6.62×10^{-4}
ESP Outlet	6.96×10^{-4}	6.31×10^{-4}
FGD Inlet*	2.78×10^{-4}	0.63×10^{-4}
FGD Outlet*	2.30×10^{-4}	0.51×10^{-4}
Stack	6.48×10^{-4}	6.19×10^{-4}

* Calculated using a 60% bypass for Condition A and 90% bypass for Condition B.

The measured mercury leaving the plant was as follows:

- 6.19×10^{-4} lb/min with the flue gas
- 0.33×10^{-4} lb/min with the fly ash
- 0.21×10^{-4} lb/min with the blowdown solids
- 0.05×10^{-4} lb/min with the blowdown water

This gave a total mercury flow leaving the plant of 6.78×10^{-4} lb/min or an overall mercury balance (inlet/outlet) of 147.1%. However, if the coal measurement for Condition A was used the mercury balance was 102.0%. To get good representative coal mercury measurements (standard deviation <20%) at the crushers, it is necessary to analyze many more samples than we were able to take during this test. In general, ~95% (97% for Condition A and 93% for Condition B) of the mercury in the coal is emitted at the stack. This is due to the low concentration of Hg^{2+} and the high percentage of FGD bypass.

The mercury balances across the ESP and FGD systems are shown in Tables 4-11 and 4-12. With the exception of mercury balance for Condition B, which was based on the fuel analyses, all the mercury balances were very good (<±20%).

4.5 Mercury Stability in Fly Ash

It appears that once mercury is collected on the fly ash generated by firing the BNI lignite, it stays in place. This was true in the slurries collected at both the fly ash reaction tank and the

TABLE 4-11
Mercury Balance Across ESP

	Condition A	Condition B
Hg at the Inlet to ESP, 10^{-4} lb/min	6.64	6.63
Hg at the Outlet to ESP, 10^{-4} lb/min	6.96	6.31
Hg in the Hopper Ash, 10^{-4} lb/min	0.34	0.33
Outlet/Inlet Balance	109.9%	100.2%

TABLE 4-12
Mercury Balance Across FGD System

	Condition A	Condition B
Hg at the Inlet to FGD, 10 ⁻⁴ lb/min	2.78	0.63
Hg in the Fly Ash or Lime Slurry, 10 ⁻⁴ lb/min	0.94	0.06
Hg at the Outlet to FGD, 10 ⁻⁴ lb/min	2.30	0.51
Hg in Blowdown, 10 ⁻⁴ lb/min	0.67	0.26
Outlet/Inlet Balance	80.5%	111.6%

FGD module. The mercury concentration in the water from these slurries was very low. In the fly ash slurry tank, the slurry pH is high because of the high alkali concentration in North Dakota lignites. Yet the concentration of mercury measured in the water taken from the this tank was lower than the detection limit of the analyzer. Also, the concentration of mercury on the solid material collected from the fly ash slurry tank was similar to the concentration of mercury measured in the ESP hopper fly ash, 133 ppb compared to 99 ppb, respectively. The same results were observed in the blowdown water from the scrubber module. The scrubber blowdown slurry is acidic, with a pH of 4 to 6. In this slurry, the solids had a mercury concentration of 129 ppb. Although the mercury concentration was measurable in the blowdown slurry water, it was several orders of magnitude less than in the solid. This would indicate that for North Dakota lignites, mercury captured in the fly ash or scrubber sludge is very stable and more than likely would not be mobilized in a landfill situation.

5.0 CONCLUSIONS

On the basis of the results from the sampling program at the Milton R. Young Station, the following conclusions can be made:

- The mercury emitted at stack was about 10% Hg²⁺ and 90% Hg⁰.

- About 5% of the mercury was captured on the filter sample at the ESP inlet. This was very similar to the amount of mercury measured in the ESP hopper ash.
- It is possible that about 5% of the Hg^0 measured at the ESP inlet is converted to Hg^{2+} across the ESP.
- The FGD system, whether utilizing fly ash or lime as the sorbent, removes almost all the Hg^{2+} but little if any Hg^0 .
- At the high temperatures encountered at the inlet to the air preheater, all the mercury was measured as Hg^0 .
- The Semtech Hg 2000 gave total mercury results very comparable to those obtained using the Ontario Hydro mercury speciation sampling method.
- The mercury emission factor for Unit 2 was $8.74 \pm 0.81 \text{ lb}/10^{12} \text{ Btu}$.
- Approximately 95% of the mercury in the coal is emitted at the stack.
- The mercury balance across Unit 2 was near 100% when only two of the fuel analyses were used (Condition A). In general, getting representative fuel analyses for mercury is a difficult proposition. These results depend greatly on how representative the fuel mercury analysis is.
- Good mercury balances were obtained around the ESP and FGD systems for both test conditions.
- Mercury captured on the fly ash or scrubber sludge tended to stay there, even when mixed in highly basic or acidic solutions.
- The mercury levels in the ash sluice water and the ash pond water were very low, at or near the detection limits of the CVAA.
- The chloride concentration in the flue gas was very low as is the case with all western coals. It was measured at $< 2 \text{ ppm}$.

6.0 REFERENCES

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