Comprehensive Assessment of Air Toxics Emissions

DOE Contract No DE-AC22-93PC93254

FINAL REPORT

TESTS ON A COAL WASHING PLANT AND THE ASSOCIATED CYCLONE-FIRED UNIT EQUIPPED WITH A WET VENTURI SCRUBBER

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SOUTHERN RESEARCH INSTITUTE

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TESTS ON A COAL WASHING PLANT AND THE ASSOCIATED CYCLONE-FIRED UNIT EQUIPPED WITH A WET VENTURI SCRUBBER

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Submitted by

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Submitted to

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Comprehensive Assessment of Air Toxics Emissions: Tests on a Coal Washing Plant and the Associated Cylcone-Fired Unit Equipped with a Wet Venturi Scrubber

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ABSTRACT

Southern Research Institute (Southern) conducted a test program from October 24 to October 29, 1994, at the coal washing plant and Unit 1 of a coal-fired power plant in the southeastern United States. Three defining features of the plant were the on-site coal washing plant, cyclone burners, and the wet, limestone venturi scrubber for emissions control. Southern collected the samples required to measured concentrations of anions and trace elements (with special emphasis on mercury) in the coal washing plant, and around two scrubber modules and in the stack of Unit 1.

Southern studied in detail the coal washing plant performance during one shift. We also studied the variability of the coal washing process for four consecutive days. The cleaning process resulted in a reduction in ash by 56%, and sulfur by 26%. The heating value of the coal was increased by 13%. Normalized by calorific content, the relative reductions of anions was 2% for chlorine, 36% for sulfur, and 60% for fluorine. Five major elements quantified in the coal and refuse streams showed between 58 and 72% relative reduction between the raw coal and the cleaned coal on a weight basis. Trace element data showed a wide range of reductions for 16 target elements. The washing reduced mercury content in the coal an average of 29.6% on the basis of weight, or 39.2% on the basis of calorific value.

Southern made measurements across two scrubber modules on Unit 1 to examine the effects of liquid-to-gas ratio and slurry pH on the removal of trace elements and anions from the flue gas. Measurements in the stack quantified emissions rates of anions and trace elements. The average mercury concentration in the as-fired (washed) coal was 0.0837 μg/g, which for this coal would yield 9.7 $\mu g/Nm^3$ in the flue gas. This expected concentration agreed very well with the flue gas measurements.

We used two different sampling methods to determine the concentration of mercury in the flue gas — Method 29 and the modified Method 101A developed by Ontario Hydro Technologies. The percentage of the total mercury found in the particulate state was 1% or less of the total. The two methods were in good agreement on the total concentration of mercury. Both methods indicated that the scrubber removed most of the ionic mercury. The methods differed substantially on the proportions of mercury in the ionic and elemental states. At each sampling location Method 29 gave the higher percentage in the ionic state, and seemed to show that part of the ionic mercury at the scrubber inlet was converted to the elemental form at the outlet. We suspect inaccurate speciation by Method 29.

Removal efficiencies across the scrubber averaged 84% for sulfur and 95-98% for chlorine and fluorine. The measured efficiency for total particulate averaged 93%. For five major metals, the range was 95-98%. Eleven of the trace elements had removal efficiencies in the range 90-99%. The average removal of mercury was 45%.

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EXECUTIVE SUMMARY

Southern Research Institute (Southern) conducted a test program from October 24 to October 29, 1994, at the coal washing plant and Unit 1 of a coal-fired power plant in the southeastern United States. Two features of the plant were of specific interest: the on-site coal washing plant, and the wet, limestone scrubber on Unit 1. The test schedule was chosen to permit us to collect samples during a period of consecutive days with a constant coal source. During the test period, coal was provided to Unit 1 from only one seam of the Costain mine.

Southern collected the samples required to measured concentrations of anions and trace elements (with special emphasis on mercury) in the coal washing plant, and around two scrubber modules and in the stack of Unit 1. Anions of interest were Cl^-, F^-, and $SO_4^=$. We analyzed samples for five major elements (Al, Ca, Fe, Mg, and Ti) and 16 trace elements (As, B, Ba, Be, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, and V).

Measurements in the coal washing plant had two objectives: 1) determine the degree to which washing the coal alters the concentrations of the anions and trace elements in the cleaned coal compared to the raw coal, and 2) quantify separately the compositions of the several other input and waste streams in the washing process. Southern studied in detail the coal washing plant performance during one shift of typical operation with the Costain coal used for the Unit 1 testing. We also studied the variability of the coal washing process for four consecutive days of operation. During the Unit 1 test days we acquired samples of raw coal and cleaned coal to examine coal feed and cleaning variability.

Southern made measurements across two scrubber modules on Unit 1. Across one module we examined the effects of changes in the liquid-to-gas ratio (L/G) on the efficiency with which the scrubber removes trace elements and anions from the flue gas. Across another module we examined the effects of slurry pH on the removal of trace elements and anions from the flue gas. Measurements in the stack quantified emissions rates of anions and trace elements.

For the Unit 1 tests special emphasis was placed on measurements of mercury concentrations. Southern sampled with two methods designed to measure mercury in flue gases -- EPA Method 29, and a proprietary modification to EPA Method 101A developed by Ontario Hydro Technologies.

WASH PLANT

The Coal Washing Plant has a maximum capacity of approximately 2000 tph of raw coal, which is divided into four separate modules each with a throughput of 500 tph. Raw coal is conveyed from a raw coal silo into the plant. Coal cleaning is accomplished in coarse, middling, and fine coal circuits. Cleaning of the different size fractions is accomplished through a number of devices including screens, heavy media drum, cyclones, and froth cells. Raw coal is initially separated into two different size fractions.

The coarse fraction is then passed through heavy media vessels in which magnetite promotes segregating the coal from refuse based on density. The finer fraction is further segregated by screens into middling and fine fractions. The middling fraction is passed through heavy media cyclones, where magnetite is also used to enable a density separation of the coal and refuse. The fine fraction is passed through classifying cyclones, sieves, and froth flotation cells. An oil is used as an aid to frothing in the flotation cells. Fine coal is captured on rotating filters, and the fine reject is pumped to static thickeners. An anionic polymer is used in the thickener to promote settling of solids and clarification of the water. Fine refuse is transported in a slurry line from the thickener to a settling pond. Clean coal is ultimately one product stream comprised of the coal fractions from the coarse, middling and fine washing circuits.

Our intensive sampling at the coal wash plant was conducted on October 24, 1994. Modules B and D were in service. The totalized weight of raw coal fed during the shift was 4863 tons. The plant operated for approximately 5½ hours during this shift, which yields an average raw coal feed rate of 884 tph (442 tph per belt). The weight of cleaned coal fed to the Unit 1 coal bunkers during the 11-7 shift was 3577 tons. Thus, 26.4% of the raw coal was removed as refuse in the coal washing process on this shift.

Coal wash plant tonnage for the 24th through the 28th indicated the following refuse percentages: 26.4, 26.4, 26.6, 27.8, and 26.3%. These data suggest consistent performance of the coal wash plant on the Costain coal, even though the refuse rate is higher than the plant was designed to yield.

Results of proximate analyses on the coal and refuse samples taken from the Coal Wash Plant show the coarse and middlings refuse were high ash, low Btu, and high sulfur wastes. But, the fine refuse was relatively high carbon, high Btu material. This suggests inefficient operation of the flotation cells in the fine circuit during our test, causing a higher-than-normal waste of fine coal in this circuit.

The cleaning process resulted in a reduction in ash by 56%, and sulfur by 26%. The heating value of the coal was increased by 13%. On a weight basis, chlorine was enriched by 13% in the coal washing process, sulfur was reduced by 26%, and fluorine was reduced by 54%. When the data are normalized by calorific content, the relative reductions of anions was 2% for chlorine, 36% for sulfur, and 60% for fluorine.

Five major elements quantified in the coal and refuse streams show between 58 and 72% relative reduction between the raw coal and the cleaned coal on a weight basis. Aluminum and titanium are apparently reduced by ~60%, and calcium, magnesium, and iron by ~70%. If we assume no bias in the analyses for these elements, the data suggest that more of the iron, calcium, and magnesium are extraneous to the coal than is the case for aluminum and titanium.

Trace element data show a wide range of reductions for the 16 target elements:

Reduction (calorific basis)	Elements
- to 0%	Be, Cd, Mo
20 to 39%	Hg, Sb
40 to 49%	Cr, Ni
50 to 59%	V
70 to 79%	Ba, Cu, Mn
80 to 100%	B, Pb

Concentrations below detection prohibited calculation of the reductions in As, Co, and Se. There consistently were analytical difficulties with Be, Cd, Mo, and Sb. Apart from analytical problems, another reason for variations would be the distributions of the elements in the mix of coal and extraneous matter.

There was special interest in mercury throughout our test program. We have reason to believe the mercury value reported by analytical subcontractor Galbraith Laboratories (GL) for the cleaned coal is low. We had some samples of cleaned coal analyzed by Brooks Rand, Ltd. (BR). For the period October 25-28, the concentrations of mercury in the washed coal average 0.0837 µg/g in the analyses at BR but only 0.0578 µg/g in the analyses at GL. We believe the reason for this difference is the use of different sample digestion procedures by the two labs. Only the higher concentrations reported by BR could have produced the highly consistent flue-gas concentrations that were measured.

The effects of washing on mercury content in the coal for the period October 25-28 show an average reduction on the basis of weight of 29.6%; that based on calorific values is 39.2%. An unusually low and perhaps erroneous concentration in the raw coal on October 28 is responsible for these results on reduction that are lower than those for other elements. There is the possibility that the actual reductions are higher, because the data for raw coal from Galbraith may all be biased to the low side just as the data for the clean coal from that laboratory appear to be.

Magnetite is the only process additive that has sufficient concentrations of any of the target analytes to be a potential source of the analytes in the cleaned coal. Reduction of the elements in the cleaned coal (note iron in particular) is apparently unaffected by the magnetite, suggesting efficient recovery of magnetite in the washing process. Of particular interest in our study, mercury levels in the water and process additives were typically four orders of magnitude lower than in the wash plant solids.

Without measured flow rates for all the input and output streams, and with the uncertainties in the thickener underflow, we decided to calculate multiple mass balances based on different combinations of measurements and assumptions. These scenarios represent a wide range of combinations for the refuse. Nevertheless, combined refuse represents only 26.4% of the material, so variations in the distribution of the refuse may be hidden by analytical variability.

Three mass balances were calculated for each element yielding recoveries, defined as the sum of the output streams (clean coal + combined refuse) divided by the input stream (raw coal). Averages of the three calculated recoveries were as follows:

Recovery Range	Elements
< 50%	B, Co
50 to 74%	Hg, Pb, Sb
75 to 99%	As, Ba, Cu, V, Al, Ca, Fe, Ti
100 to 125%	Cr, Mn, Mg
> 125%	Be, Cd, Mo, Ni

The elements for which recoveries were affected by non-detects were As, Cd, Co, Mo, and Sb. Non-detects precluded calculation of recoveries for Se.

The low mercury recoveries (averaging 71%) are probably the results low concentrations in the coal analyzed by GL because of incomplete sample digestion, as discussed above. This uncertainty must also cloud some of the other analytical results.

Data from the analyses show that the coarse circuits are responsible for the vast majority of the removal of non-volatile material, including anions and trace elements, from the raw coal. Concentrations of trace elements in the extraneous matter that is mingled with the coal are higher than in the coal itself. From our test results, the fine circuit did not significantly contribute to the reduction of sulfur or trace elements in the coal.

POWER PLANT UNIT 1

Unit 1 of the power plant tested is nominally 700 MW, and is equipped with cold-side electrostatic precipitators (ESPs) for the removal of fly ash and venturi scrubbers for the removal of both fly ash and SO_2 from the flue gas. Features of Unit 1 that affect emissions of the chemical substances of interest are:

1) The coal is beneficiated by washing to remove a substantial fraction of mineral matter and sulfur.
2) The coal is burned in a cyclone furnace, with the attendant high temperature of combustion and the emission of a high concentration of nitrogen oxides, but the emission of a lower fraction of the ash than occurs with wall or tangential firing. (During a test in August, 1993 it was determined that 66 to 73% of the coal ash was accounted for as bottom ash and 27 to 34% as fly ash.)
3) The fly ash evolved from the boiler is first subjected to collection in an ESP. The ESP, however, is not a unit with high collection efficiency.

4) The residual fly ash at the outlet of the ESP and the SO_2 are subject to capture in a venturi scrubber with limestone as the basic reactant. Design specifications of the scrubber are to achieve particulate removal by 94% and SO_2 removal by 84%.

The scrubber consists of six venturi modules. Normally, five scrubber modules are in service, and one is in maintenance. Customarily four of the active modules are operated at "high" pH and the fifth is operated at "low" pH. During this test the high pH was typically 5.7 and the low pH was typically 5.1. Scrubber sorbent is prepared at the plant by pulverizing limestone in a wet ball mill. Additional water is added to this slurry to maintain a solids concentration in the recycle tanks around 12%. The actual feed rate of limestone is governed by the pH of the recycle tanks. Fresh limestone slurry is supplied only to the high-pH modules; spent slurry from the high-pH modules performs the scrubbing in the low-pH module. Fresh limestone slurry is added at Ca/S mole ratio of about 1.05, or perhaps sometimes as high as 1.10. The scrubber is operated with forced oxidation to produce a waste product in which gypsum rather than calcium sulfite is dominant. Waste liquor and solids from the recycle tanks are pumped to an effluent tank and then to an ash pond.

The main constraint placed on Unit 1 by our test program was the exclusive use of Costain coal. 31,804 tons of Costain coal were unloaded and 23,335 tons of cleaned Costain coal were fed to the Unit 1 boiler during our test period. This supply was adequate to cover the entire elapsed time of our test. The gross generating load on Unit 1 was kept at 652 MW ± 3 MW throughout our sampling periods. In addition to holding the load constant, soot blowing of air heaters was suspended during our sampling times to eliminate the effect of this erratic ash loading from our flue gas measurements.

Our test program called for three operating conditions in the scrubber. We tested across a scrubber module at the normal liquid-to-gas ratio (L/G) and at a higher L/G each day of our test. The adjustment in L/G was made by reducing the flue gas flow through a scrubber module (Module E) while maintaining the slurry feed rate. The flue gas flow was reduced by closing a louver-type damper at the inlet to the module. We also tested across another scrubber module operated at low and high pH levels on alternate days. The change in scrubber pH was made over night on Module F. The module operated at low pH on the first and third days of our test, and high pH on the second and fourth test days.

Other than the operational changes in the scrubber modules and the restrictions on sootblowing, Unit 1 boiler and scrubber systems operated during our test program as they would normally operate. The operators maintained very stable conditions during our test periods.

Samples taken during this program were comprised of both flue gas and process liquids and solids. Flue gas samples were taken at four locations:

1) the inlet to Scrubber Module E,
2) the outlet of Scrubber Module E,
3) the outlet of Scrubber Module F, and
4) the stack.

The sampling methods we used for flue gases were as follows:

- Major metals and trace metals (including mercury) in both particulate and vapor forms were sampled using EPA Draft Method 29.

- Mercury was also collected as the single analyte by an impinger train developed by Dr. Keith Curtis of Ontario Hydro Technologies. The Ontario Hydro mercury train is a modification to the EPA Method 101A sampling train.

- Anions were sampled by use of the Method 5 train in which solids on the filter as well as sodium carbonate/bicarbonate impinger solutions were retained for analysis.

- Samples collected for metals analysis in three ranges of particle size were taken using teflon-coated cyclones I and II of the Southern/EPA Five Series Cyclone sampling system.

Mercury Concentrations

Special emphasis was placed on the measurement of mercury in this test program. Mercury was determined in all process solids and liquids. We determined mercury in the as-fired (washed) coal to assess the plausibility of the mercury concentrations measured in the flue gas. The average mercury concentration in the washed coal was 0.0837 μg/g, which for this coal would yield 9.7 μg/Nm^3 in the flue gas. This concentration agrees very well with the measured concentrations of mercury in the flue gas.

We used two different sampling methods to determine the concentration of mercury in the flue gas. Both methods, Method 29 and the modified Method 101A, ostensibly provide distinct measures of two ionic species of mercury — Hg^{++} and Hg(0).

Evidently, there is no way to speciate mercury in solid matter; however, it seems plausible that the mercury in this state is ionic (perhaps as the compound HgO), not elemental. The percentage of the total mercury found in the particulate state was 1% or less of the total, confirming the expectation that mercury would occur mainly in the vapor state.

The average mercury concentrations in the vapor state are tabulated below for ready comparison. The concentrations are in the units μg/Nm^3; the percentages of the two forms of mercury are shown in parentheses:

	Method 29	Modified Method 101A
Inlet, E Module	μg/Nm^3	μg/Nm^3
Ionic	7.39 (74.3%)	4.74 (48.1%)
Elemental	2.56 (25.7%)	5.12 (51.9%)
Total	9.95	9.86
Outlet, E Module	μg/Nm^3	μg/Nm^3
Ionic	1.15 (20.8%)	0.56 (9.3%)
Elemental	4.37 (79.2%)	5.56 (90.7%)
Total	5.52	6.13
Outlet, F Module	μg/Nm^3	μg/Nm^3
Ionic	-	0.51 (8.5%)
Elemental	-	5.54 (91.5%)
Total	-	6.06
Stack	μg/Nm^3	μg/Nm^3
Ionic	1.35 (22.6%)	0.52 (7.9%)
Elemental	4.63 (77.4%)	6.13 (92.1%)
Total	5.98	6.66

The more important observations from the above tabulation are as follows:

1. The two methods were in good agreement on the total concentration at each location where both methods were used. The differences range only from 0.1 to 0.6 μg/Nm^3.

2. Both methods indicate that the scrubber removed most of the ionic mercury. Either method shows good agreement between the outlet of Module E and the stack; Method 101A also shows good agreement between the outlets of Modules E and F.

3. The methods differ substantially on the proportions of mercury in the ionic and elemental states. At each sampling location Method 29 gave the higher percentage in the ionic state. Moreover, Method 29 seemed to show that part of the ionic mercury at the scrubber inlet was converted to the elemental form at the outlet.

The explanation for the difference in speciation cannot be explained unequivocally. It may have to do, however, with the lack of specificity of the peroxide impinger in Method 29 for capturing the ionic form of mercury. The combination of hydrogen peroxide and nitric acid in the so-called peroxide impinger surely has the oxidizing potential for converting part of the elemental mercury to the ionic state. The suggestion that ionic mercury shifts from the ionic state to the elemental state across the scrubber

is contrary to the predictions of thermodynamics. Therefore, these data suggest Method 29 did not accurately differentiate the species of mercury.

Concentrations of Other Metals

The measured concentrations of all trace elements are as follows:

	Concentration, μg/Nm^3		
Metal	Inlet, Module E	Outlet, Module E	Stack
As	198	28.0	31.8
B	7522	439	457
Ba	769	42.7	42.0
Be	29.1	1.0	1.20
Cd	22.5	2.3	2.82
Co	58.4	<5.7	3.68
Cr	503	37.7	42.6
Cu	261	14.9	15.4
Hg	10.20	5.6	6.02
Mn	414	5.5	7.53
Mo	221	46.3	47.0
Ni	267	3.9	11.3
Pb	228	21.6	15.0
Sb	45.4	<12.9	6.4
Se	63.8	45.6	41.8
V	1331	99.2	110.0

The percentages of vapor of each metal present to a large degree in the vapor state are:

	Inlet, Module E	Outlet, Module E	Stack
Boron	85	91	81
Mercury	99.2	99.6	99.5
Selenium	27	30	29

Anions

Three non-metals under study — fluorine, chlorine, and sulfur — are reported as the corresponding anions — fluoride, chloride, and sulfate. The vapors presumed to have been present in the flue gas were the compounds HF, HCl, and SO_2; the first two compounds are simply captured by acid-base reactions in the alkaline impinger solutions, whereas SO_2 undergoes oxidation and neutralization to occur as sulfate. The calculated concentrations of the vapors in the units ppmv were:

LOCATION	HCl, ppmv	HF, ppmv	SO_2, ppmv
Module E Inlet	134	2.8	1843
Module E Outlet	1.9	0.1	333
Module F Outlet	1.9	0.2	320
Stack	1.5	0.1	308

The only solids analyzed for the anions corresponding to the acid gases were from the stack samples. The filters from the sampling train were extracted with water and the extracts analyzed. Apparent weight-based concentrations of the anions in the filter solids were as follows:

	Cl^-, mg/g	F^-, mg/g	SO_4^{-2}, %
October 25	140	48	57.1
October 26	160	36	54.3
October 27	170	44	52.4
October 28	-	55	63.8

The concentrations of chloride and fluoride are not high enough to be remarkable; those of sulfate, on the other hand, are quite remarkable. From these data, the calculated vapor concentrations are: HCl, 0.0139 ppmv; HF, 0.0073 ppmv; and SO_2, 19.2 ppmv. The stack solids thus contain negligible concentrations of the anions compared to the vapor concentrations that were observed.

Small concentrations of the anions might be explained as the result of interaction between the acid gases and alkali in the solids; the average sulfate concentration of approximately 60% surely cannot be explained this way. The probable explanation for the sulfate is the condensation of sulfuric acid vapor during cooling of flue gas in the scrubber, with little capture of the condensed mist occurring in the scrubber. The average stack particulate concentration was 128 mg/Nm^3. Sixty percent of this figure is 77 mg/Nm^3; this corresponds to a sulfuric acid vapor concentration of 19 ppmv. Such a level of sulfuric acid vapor is easily attainable with a coal containing 2.8% sulfur.

If sulfate accounts for 60% of the solid in the stack, fly ash is not likely to account for the remaining 40%. Sulfate has a formula weight of 96 and sulfuric acid in the anhydrous state has a formula weight of 98; however, the acid as the dihydrate often said to occur as the condensate in a flue-gas environment has a formula weight of 134. Thus, the condensate may weigh 134/96 or 1.4 times as much as the sulfate, leaving perhaps as little as 20% of the stack particulate as the mineral matter that constitutes fly ash.

Absorption of the acid gases HCl, HF, and SO_2, with forced oxidation of SO_2, produced very large enhancements in the fluoride, chloride, and sulfate concentrations in aqueous solution. Chloride, being more soluble in the presence of calcium than sulfate, and being present at a higher concentration than fluorine in the flue gas, reached the highest concentration in the liquid phase — somewhat over 2000 ppm.

Sulfate, on the other hand, experienced the greatest enhancement in the solid phase. It was found at 42% in the solid phase of the recycle slurry or 51% in the solid phase of the discharge slurry. The latter is the more plausible value; sulfate is 56% of gypsum.

Mass Balances

Coal vs. Scrubber Inlet

The plan of the investigation did not include collection of samples of bottom ash or ESP ash. Moreover, the plan did not include measurement of the proportions of ash leaving the boiler as bottom ash and fly ash or the measurement of ash removal in the ESP. The only task relevant to these general considerations that can be undertaken is a comparison of the concentrations of substances flowing in the duct leading to the E Module against the concentrations that would have been observed if all of these substances originally in the coal had been entrained uniformly in the inlets to all five operating modules.

The average metal concentrations based on the coal analysis were compared with the averages found at the E Module inlet. There was a wide range of recovery values (ratio of scrubber inlet to coal-derived concentrations), which makes inescapable the conclusion that there are some poor data underlying the recovery data.

The following tabulation gives an overall assessment of the recoveries :

Recovery range	Metals	Comment
<10%	Cd, Cu, Mo, Sb	Not plausible
10-20%	Ba, Be	Probably lower than actual, but perhaps indicative of selective discharge in bottom ash
20-35%	Cr, Mn, Ni, V Al, Ca, Fe, Mg, Ti	Plausible
>35%	As, B, Hg, and Pb	Only Pb not believable

For the major metals recoveries range approximately from 23-32%. For fly ash at the inlet of the E Module, the recovery might be expected to fall somewhere within this range. It is consistent with what was learned in earlier studies performed by Southern at Paradise Unit 1. First, the distribution of ash between bottom ash and fly ash was found to make the latter about 30% of the total. The efficiency of the ESP was found to be negligible, or at most 40%. If 30% of the coal ash were fly ash and 40% or less of the fly ash were collected in the ESP, the recovery at the inlet of Module E would be 18% or more.

Reasons thus need to be found to explain recoveries of trace metals that differ a great deal from values in the range 20-30%. There cannot be any justification for values such as 0.4% for cadmium or other values below 10%. Co and Se in the coal were at concentrations below detection limits, and Mo, Pb, and Sb concentrations were suspect for other reasons. Faulty coal analysis is suspected as the more probable source of erroneous data than the flue-gas analysis, but this is an opinion that cannot be rigorously supported.

The recovery of mercury is 105%. The result for this metal is highly gratifying. A few metals other than mercury can be explained at recoveries above the range given for the major metals. One is boron, which is volatile as boric acid; the recovery of 73% is plausible. The recovery of 54% for arsenic can be justified because this metal is probably too volatile at boiler temperatures to be discharged in the bottom ash.

The average recoveries for acid gases were about 82% for HCl and SO_2 but only 34% for HF.

Scrubber Module E Inlet vs. Outlet

We were able to calculate a mass balance around the scrubber Module E. Values fixed at the outset of calculations at 100% were recoveries for calcium, sulfate, and water. These assumptions were required in the absence of measured flow rates for scrubber slurries. We achieved a balance of 99% for heat across the scrubber with these assumptions, which is to a degree independent of the assumed closure for water;

the result is highly gratifying. Beyond these four results, the balance across Scrubber Module E can be classified as follows:

	Number of closures		
	<75%	75-125%	>125%
Trace metals	7	7	2
Major metals	0	3	1
Anions	0	2	1

The value for mercury, 91%, can justifiably be singled out as quite good. All of the mercury data in the calculations having to do with flue gas, it must be said, are based on Method 29.

The inlet flue gas dominates input in every aspect except for calcium, where the limestone is dominant. The discharge slurry dominates output for every element.

Effects of Scrubber Operation

Measurements at the inlet and outlet of the E Module provided data at two L/G ratios: the customary value around 85 gal/kacf and an increased value of about 100 gal/kacf. For most of the substances measured, the efficiency of removal in the scrubber was not greatly affected by the change in L/G. Only the removal of SO_2 was significantly enhanced at the higher L/G ratio. At the higher ratio, 87% of the SO_2 was removed; at the lower ratio, 82% was removed. Each of these two removals is outside the range of the other plus or minus two standard deviations. This statement cannot be made for any other element.

The data on mercury based on Method 29 or based on the modification of Method 101A lead to the same conclusion — that mercury removal in the scrubber is not altered by changing L/G.

Concentrations of HCl, HF, and SO_2 at the outlet of the F Module when scrubbing occurred at recycle pH values of 5.7 and 5.1 makes it impossible to say that the removal of any of the gases was affected by a change in pH.

A tabulation is given below for mercury (concentrations are in $\mu g/Nm^3$):

	Higher pH	Lower pH
Ionic	0.67, 0.50	0.37, 0.50
Elemental	4.75, 5.70	6.45, 5.26

The data are not decisive enough to show any difference due to pH.

Removal Efficiencies

For the anions, the removal efficiencies in the E Module appear to be credible — on the average, 84% removal for sulfur and 95-98% for chlorine and fluorine. The stronger acidities of HCl and HCl (compared to SO_2) make higher removals for the two halogen compounds believable.

The average removal of mercury is 45%; this is the result for data from Method 29, but the result would be about the same for data from modified Method 101A. For the five major metals, the range is 95-98%. An efficiency in this range, it may be imagined, should match the efficiency for removal of total particulate matter, inasmuch as there is likely to be a 1:1 correspondence between the five major metals and total particulate. In actuality, the measured efficiency for total particulate averaged 93%. Among the 13 trace metals that remain when cobalt, mercury, and selenium are not counted, 11 have removal efficiencies in the range 90-99%.

Emissions Factors

	Units, $g/10^{12}$ J	Units, $lb/10^{12}$ Btu
Mercury	1.85	4.30
Other trace metals		
Minimum (Be)	0.30	0.70
Maximum (Ba)	141	327
Major metals		
Minimum (Mg)	60.8	141
Maximum (Fe)	1099	2556
Acid gases		
HCl	706	1643
HF	24.9	58.0
SO_2	259,000	603,000

1.0 REPORT ORGANIZATION

This report is organized into six sections, including the preceding, unnumbered Executive Summary and this description of the report contents. Section 2 gives an overview of the project and a discussion of the project objectives. Section 3 describes the relationships among the participants, and the organizational lines of authority used in managing this project. The main body of the report is presented in Sections 4 and 5. Section 4 is devoted to the testing done at the coal washing plant. A description of the plant, lists of samples we collected, and the analyses we performed are included in Section 4. Section 5 describes the testing done on Unit 1 of the power plant, and includes the following subsections: descriptions of the boiler and scrubber; tabulated and plotted plant operating data collected during our test; descriptions of the methods we used to collect all samples from solid, liquid, slurry, and gas streams; the sampling schedule; the analytical methods used on all of the collected samples; all of the analytical results; and review and interpretation of the results.

There are five appendices to the report. They contain descriptions of supporting information on sampling and analytical protocols, quality assurance and quality control procedures and results auditing exercises, tabulated plant operating data, and details of analyses of daily samples.

2.0 TEST OVERVIEW AND OBJECTIVES

Southern Research Institute (Southern) conducted a test program from October 24 to October 29, 1994, at the coal washing plant and Unit 1 of a coal-fired power plant in the southeastern United States. Two features of the plant were of specific interest: the on site coal washing plant, and the wet, limestone scrubber on Unit 1. The test schedule was chosen to permit us to collect samples during a period of consecutive days with a constant coal source. During the test period, coal was provided to Unit 1 from only one seam of the Costain mine. The test period was also selected to coincide with an outage on Unit 2 at the plant, which permitted the host utility to collect samples of the flue gases in the plume of Unit 1 without interference from the Unit 2 exhaust gases.

Southern collected the samples required to measured concentrations of anions and trace elements (with special emphasis on mercury) in the coal washing plant, and around two scrubber modules and in the stack of Unit 1. Anions of interest were sulfate, chloride, and fluoride. Trace elements studied were

- antimony
- arsenic
- barium
- beryllium
- boron
- cadmium
- chromium
- cobalt
- copper
- lead
- manganese
- mercury
- molybdenum
- nickel
- selenium
- vanadium

Measurements in the coal washing plant had two objectives: 1) determine the degree to which washing the coal alters the concentrations of the anions and trace elements in the cleaned coal compared to the raw coal, and 2) quantify separately the compositions of the several other input and waste streams in the washing process. Southern studied in detail the coal washing plant performance during one shift of typical operation with the Costain coal used for the Unit 1 testing. During this intensive study, Southern collected samples and data to describe the input and output streams of the coal washing plant. These data revealed the sources and sinks of the analytes of interest. The results ought to indicate where in the coal washing process effort should be focused to optimize the removal of these analytes. We also studied the variability of the coal washing process for four consecutive days of operation. During the Unit 1 test days we acquired samples of raw coal and cleaned coal to examine coal feed and cleaning variability.

Southern made measurements across two scrubber modules on Unit 1. Across one module we examined the effects of changes in the liquid-to-gas ratio (L/G) on the efficiency with which the scrubber removes trace elements and anions from the flue gas. Across another module we examined the effects of slurry pH on the removal of trace elements and anions from the flue gas. Measurements in the stack quantified

emissions rates of anions and trace elements. We collected quadruplicate samples (one set of samples per day for four days) to characterize stack emissions, quadruplicate samples (two sets of samples per day for four days) to characterize scrubber performance at two levels of L/G, and duplicate samples (one set of samples per day) to characterize scrubber performance at two levels of slurry pH.

For the Unit 1 tests special emphasis was placed on measurements of mercury concentrations. We coordinated our test program with measurements by the host utility of mercury concentrations in the Unit 1 plume, and additional measurements by Brooks Rand, Ltd. (under contract to the host utility) of mercury concentrations at various sampling locations, including some of the locations at which we were sampling. Southern sampled with two methods designed to measure mercury in flue gases -- EPA Method 29, and a proprietary modification to EPA Method 101A developed by Ontario Hydro Technologies. Southern results supplement or compliment results obtained by the host utility and Brooks Rand during the test period. (This report describes only the Southern sampling and results.)

3.0 CONTRACTOR ORGANIZATION

This project was performed by the staff of the Environment & Energy Division of Southern Research Institute, supplemented by eight subcontracted organizations or consultants. The project management structure is described below. Subcontractors and their responsibilities were as follows:

- Dr. Keith E. Curtis of Ontario Hydro Technologies, Inc. was contracted to provide Southern with instructions on the preparation, sampling, recovery, and analysis of a mercury sampling train that he developed. Dr. Curtis was on site for the initial sampling preparations and for the first two sampling days.
- Guardian Systems, Inc. provided two field sampling crew members to supplement Southern staff. Their duties were operation of one of the mercury sampling trains, Orsat measurements of O_2 and CO_2 in the flue gas, and pitot measurements at one sampling location.
- Seatec, Inc. provided two field sampling crew members to assist in flue gas sampling and in plant process solids and liquids sampling.
- Commercial Testing & Engineering, Inc. was contracted to do the proximate, ultimate, chlorine, and fluorine analyses on the coal and coal refuse samples from the coal washing plant. CT&E also measured the size distribution of samples from the coal washing plant, and crushed and riffled them into -60 mesh composites.
- Galbraith Laboratories, Inc. was the major analytical subcontractor. They analyzed all process solids for all of the target trace elements and major metals, all metals train impinger solutions for antimony, arsenic, and selenium, and all metals and mercury train impinger solutions for mercury.
- University of Missouri-Columbia measured trace elements in the coal wash plant composite samples using neutron activation analysis.
- Brooks Rand, Ltd. measured mercury in coal samples for each of the Unit 1 test days.
- Dr. Edward B. Dismukes was hired as a consultant to assist in the review and interpretation of the analytical data, and in the preparation of the report.

Five individuals were classified as key personnel for this project:

P. Vann Bush, Program Manager and Principal Investigator

Joseph D. McCain, Sampling Coordinator

William K. Fowler, Analytical Coordinator

Larry S. Monroe, QA Auditor

The following paragraphs describe the roles of the key personnel.

Program Manager and Principal Investigator The Program Manager had the duties of liaison with the DOE Contracting Officer's Representative, liaison with other participants of the project including the host site representatives and other DOE contractors where needed, scheduling the activities of project personnel, and monitoring and reporting the project performance relative to the schedule and budget. The Program Manager scheduled and conducted pre-test site evaluations required for the preparation of site-specific sampling and analytical plans. The Program Manager was on site during the field sampling, participated in review and interpretation of analytical results including mass balance determinations, and directed the preparation of the project reports.

Sampling Coordinator The Sampling Coordinator participated in the pre-test site survey and the preparation of the site-specific sampling and QA plans. The Sampling Coordinator supervised the preparation of sampling equipment, the on-site sampling, and delivery of samples for post-test analyses. The Sampling Coordinator was responsible for the reduction of data from the sampling trains, and assisted in writing the report.

Analytical Coordinator The Analytical Coordinator assisted in the preparation of site-specific analytical plans. The Analytical Coordinator was on site during part of the field sampling, assumed custody of the samples collected upon their delivery to the laboratory in Birmingham, and supervised the disposition and analyses of all samples. The Analytical Coordinator was responsible to summarize the analytical results, assist in the interpretation of results, and help prepare the report.

Quality Assurance Auditor The Quality Assurance Auditor reviewed the standard operating procedures (SOPs) for each of the sampling trains and analytical instruments. The Auditor monitored the sampling at the power plant and conducted independent checks of procedures against the SOPs and test objectives. The Auditor compiled the quality assurance documentation from pre-test and post-test calibrations of test equipment, and the quality control data records from the analytical work.

3.1 Sampling Team

Southern had 21 people on site for the test program, plus two subcontracted sampling team members from Guardian Systems, Inc. and two from Seatec, Inc. The staff were divided as follows:

Coal Washing Plant:

1 test coordinator
1 QA/QC coordinator
3 (plus the test coordinator) to collect plant samples

Unit 1:

4 in the mobile laboratory,
6 at the Unit 1 scrubber module E inlet sampling location,
5 full-time + 1 half-time at the Unit 1 scrubber module E outlet sampling location,
2 half-time at the Unit 1 scrubber module F outlet sampling location,
2 full-time + 1 half-time at the Unit 1 stack sampling location,
1 to make pitot measurements and run Orsat samples,
1 to collect plant samples,
1 flue gas sampling coordinator,
1 plant process sampling coordinator,
1 QA auditor, and
1 test supervisor.

The organization of the sampling team is shown in Figure 3-1. Dr. Michael J. Baird of DOE/PETC was on site throughout the testing.

3.2 Analytical Team

The analytical team for this project was organized as shown in Figure 3-2. As indicated in the figure, Dr. Fowler personally directed the in-house analyses of anions and trace elements. He submitted the samples to, and reviewed the results from, the subcontracted analytical laboratories. Dr. Dismukes assisted in the review of the analytical work.

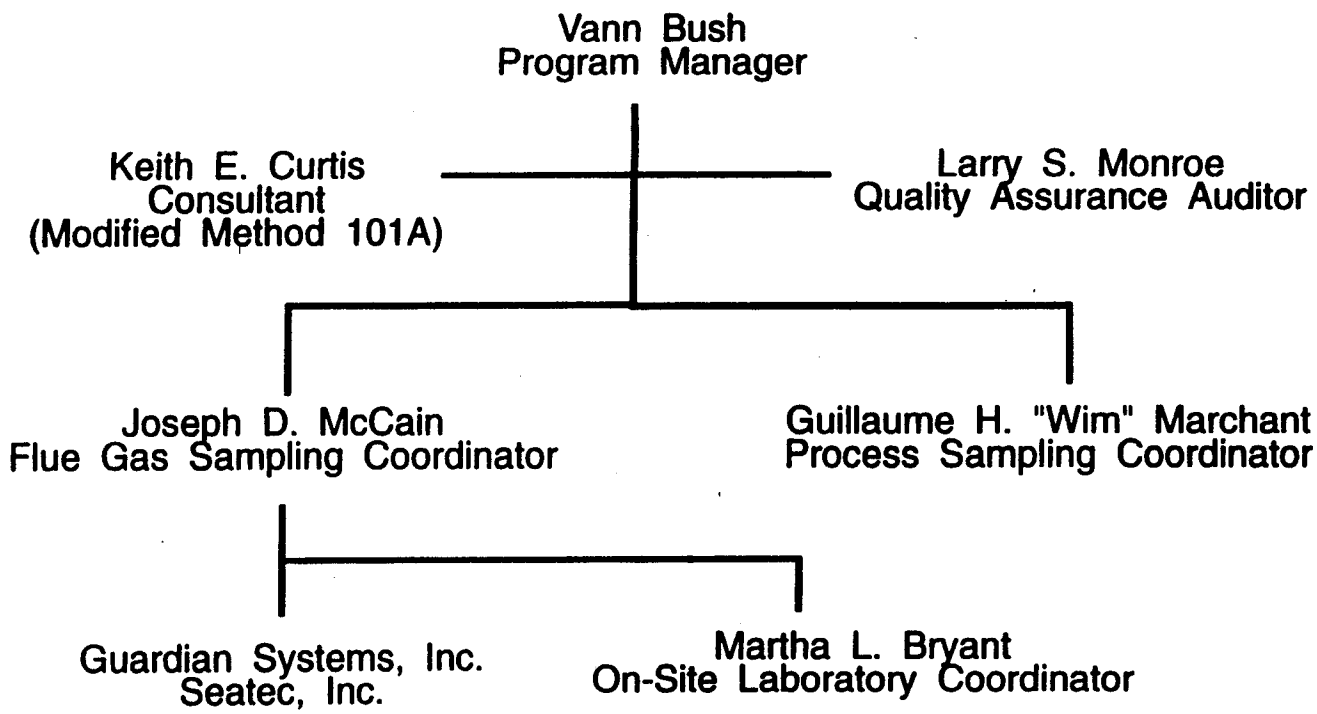


Figure 3-1. Sampling Team Organization

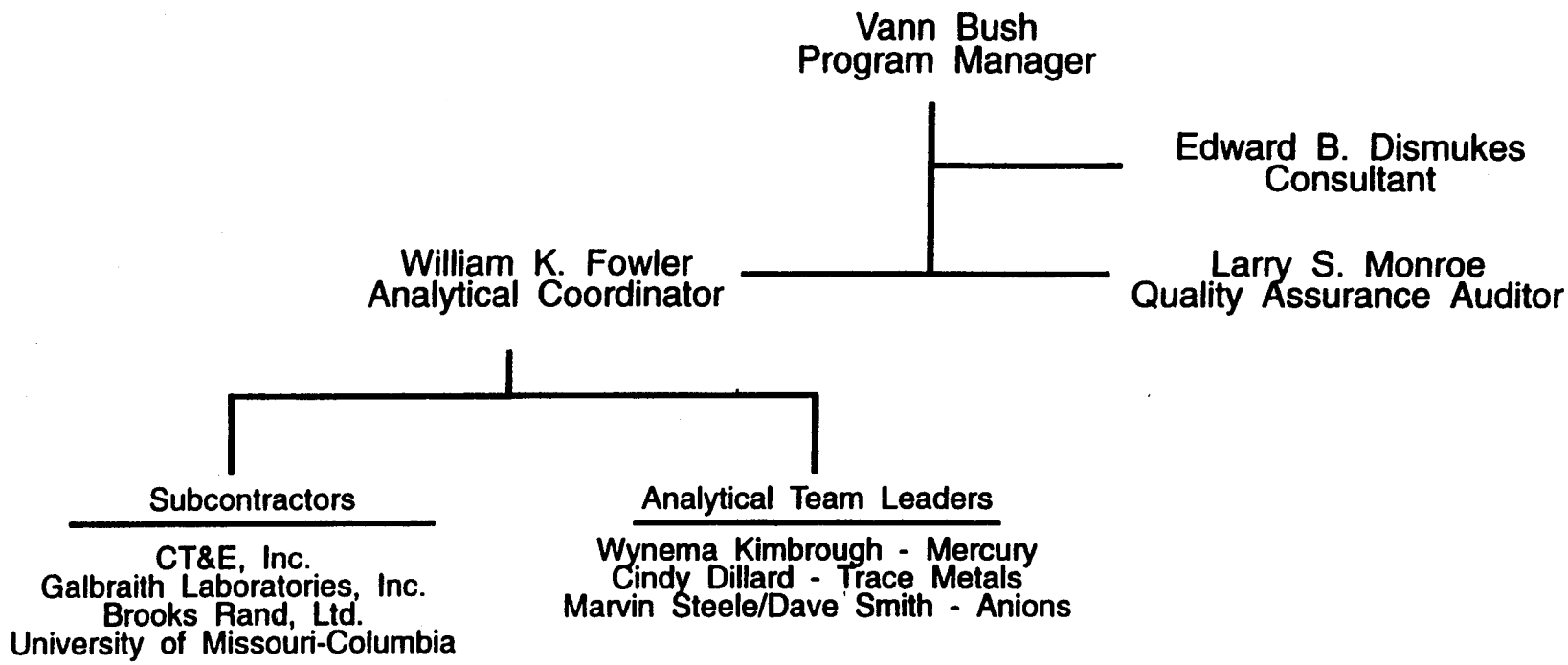


Figure 3-2. Analytical Team Organization

4.0 COAL WASHING PLANT TEST

4.1 Plant Description

Part of the normal operation of the host site of this test is the beneficiation of coal by washing. The sulfur content of coal used at this plant is limited to the level that produces SO_2 at no more than 5.2 lb/MMBtu. This limit is governed by the requirements of a unit which has no scrubber. The coal yard does not segregate coal according to the requirements of the individual units; thus, the unscrubbed unit determines the maximum in sulfur for the entire plant, although other units with scrubbers could tolerate higher sulfur levels.

The Coal Washing Plant has a maximum capacity of approximately 2000 tph of raw coal, which is divided into four separate modules each with a throughput of 500 tph. Figure 4-1 is a simplified schematic drawing of one module of the coal washing plant. Raw coal, typically 3" X 0", is conveyed from a raw coal silo into the plant. The two belts conveying the raw coal are equipped with an automatic sampler that uses an ASME method in which a sample of the coal is taken from the moving belts at three-minute intervals throughout the conveying period.

Coal cleaning is accomplished in coarse, middling, and fine coal circuits. Cleaning of the different size fractions is accomplished through a number of devices including screens, heavy media drum, cyclones, and froth cells. Raw coal is initially separated into two different size fractions, greater than and less than $^5/_{16}$ inch. The coarse fraction is then passed through heavy media vessels in which magnetite promotes segregating the coal from refuse based on density. The fraction less than $^5/_{16}$ inch is further segregated by screens into middling and fine fractions. The middling fraction is passed through heavy media cyclones, where magnetite is also used to enable a density separation of the coal and refuse. Sampling of coarse and middling rejects can be done from the vessel and cyclone refuse screens. The fine fraction is passed through classifying cyclones, sieves, and froth flotation cells. An oil is used as an aid to frothing in the flotation cells. Fine coal is captured on rotating filters, and the fine reject is pumped to static thickeners. An anionic polymer is used in the thickener to promote settling of solids and clarification of the water. Fine refuse is transported in a slurry line from the thickener (thickener underflow) and sampled at the discharge point at the pond. Clean coal is ultimately one product stream comprised of the coal fractions from the coarse, middling and fine washing circuits. This clean coal product stream is equipped with an automatic sampling device of the same type as used on the raw coal.

Figure 4-1 does not show the water sources. The raw coal is wetted almost as soon as it enters the coal washing plant. Water is recirculated between the plant, the thickener, and the settling pond. The plant also uses fresh water make-up. There are thus three water sources – fresh makeup water, pond return water, and thickener clarified water.

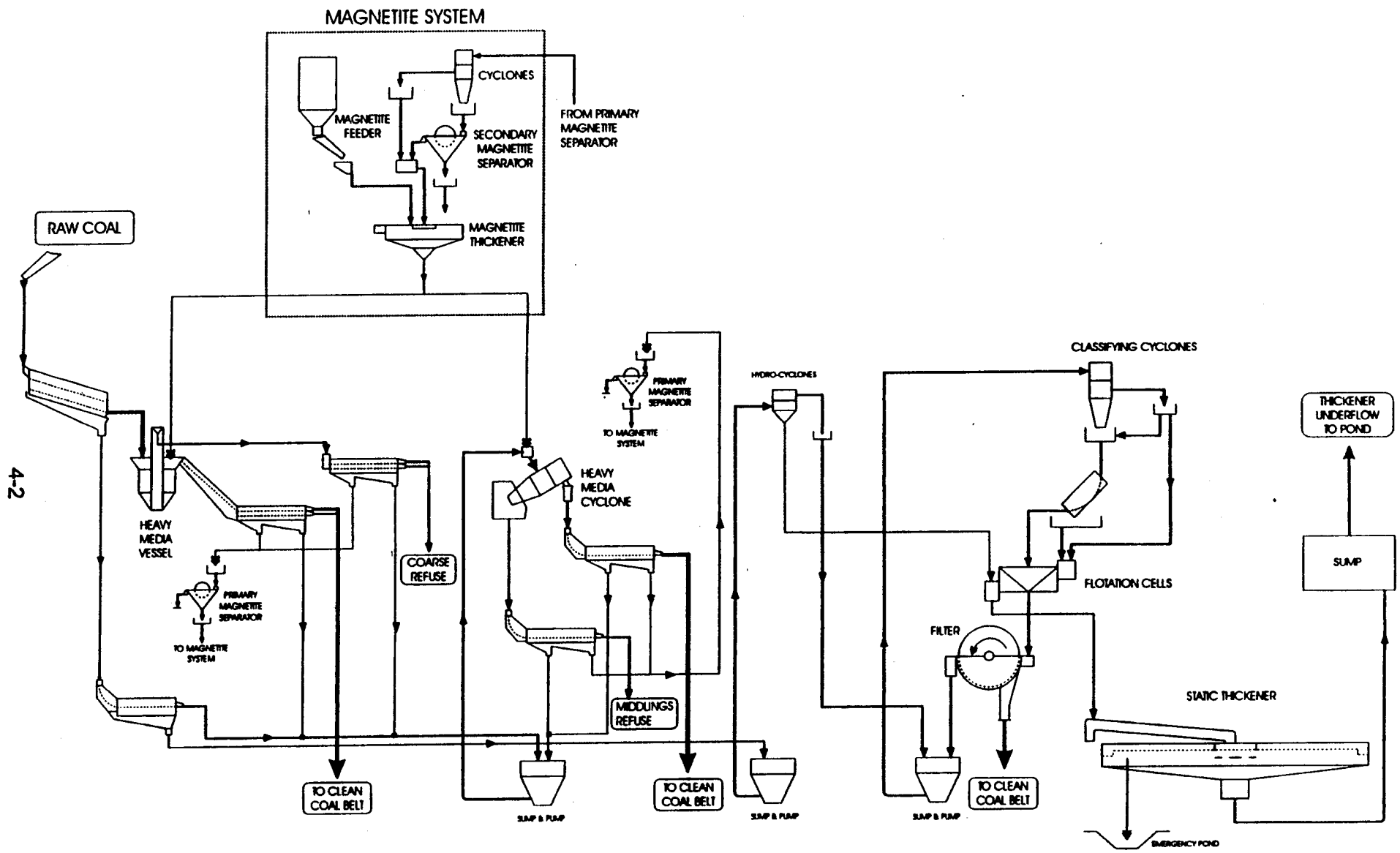


Figure 4-1. Simplified Process Diagram for the Coal Washing Plant

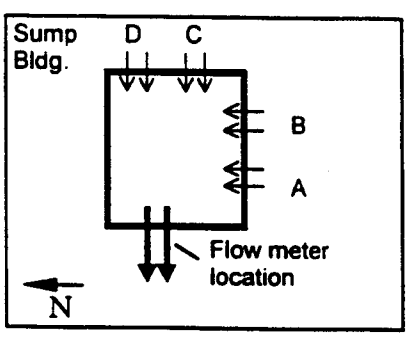
4.2 Plant Operation

Throughout our tests at the power plant, the coal washing plant processed approximately 1000 tph of Costain coal during the 11 pm to 7 am shift. Our intensive sampling at the coal washing plant was conducted on October 24, 1994. Modules B and D were in service. The two raw coal conveyer belts were on line at 0125. We stopped these belts for about 10 minutes at 0140, and again at 0630 to collect samples. Otherwise, the coal washing proceeded at a raw coal feed rate in the range from 375 to 450 tph per belt.

The totalized weight of raw coal fed during the shift was 4863 tons. The plant operated for approximately 5½ hours during this shift, which yields an average raw coal feed rate of 884 tph (442 tph per belt). The weight of cleaned coal fed to the Unit 1 coal bunkers during the 11-7 shift was 3577 tons. Thus, 26.4% of the raw coal was removed as refuse in the coal washing process on this shift. This is a higher refuse fraction than is typically reported at the wash plant. An operator at the plant related two facts that could contribute to a high refuse fraction during our sampling: the Costain coal had a high percentage of fines (this over-worked the fine circuit, limiting coal feed rate through the modules), and module B had a chemical pump out of service resulting in inefficient separation in the flotation cells and abnormally high fine refuse.

Coal washing plant tonnage for the 24th through the 28th indicated the following refuse percentages: 26.4, 26.4, 26.6, 27.8, and 26.3%. These data suggest consistent performance of the coal washing plant on the Costain coal, even though the refuse rate is higher than the plant was designed to yield.

Southern installed a portable ultrasonic flow meter to measure the fine coal refuse (thickener underflow) discharged to the pond. Our flow meter was installed at the discharge of the sump into which the underflow was pumped. This was the only process flow rate other than the raw and cleaned coal weights that was measured. The location of inputs and outputs to this sump building are shown below:



Inputs from Modules A, B, C, and D are labeled. There were two discharge pipes each seven inches in diameter. The flow meter was used to measure the flow rate and cumulative flow through the northernmost discharge pipe for the first half of our sampling period, and the southernmost discharge pipe for the last half of the sampling period. Data from the ultrasonic flow meter are shown in Table 4-1. The measured flow rate of the thickener underflow indicates that 61% of the refuse was discharged in the thickener underflow (15.84% of the raw coal). We think this is an erroneously high value, even though the fine refuse fraction may have been atypically high for reasons given above. The error is probably due to sampling location more than flow meter errors. We know that there was a third module

Table 4-1
Fine Refuse Slurry Flow

Time	Pipe 1 (gpm)	Pipe 2 (gpm)	Total Flow (gallons)	Average Flow (gpm)
2:15	1803		194128	
2:30	1772		222527	1893.23
2:45	1842		249662	1809.05
3:00	1814		276899	1815.81
3:15	1779		303378	1765.24
3:30	1777		329885	1767.14
3:45	1835		357041	1810.42
4:00	1790		384459	1827.83
4:05		2019	396235	
4:15		1983	416284	2004.93
4:30		1962	446283	1999.95
4:45		2023	476863	2038.66
5:00		2047	507643	2051.99
5:15		2043	538388	2049.70
5:30		1971	568624	2015.73
5:45		1959	598246	1974.80
6:00		2053	628368	2008.09
AVERAGE	**1802**	**2006**	**405583**	**1922**

Average Flow Rate of Thickener Underflow	Measured Percent Solids in Flow	Assumed Density of Slurry, lb/gal
3844 gpm	13.8	8.8

Mass Flow of Solids, lb/h	Mass Flow of Solids, tph
280089	**140.04**

Assumed solids density equal to 1.4 g/mL, a typical density for coal.

of the wash plant being cleaned during our sampling period and that rinse stream contributed to the total discharge where we measured it. Reducing the measured sump discharge rate by one-third would still give ~41% of the total refuse as thickener underflow (10.6% of the raw coal).

4.3 Sampling Performed

We adopted a protocol for sampling at coal beneficiation plants developed by CONSOL, Inc. The protocol was designed to assure representative samples that characterize the coal cleaning process. The major feature of this protocol is the collection of large grab samples from process streams at 15-minute intervals over a four-hour period of stable plant operation. In addition, we incorporated suggestions by CQ, Inc. to collect some supplementary samples. Table 4-2 lists the specific samples that were collected at the coal washing plant.

Table 4-2
Samples from Coal Washing Plant

	Sample	Sampling Location	Sampling Method
1	Raw Coal	raw coal conveyer	ASME autosampler
2	Raw Coal	raw coal conveyer belt	stop-belt manual sampling
3	Raw Water Makeup	water tap in plant	multiple grab samples
4	Magnetite	magnetite feeder bin	1 grab sample
5	Oil (frothing additive)	storage tank in plant	1-quart grab sample
6	Anionic Polymer (thickener additive)	storage tank in plant	1-quart grab sample
7	Static Thickener Clarified Water	water tap in plant	multiple grab samples
8	Pond Return Water	pond	single grab sample
9	Coarse Refuse	refuse screen, level 3 in plant	multiple grab samples
10	Middling Refuse	refuse screen, level 3 in plant	multiple grab samples
11	Fine Reject Slurry	pond discharge	multiple grab samples
12	Cleaned Coal	clean coal conveyer belt	stop-belt manual sampling
13	Cleaned Coal	bunker coal conveyer	ASME autosampler

All 13 types of samples taken from the coal washing plant process streams were grab samples. The sampling methods used were as follows:

SAMPLE	SAMPLING METHOD
1) & 13)	Automatic Sampler - ASME method collecting samples at 3-minute intervals. The host utility provided Southern with splits of the samples taken during the shift beginning one hour after startup of the wash plant.
2) & 12)	Southern collected these samples. The host utility stopped the conveyer belts and we shoveled coal off of a section of the belt. The coal was placed in lined bags. Two raw coal samples were taken -- one at the beginning and one at the end of the four-hour sampling period -- and then transferred into separate, lined, 55-gal drums. The clean coal belt samples were taken at the end of the four-hour sampling period and kept in lined bags.
3) & 7)	Southern collected these samples. These water streams were sampled by manually opening valves located on water lines in the plant. Samples of each stream were taken at 15-minute intervals over a four-hour period of stable plant operation (0200 to 0600).
4), 5) & 6)	The host utility collected a one-quart jar of each of these samples from the batch of each additive being used during our test. (An initial set of samples was collected in glass jars with metal lids. We supplied the host utility with clean, neoprene bottles and they collected a replacement set of these samples in the plastic bottles. The initial set was discarded.)
8)	Southern collected this sample. Because this is an intermittent stream from the clarifying pond, and the clarified water is derived from a long period of wash plant operation, we collected a single sample of this water three days after the coal washing plant test.
9) & 10)	Southern collected both of these samples. Coal refuse was collected with a bucket on a pole as the refuse is dumped off of refuse screens before the coarse and middling refuse are combined and conveyed to a refuse silo. The coarse refuse screen discharges waste from the heavy media vessel, and the middlings refuse screen discharges waste from the heavy media cyclones (see Figure 4-1). Each sample was 50 to 80 lbs of refuse collected in a lined, burlap-type bag. Samples of each stream were taken at 15-minute intervals over a four-hour period of stable plant operation (0200 to 0600).
11)	Southern collected this sample. Fine refuse slurry was sampled at the thickener underflow discharge pipes at the wash plant sump building. A three-quart pitcher was passed through each discharge stream to get a sample and then the catch was transferred to a 5-gal plastic bucket with a sealable lid. Samples of this stream were taken at 15-minute intervals over a four-hour period of stable plant operation (0200 to 0600).

4.3.1 Deviations from the Sampling Plan

The sampling team arrived at the coal washing plant about 2230 on 10/23/94 to prepare the necessary equipment. Modules B and D were in service. We decided to do the bulk solids and water sampling from Module B.

The raw coal feed conveyer belts were on line at 0125. We collected stop-belt samples off of both main raw coal feed belts between 0140 and 0150. We collected approximately equal amounts from both belts; a total of seven bags estimated to weigh 75 pounds each. The four-hour stable operating period for our sampling began at 0200, with the first samples collected at 0215.

Our initial coarse refuse sample was not getting all of the coarse reject. A dual screen is used for this waste stream (see Figure 4-1), and we were accessing only the coarser fraction (~>1 inch) at the upper screen sampling location we had selected. At 0330 we began sampling at a location beneath the lower screen discharge, after the coarser and finer refuse fractions had combined, giving us a true composite fraction of the coarse refuse. We segregated and used only those samples taken from 0330 to 0600 in analyses of the coarse refuse. The unrepresentative coarse samples were held as backup only.

Thickener underflow was apparently flowing from 2 pipes at east side of the slurry bldg. These were the middle two pipes. Discharge from the pipe farthest to the south was much less dense. A wash plant operator informed Southern that one of these sample lines was from C module (out of service and being cleaned), and thus contained very little solids. Therefore the samples collected from 0215 to 0345 had equal parts from D and C module. They were thus diluted with the wrong stream. We discarded these samples. At 0400 we began taking samples from B and D modules in equal parts. This was the sample retained for analyses.

4.3.2 Sample Preparation

Southern prepared Chain of Custody labels for all of the samples collected at the Coal Washing Plant. Two bulk samples (coarse refuse and middling refuse) were taken to Commercial Testing and Engineering Company in Birmingham, AL. There both of these samples were sized, crushed and riffled, and then pulverized to -60 mesh and riffled to yield composite samples. We took 1000 to 1300 lbs of each of these refuse samples and retrieved approximately 2 lb of each of the prepared composite samples.

The raw and cleaned coal samples were divided by Southern in Birmingham to generate splits for the various analyses to be performed on the samples. Slurry and liquid samples were returned to Birmingham in sealed containers. We determined the solids content in the slurries, and prepared composites of each of these samples from which splits were taken for the various analyses to be performed.

4.4 Analytical Results

4.4.1 Size Distributions

Commercial Testing and Engineering Company (CT&E) determined the size in three fractions of the raw coal, coarse refuse, middlings refuse, and cleaned coal. This was done in order to permit us to estimate the relative flow rates of the coarse and middlings streams. The size fractions were selected based on screen sizes used in the coal washing plant to segregate and route the coal to specific circuits. The size data are presented in Table 4-3.

Table 4-3
Size Distributions of Wash Plant Solids

	Percent of Weight in Size Fraction			
Cut point	Raw Coal	Coarse Reject	Middlings Reject	Clean Coal Belt
>8 mm	42.18	88.78	0.07	18.04
8 mm >x>0.8 mm	42.77	10.83	98.68	55.93
<0.8 mm	15.05	0.39	1.25	26.03

The data show that there is an efficient segregation of the raw coal stream into the coarse, middlings, and fine circuits of the coal washing plant. The cleaned coal is also significantly finer than the raw coal. These data were used to estimate the relative proportions of coarse and middling material in the raw coal (described in Section 4.5).

4.4.2 Proximate and Ultimate Analyses

CT&E performed proximate and ultimate analyses on the coal and refuse samples taken from the coal washing plant. Results of proximate analyses are shown in Table 4-4. These data show the coarse and middlings refuse were high ash, low Btu, and high sulfur wastes. But, the fine refuse was relatively high carbon, high Btu material. This agrees with the observations made in Section 4.2 about the inefficient operation of the flotation cells in the fine circuit during our test, causing a higher-than-normal waste of fine coal in this circuit.

We compared the results of the proximate analyses on a dry basis. (This basis is not subject to sample handling artifacts. Furthermore, the moisture contents of the clean coal and raw coal were nearly equal anyway.) The comparison of clean versus raw coal is shown in Table 4-4. The cleaning process resulted in a reduction in ash by 56%, and sulfur by 26%. The heating value of the coal was increased by 13%.

The ultimate analyses are shown in Table 4-5. The relatively high carbon content of the fine refuse is evidence of inefficient separation of coal and waste in this circuit.

Table 4-4
Coal Data - Proximate Analysis
Coal Washing Plant - October 24, 1994

As Received	Raw Coal	Coarse Reject	Middlings Reject	Fine Reject	Clean Coal
% Moisture	2.79	2.89	4.93	1.13	3.22
% Ash	20.15	58.08	60.89	34.56	8.81
% Volatile	34.74	19.37	17.34	27.78	38.71
% Fixed Carbon	42.32	19.66	16.84	36.53	49.26
Btu/lb	11470	4917	3645	9420	13166
% Sulfur	4.13	8.65	11.37	3.33	3.05
Dry Basis					
% Ash	20.73	59.81	64.05	34.95	9.10
% Volatile	35.74	19.95	18.24	28.10	40.00
% Fixed Carbon	43.53	20.24	17.71	36.95	50.90
Btu/lb	11799	5063	3834	9528	13604
% Sulfur	4.25	8.91	11.96	3.37	3.15
MAF Btu	14885	12598	10665	14647	14966

Table 4-5
Coal Data - Ultimate Analysis
Coal Washing Plant - October 24, 1994

As Received	Raw Coal	Coarse Reject	Middlings Reject	Fine Reject	Clean Coal
% Moisture	2.79	2.89	4.93	1.13	3.22
% Carbon	61.91	26.21	19.22	51.70	71.87
% Hydrogen	4.24	2.11	1.66	3.55	4.87
% Nitrogen	1.25	0.69	0.52	1.00	1.39
% Sulfur	4.13	8.65	11.37	3.33	3.05
% Ash	20.15	58.08	60.89	34.56	8.81
% Oxygen (difference)	5.53	1.37	1.41	4.73	6.79
Dry Basis					
% Carbon	63.69	26.99	20.22	52.29	74.26
% Hydrogen	4.36	2.17	1.75	3.59	5.03
% Nitrogen	1.29	0.71	0.55	1.01	1.44
% Sulfur	4.25	8.91	11.96	3.37	3.15
% Ash	20.73	59.81	64.05	34.95	9.10
% Oxygen (difference)	5.68	1.41	1.47	4.79	7.02

4.4.3 Major Elements, Trace Elements, and Anions

CT&E analyzed samples for chlorine, fluorine, and sulfur. Two laboratories analyzed samples for trace and major elements: Galbraith Laboratories, Inc. (GLI) analyzed all solid samples for all 21 target trace and major elements, University of Missouri-Columbia (UM) analyzed all samples for 13 of the trace and major metals measurable by neutron activation analysis.

Results of the analyses of coal and solid refuse samples by CT&E and GLI are given in Table 4-6. (In these calculations, we have used a value of zero for the concentration of elements that were below detection limits. This approach gives minimum recoveries for those elements with indeterminate concentrations.) There are two ways to calculate changes in concentration: on the basis of weight, or on the basis of calorific value. The weight basis is the most straightforward calculation, but the calorific basis is the most meaningful calculation since the heating value of the coal determines its rate of consumption in the generation of steam and power.

On a weight basis, chlorine was enriched by 13% in the coal washing process, sulfur was reduced by 26%, and fluorine was reduced by 54% (a reduction almost equal to the reduction of major elements). These sort of results are similar to our findings at Blacksville No. 2 Coal Washing Plant. When the data are normalized by calorific content, the relative reductions of anions was 2% for chlorine, 36% for sulfur, and 60% for fluorine.

Five major elements quantified in the coal and refuse streams show between 58 and 72% relative reduction between the raw coal and the cleaned coal on a weight basis. If the coal was homogeneous, we would expect the changes in concentrations of each of the major elements to be equal (with the possible exception of iron, which represents as much as 10% of the refuse and should be very efficiently segregated from coal with magnetite-assisted density separation). However, aluminum and titanium are apparently reduced by ~60%, and calcium, magnesium, and iron by ~70%. These results could be due to analytical biases, or suggest different forms of these minerals (either as inclusions in the coal or as extraneous matter). If we assume no bias in the analyses for these elements, the data suggest that more of the iron, calcium, and magnesium are extraneous to the coal than is the case for aluminum and titanium.

Trace element data in Table 4-6 show a wide range of reductions for the 16 target elements. Two reasons for the scatter in the results are 1) data near or below detection limits in some cases, and 2) element-specific variations in the analytical uncertainties. Concentrations below detection prohibited calculation of the reductions in As, Co, and Se. There consistently were analytical difficulties with Be, Cd, Mo, and Sb. Another reason for differences would be the distributions of the elements in the mix of coal and extraneous matter. The best way to judge the reasonableness of the data is through material balance calculations. A discussion of material balances is presented in Section 4.5.

Table 4-6
Coal Data - Trace Elements
Data From Galbraith Laboratories and CT&E

Data From Galbraith Laboratories and CT&E

	Raw Coal	Coarse Reject	Middlings Reject	Fine Reject	Clean Coal	Clean Coal Belt	Raw vs Clean % Removal (weight basis)	Raw vs Clean % Removal (calorific basis)
Chlorine, %	0.199	0.091	0.083	0.17	0.224	0.190	-13%	2%
Sulfur, %	4.25	8.91	11.96	3.37	3.15	3.31	26%	36%
Fluorine, ppm	148	327	209	222	68	71	54%	60%
	ppm							
Arsenic	14.1	45.3	58.3	21	<1.6	3.5		
Boron	411	147.5	179.9	111.2	88.1	105.7	79%	81%
Barium	120	263	665	241	35.6	70.4	70%	74%
Beryllium	1.39	2.82	1.93	1.4	2.1	2.15	-51%	-31%
Cadmium	30.7	27.4	28.3	<19.4	62.1	35.1	-102%	-75%
Cobalt	5.1	12.1	8.7	4.6	<3.0	<2.8		
Chromium	30.5	118	86.4	38.7	20.3	17.9	33%	42%
Copper	19.9	55.3	65.6	8.2	6.8	8.2	66%	70%
Mercury	0.184	0.39	0.41	0.0933	0.072	0.105	61%	66%
Manganese	62	209	190	217	18	53.8	71%	75%
Molybdenum	37.8	51.6	<25.4	<23.1	64.2	30.5	-70%	-47%
Nickel	18.3	73.7	51.9	48.2	11	53.6	40%	48%
Lead	18.2	61.3	48	16.4	1.4	6.45	92%	93%
Antimony	51.4	<8.0	10.8	9.8	47	19.9	9%	21%
Selenium	<0.99	3.5	<1.0	<0.94	<1.1	<1.1		
Vanadium	95.2	324	205	73.3	44.5	50.3	53%	59%
Aluminum	20600	58800	55800	36100	8120	10700	61%	66%
Calcium	3350	6210	7460	9880	1000	1450	70%	74%
Iron	27900	81100	100700	33000	8350	13800	70%	74%
Magnesium	1350	4830	4650	2510	377	608	72%	76%
Titanium	1122	2940	3085	1836	474	619	58%	63%

* dry basis

The clean coal belt sample (a snapshot sample taken at the end of our sampling) provides more reasonable reduction values for lead and antimony, and a value for arsenic. This sample, however, should not really provide the best correspondence with the raw coal sample. These data demonstrate the variability in either the sample consistency or analytical method.

Table 4-7 lists the measurements by UM of the concentrations of the major and trace elements in our target list. These data show a distribution of the elements among the process samples equivalent to what is seen in the GLI data. Mercury is a notable exception to this general finding: the level of mercury in the raw coal as measured by UM is implausibly low. Neutron activation analysis has usually provided poor accuracy for mercury.

Table 4-8 lists the compositions of the additives and water used in the coal washing plant. Magnetite is the only one of this group of samples that has sufficient concentrations of any of the target analytes to be a potential source of the analytes in the cleaned coal. Based on the data in Table 4-6, the reduction of the elements in the cleaned coal (note iron in particular) is apparently unaffected by the magnetite, suggesting efficient recovery of magnetite in the washing process. Furthermore, there is no evidence that the relatively high manganese, cadmium, and fluorine concentrations in the magnetite contaminated the cleaned coal. Of particular interest in our study, mercury levels in the water and process additives were typically four orders of magnitude lower than in the wash plant solids.

4.5 Data Analysis and Interpretation

4.5.1 Mass Balances

The requisite information for conducting mass balances for any process is independent measures of mass flow rates for all process streams that cross a boundary containing the process. That is, internally circulating streams need not be measured, but flows are required for all external input and output streams. For the coal washing plant, the streams for which flows are required for a rigorous mass balance are: 1) raw coal feed, 2) makeup water (raw water and pond return water), 3) solid refuse (coarse plus middlings refuse), 4) slurry discharge (thickener underflow), and 5) cleaned coal product. Section 4.2 describes the plant data we obtained.

Southern measured the flow rate for slurry discharge (thickener underflow) with an ultrasonic mass flow meter. The host utility measured the flow rates of raw coal and cleaned coal. The two streams which were not measured were input water stream, and output solids refuse. Thus, we made two assumptions for the unmeasured streams. We accounted for the mass discharge rate of the solids refuse by assuming a mass balance: solids refuse discharge was set equal to the total refuse (raw coal feed minus the clean coal discharge) minus the fraction of total refuse accounted for in the

Table 4-7
Coal Data - Trace Elements
Data From University of Missouri (INAA)

Data From University of Missouri (INAA)

	Raw Coal	Coarse Reject	Middlings Reject	Fine Reject	Clean Coal	Clean Coal Belt	Raw vs Clean % Removal (weight basis)	[illegible]
Chlorine, %								
Sulfur, %								
Fluorine, ppm								
	ppm							
Arsenic	6.6	24	28.3	9.5	4	3.8	39%	
Boron								
Barium	86	209	568	340	30	61	65%	
Beryllium								
Cadmium								
Cobalt	4.38	13.84	11.29	6.28	2.79	2.89	36%	
Chromium	30.3	118.8	82.5	41.1	12.7	16.1	58%	
Copper								
Mercury	0.049	0.216	0.129	0.088	0.109	0.036	-122%	
Manganese	47.4	198.7	183.2	153.6	20.4	27.1	57%	
Molybdenum	17.9	79	38.8	13.3	5.5	6.7	69%	
Nickel								
Lead								
Antimony	1.32	4.09	2.84	1.26	0.85	1.00	[illegible]	44
Selenium	3.14	16.05	8.08	2.82	1.13	1.85	[illegible]	69%
Vanadium	62	307	191	74	29	50	[illegible]	59%
Aluminum	15600	50600	53400	34000	8900	10100	43%	51%
Calcium	1800	6800	7200	9800	700	[illegible]	61%	66%
Iron	25800	89100	97900	39500	16500	[illegible]	36%	45%
Magnesium								
Titanium	800	2600	2500	1700	500	[illegible]	38%	46%

* Numbers are on dry basis

Table 4-8
Wash Plant Water & Additives Data - Trace Elements
Coal Washing Plant - October 24, 1994

	Feed Water	Anionic Polymer	Frothing Oil	Magnetite	Pond Return Water	Thickener Underflow Liquid
Chlorine, %	0.00121	0.06	0.04	0.0205	0.00120	0.0175
Sulfate, %	0.00343	0.39	<0.01	0.117	0.0066	0.0636
Fluorine, ppm	0.16	11	39	205	0.19	0.45
				ppm		
Arsenic	<0.00300	<0.098	<0.100	9.1	0.00440	0.0038
Boron	<0.228	4.72	2.40	995	<0.228	<0.228
Barium	0.0316	<1.20	<1.22	143.7	0.03360	0.0236
Beryllium	<0.00626	<1.31	<1.34	3.4	0.00701	0.00656
Cadmium	0.0028	<0.74	<0.76	101.9	<0.00136	<0.00136
Cobalt	<0.00473	<1.69	<1.72	18.5	0.00550	<0.00473
Chromium	<0.00340	0.20	<0.24	20.5	0.00701	<0.00340
Copper	<0.00605	5.51	<1.62	35.9	0.0118	<0.00605
Mercury	1.14E-05	1.16E-04	1.20E-05	3.28E-05	<0.0000104	0.0000146
Manganese	<0.00215	0.39	0.80	1954.80	<0.00215	0.0679
Molybdenum	<0.00473	<5.9	<6.02	<2.4	0.00743	0.0434
Nickel	<0.00370	<2.9	<3.01	75.3	0.00379	0.00679
Lead	<0.0610	<0.100	0.120	25.7	<0.0610	<0.0610
Antimony	0.00380	<9.05	<9.23	19.6	<0.0498	<0.0498
Selenium	<1.0	<1.3	<1.2	67.5	<0.5272	<0.5272
Vanadium	<0.00258	<0.72	0.60	480.3	0.00261	0.00366
Aluminum	<0.123	<7.28	<7.42	957	<0.123	<0.123
Calcium	47.6	<2.55	<2.61	2070	49.5	119
Iron	0.218	8.66	75.1	7.27E+05	<0.143	<0.143
Magnesium	9.28	0.59	<0.50	1091	10.5	15.6
Titanium	<0.00184	<1.96	<2.00	752	<0.00184	0.0157

thickener underflow. We do not have a measure of the makeup water flow rate. We assumed the makeup water flow rate was equal to the flow rate of water discharged in the thickener underflow. (See Table 4-1 for the calculated flow rate from the thickener underflow.)

The solids refuse represented another mass balance problem, because we sampled separately the coarse and middlings refuse streams. We had no flow rates for these streams that would permit an easy computation of the relative contributions of these separate components of refuse. Following the advice of CQ, Inc., we attempted to use the size distributions of the raw coal, coarse refuse, middlings refuse, and cleaned coal to provide a means of estimating the relative flow rates of these fractions.

There are two ways to use the size distributions shown in Table 4-3. The simplest approach is to assume the relative mass flow rates of the coarse and middlings refuse can be deduced directly from only the raw coal and cleaned coal size distributions. The raw coal data indicate that equal fractions of the coal should pass to the coarse circuit and the middlings circuit (~42% of raw coal to each). The clean coal data show there to be three times the clean coal in the middling fraction than in the coarse fraction. Therefore, you could assume there was three times the refuse in the coarse circuit as in the middlings circuit. This simple approach does not take into account any attrition of the coal in the cleaning process, but is a straightforward way to estimate relative flows.

A more rigorous approach is to solve a series of simultaneous equations using the size distributions of coarse and middlings fractions as well as the raw and cleaned coals. The unknowns of interest are the fractions of coarse and middling refuse, which combined with the clean coal to produce the raw coal size distribution. We chose to solve the equations without constraining the fraction of the clean coal, even though we had an independent measurement that indicated the clean coal mass flow rate was 73.6% of the raw coal feed rate. In addition, we did not include the thickener underflow in this calculation. The solution to these equations gave a 5:1 ratio of coarse refuse to middlings refuse.

We did not include the water streams in the mass balance calculations since trace elements in the water streams were either below detection levels or orders of magnitude lower than in the solids.

Without measured flow rates for all the input and output streams, and with the uncertainties in the thickener underflow, we decided to calculate multiple mass balances based on different combinations of measurements and assumptions. Three of the different distributions of refuse among the three refuse streams {coarse, middlings, and fine (thickener underflow)} for the mass balance calculations are as follows:

A. The calculated split of the coarse coal to the middlings coal was 5:1, determined by solving simultaneous equations based on <u>size distributions</u>. The measured thickener underflow solids was 15.84% of the raw coal, or 61% of the total refuse. Therefore, the size distribution of the samples and measured flow rate

of thickener underflow give a distribution by weight of the refuse among the three discharge streams as follows:

1. Coarse fraction = 31.2%
2. Middlings fraction = 7.8%
3. Fine rejects = 61%

B. The plant design data show a lower expected total refuse (14.8% vs. 26.4%) and a different split from the three refuse streams:

1. Coarse fraction = 37.5%
2. Middlings fraction = 51.0%
3. Fine rejects = 11.5%

C. Solving a set of simultaneous equations for the fractions of the refuse in the three refuse streams using values from proximate analyses (ash, Btu, and sulfur), and using 0.74 as the fraction the clean coal is of the raw coal, the results are as follows:

1. Coarse fraction = 70.2%
2. Middlings fraction = 0%
3. Fine rejects = 29.8%

Scenario A) can be questioned because of the uncertainty of the measured thickener underflow discharge rate. Scenario B) is unlikely to represent current operation of the wash plant with Costain coal, since we have a much higher total reject fraction than in the design basis and operators report distinctive experience with different coals. Scenario C) for material balance calculations is based on the proximate analyses in which we have good confidence. Using scenario C) presents an implausible result for the middlings fraction, however. These scenarios do represent a wide range of combinations for the refuse. Nevertheless, combined refuse represents only 26.4% of the material, so variations in the distribution of the refuse may be hidden by analytical variability.

Results of three mass balance calculations are shown in Table 4-9. We used the results from CT&E and GLI (Table 4-6) for these calculations. The results are plotted in Figure 4-2 as recovery, defined as the sum of the output streams (clean coal + combined refuse) divided by the input stream (raw coal). The elements for which recoveries were always below 70% were B and Co. Recovery of elements As, Cu, and Hg were below 70% with the size distribution scenario, and Sb was below 70% recovery with the proximate analysis scenario. The elements for which recoveries were above 130% were Be, Cd, Mo, Ni (in one scenario), and Cr (in one scenario).

We have reason to believe the mercury value reported by Galbraith Laboratories in the cleaned coal is low. We had some samples of cleaned coal analyzed by Brooks

Table 4-9
Coal Data - Trace Elements Mass Balance Summary
Coal Washing Plant - October 24, 1994

	RECOVERY		
	Scenario for Combining Refuse Streams		
	Size Distributions	Design Data	Proximate Analysis
Chlorine	101%	96%	99%
Sulfur	90%	116%	102%
Fluorine	79%	79%	89%
Arsenic	59%	92%	74%
Boron	24%	26%	25%
Barium	84%	124%	81%
Beryllium	147%	153%	159%
Cadmium	158%	170%	166%
Cobalt	38%	49%	53%
Chromium	107%	129%	134%
Copper	61%	98%	82%
Mercury	59%	81%	74%
Manganese	112%	107%	115%
Molybdenum	136%	139%	151%
Nickel	126%	130%	144%
Lead	53%	77%	78%
Antimony	71%	71%	69%
Selenium	ND	ND	ND
Vanadium	79%	99%	106%
Aluminum	86%	99%	98%
Calcium	89%	79%	82%
Iron	72%	103%	88%
Magnesium	87%	108%	105%
Titanium	85%	99%	95%

ND = non-detects preclude calculation

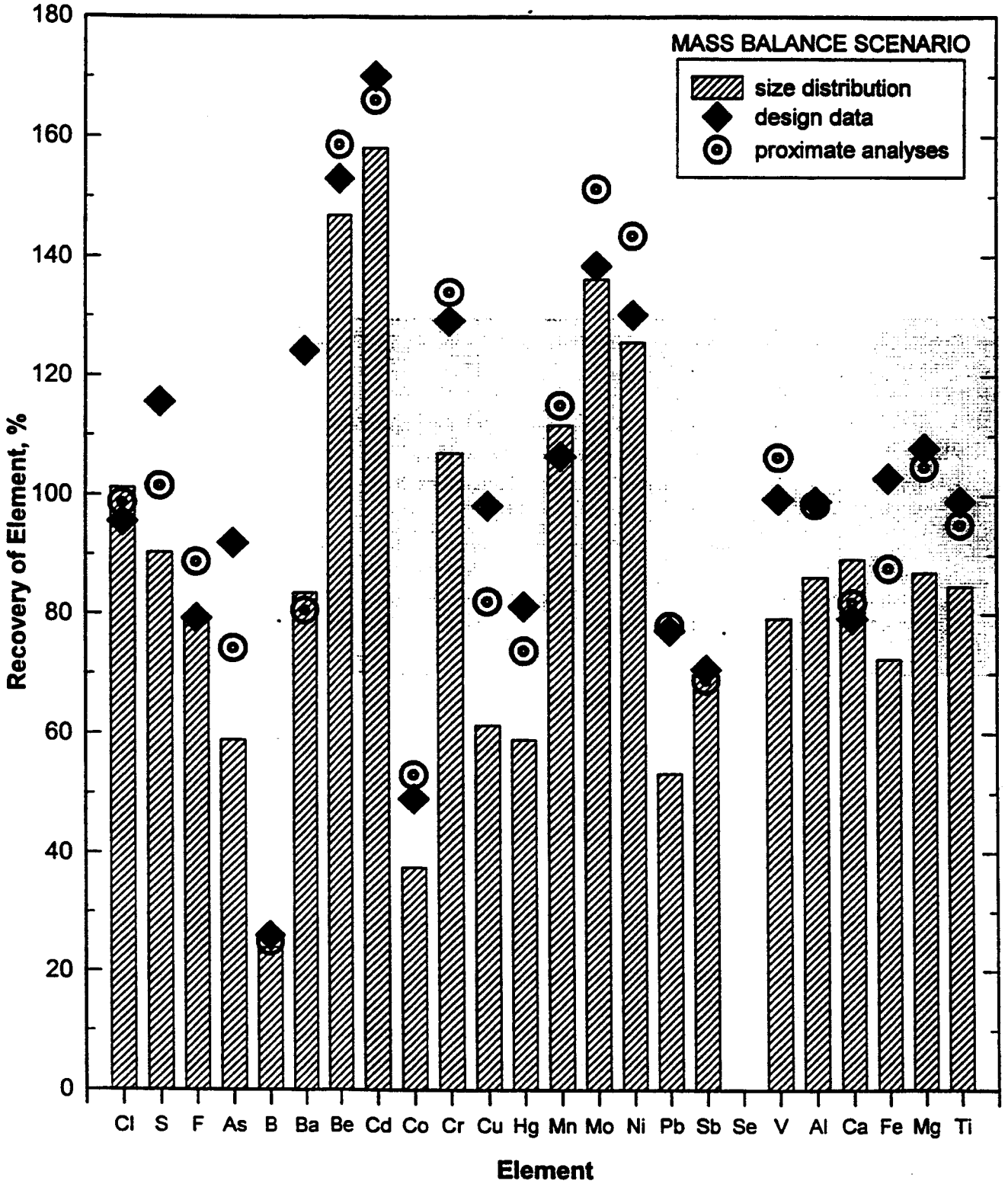


Figure 4-2. The recovery of elements, defined as the ratio of the element concentrations in outlet and inlet solids, determined by three different mass balance scenarios. (Values less than the detection limit were treated as zero concentration.)

Rand, Ltd. (BR). The results thus obtained were consistently higher than the GLI data, by as much as 35%. We believe the reason for this difference is the use of different sample digestion procedures by the two labs: the procedure by GLI does not completely digest the coal sample, whereas BR uses a more aggressive digestion with perchloric acid to achieve total digestion of the sample. Therefore, the low mercury recoveries in Table 4-9 and Figure 4-2 are probably the results of incomplete sample digestion. This uncertainty must also cloud some of the other analytical results.

4.5.2 Beneficiation Attributed to Process Subsystems

Data from the analyses show that even though we may attribute up to 61% of the refuse to the fine circuit of the wash plant, the coarse circuits are responsible for the vast majority of the removal of non-volatile material, including anions and trace elements, from the raw coal. Concentrations of trace elements in the extraneous matter that is mingled with the coal are higher than in the coal itself.

The enrichment in sulfur and iron in the middlings fraction is greater than the substantial enrichment in the coarse fraction (see Table 4-4). These findings demonstrate that both of these coarser circuits are needed to efficiently remove the extraneous mineral matter from the coal.

The coal washing plant may have operated with abnormal inefficiency in the fine circuit, as reported in Section 4.2. From our test results, the fine circuit did not significantly contribute to the reduction of sulfur or trace elements in the coal.

4.5.3 Day-to-Day Variability of Coal Cleaning

Another way to analyze the wash plant data is to consider day-to-day variability in performance. We have already reported (in Section 4.2) that the degree of cleaning in terms of the percentage weight of raw coal removed in the washing plant was consistent for a five-day period from October 24 through October 28, 1994. The refuse fraction ranged from 26.3 to 27.8%.

We analyzed a composite sample of raw coal and clean coal taken from the autosamplers on each of these streams for the four-day period. Tables 4-10 and 4-11 show the proximate and ultimate analyses, respectively. The data show very consistent raw coal quality, and very consistent cleaning. The reduction in ash content averaged 59% on a weight basis, or 65% on a calorific basis. Reductions in most of the trace elements are essentially the same as the reduction in ash content, so the data in Table 4-10 suggest a consistent reduction in trace elements by 65% on a calorific basis.

More detailed discussion of the trace element content of raw and cleaned coal over the period from October 25 through October 28 is given in Section 5.5.1.

Table 4-10
Coal Data - Proximate Analysis
Coal Washing Plant - October 24 - 28, 1994

	24-Oct		25-Oct		26-Oct		27-Oct		28-Oct		Average		σ	
As Received	Raw	Clean	Raw	Clean	Raw	Clean	Raw	Clean	Raw	Clean	Raw	Clean	Raw	Clean
% Moisture	2.79	3.22	3.64	5.68	3.21	5.86	3.58	4.55	4.00	5.32	3.44	4.93	0.46	1.08
% Ash	20.15	8.81	22.65	8.15	20.27	7.98	19.10	8.08	19.74	8.20	20.38	8.24	1.35	0.33
% Volatile	34.74	38.71	32.83	38.64	33.39	37.95	34.17	38.97	34.65	38.13	33.96	38.48	0.83	0.42
% Fixed Carbon	42.32	49.26	40.88	47.53	43.13	48.21	43.15	48.40	41.61	48.35	42.22	48.35	0.98	0.62
Btu/lb	11470	13166	10911	12791	11326	12993	11467	13001	11280	13179	11291	13026	228	158
% Sulfur	4.13	3.05	4.86	2.73	4.28	2.80	4.36	2.84	4.63	2.78	4.45	2.84	0.29	0.12
Dry Basis														
% Ash	20.73	9.10	23.51	8.64	20.94	8.48	19.81	8.46	20.56	8.66	21.11	8.67	1.41	0.26
% Volatile	35.74	40.00	34.07	40.97	34.50	40.31	35.44	40.83	36.09	40.27	35.17	40.48	0.85	0.41
% Fixed Carbon	43.53	50.90	42.42	50.39	44.56	51.21	44.75	50.71	43.35	51.07	43.72	50.86	0.95	0.32
Btu/lb	11799	13604	11323	13561	11702	13802	11893	13621	11750	13919	11693	13701	219	153
% Sulfur	4.25	3.15	5.04	2.89	4.42	2.97	4.52	2.98	4.82	2.94	4.61	2.99	0.32	0.10
MAF Btu	14885	14966	14803	14843	14801	15081	14831	14880	14791	15239	14822	15002	38	161

Table 4-11
Coal Data - Ultimate Analysis
Coal Washing Plant - October 24 - 28, 1994

	24-Oct		25-Oct		26-Oct		27-Oct		28-Oct		Average		σ	
As Received	Raw	Clean	Raw	Clean	Raw	Clean	Raw	Clean	Raw	Clean	Raw	Clean	Raw	Clean
% Moisture	2.79	3.22	3.64	5.68	3.21	5.86	3.58	4.55	4.00	5.32	3.44	4.93	0.46	1.08
% Carbon	61.91	71.87	59.32	70.58	61.20	67.91	61.74	71.03	60.96	71.63	61.03	70.60	1.03	1.59
% Hydrogen	4.24	4.87	4.02	4.66	4.23	4.67	4.33	4.78	4.28	4.77	4.22	4.75	0.12	0.09
% Nitrogen	1.25	1.39	1.18	1.35	1.26	1.33	1.23	1.35	1.18	1.38	1.22	1.36	0.04	0.02
% Sulfur	4.13	3.05	4.86	2.73	4.28	2.80	4.36	2.84	4.63	2.78	4.45	2.84	0.29	0.12
% Ash	20.15	8.81	22.65	8.15	20.27	7.98	19.10	8.08	19.74	8.20	20.38	8.24	1.35	0.33
% Oxygen (difference)	5.53	6.79	4.33	6.85	5.55	9.45	5.66	7.37	5.21	5.92	5.26	7.28	0.54	1.32
% Chlorine	0.19	0.21	0.19	0.25	0.18	0.25	0.18	0.21	0.19	0.22	0.19	0.23	0.01	0.02
% Flourine	0.0144	0.0066	0.0130	0.0065	0.0144	0.0065	0.0150	0.0063	0.0152	0.0050	0.0144	0.0062	0.0009	0.0007
Dry Basis														
% Carbon	63.69	74.26	61.56	74.83	63.23	72.14	64.03	74.42	63.50	75.66	63.20	74.26	0.96	1.30
% Hydrogen	4.36	5.03	4.17	4.94	4.37	4.96	4.49	5.01	4.46	5.04	4.37	5.00	0.13	0.04
% Nitrogen	1.29	1.44	1.22	1.43	1.30	1.41	1.28	1.41	1.23	1.46	1.26	1.43	0.04	0.02
% Sulfur	4.25	3.15	5.04	2.89	4.42	2.97	4.52	2.98	4.82	2.94	4.61	2.99	0.32	0.10
% Ash	20.73	9.10	23.51	8.64	20.94	8.48	19.81	8.46	20.56	8.66	21.11	8.67	1.41	0.26
% Oxygen (difference)	5.68	7.02	4.50	7.27	5.74	10.04	5.87	7.72	5.43	6.24	5.44	7.66	0.55	1.44
% Chlorine	0.20	0.22	0.20	0.27	0.19	0.22	0.19	0.23	0.20	0.21	0.20	0.23	0.01	0.02
% Flourine	0.0148	0.0068	0.0134	0.0069	0.0149	0.0066	0.0156	0.0052	0.0157	0.0068	0.0149	0.0065	0.0009	0.0007

5.0 POWER PLANT TEST

5.1 Plant and Scrubber Description

The host coal-fired power plant is located in the southeastern United States. This testing was conducted on Unit 1 of the power plant. Unit 1 is nominally 700 MW, and is equipped with cold-side electrostatic precipitator (ESP) for the removal of fly ash and venturi scrubber for the removal of both fly ash and SO_2 from the flue gas. The effluent from the scrubber is exhausted through an independent stack.

The plant burns coal from western Kentucky. There are several mines that supply coal by barge, rail, and truck. For this test, arrangements were made for a supply of coal adequate for seven days of continuous operation from the Costain mine. The coal was taken from a single seam in the mine to further improve the consistency of the coal for these tests.

Unit 1 was the subject of this investigation. This unit has four features that affect emissions of the chemical substances of interest:

1) The coal is beneficiated by washing to remove a substantial fraction of mineral matter and sulfur.
2) The coal is burned in a cyclone furnace, with the attendant high temperature of combustion and the emission of a high concentration of nitrogen oxides, but the emission of a lower fraction of the ash than occurs with wall or tangential firing. (During a test in August, 1993 it was determined that 66 to 73% of the coal ash was accounted for as bottom ash and 27 to 34% as fly ash.)
3) The fly ash evolved from the boiler is first subjected to collection in an ESP. The ESP, however, remains from the era prior to scrubber addition, and it is not a unit with high collection efficiency.
4) The residual fly ash at the outlet of the ESP and the SO_2 are subject to capture in a venturi scrubber with limestone as the basic reactant. Design specifications of the scrubber are to achieve particulate removal by 94% and SO_2 removal by 84%.

The general layout of the plant is depicted in Figures 5-1 and 5-2. The locations at which flue gas samples were withdrawn are also shown in these figures. The location of the ID fans at the base of the stack leads to highly negative static gas pressures at the sampling locations of interest at the inlets and outlets of the scrubber. At full load we measured the static pressure at the scrubber inlet to be -19 in. H_2O, and at the scrubber outlet -32 in. H_2O.

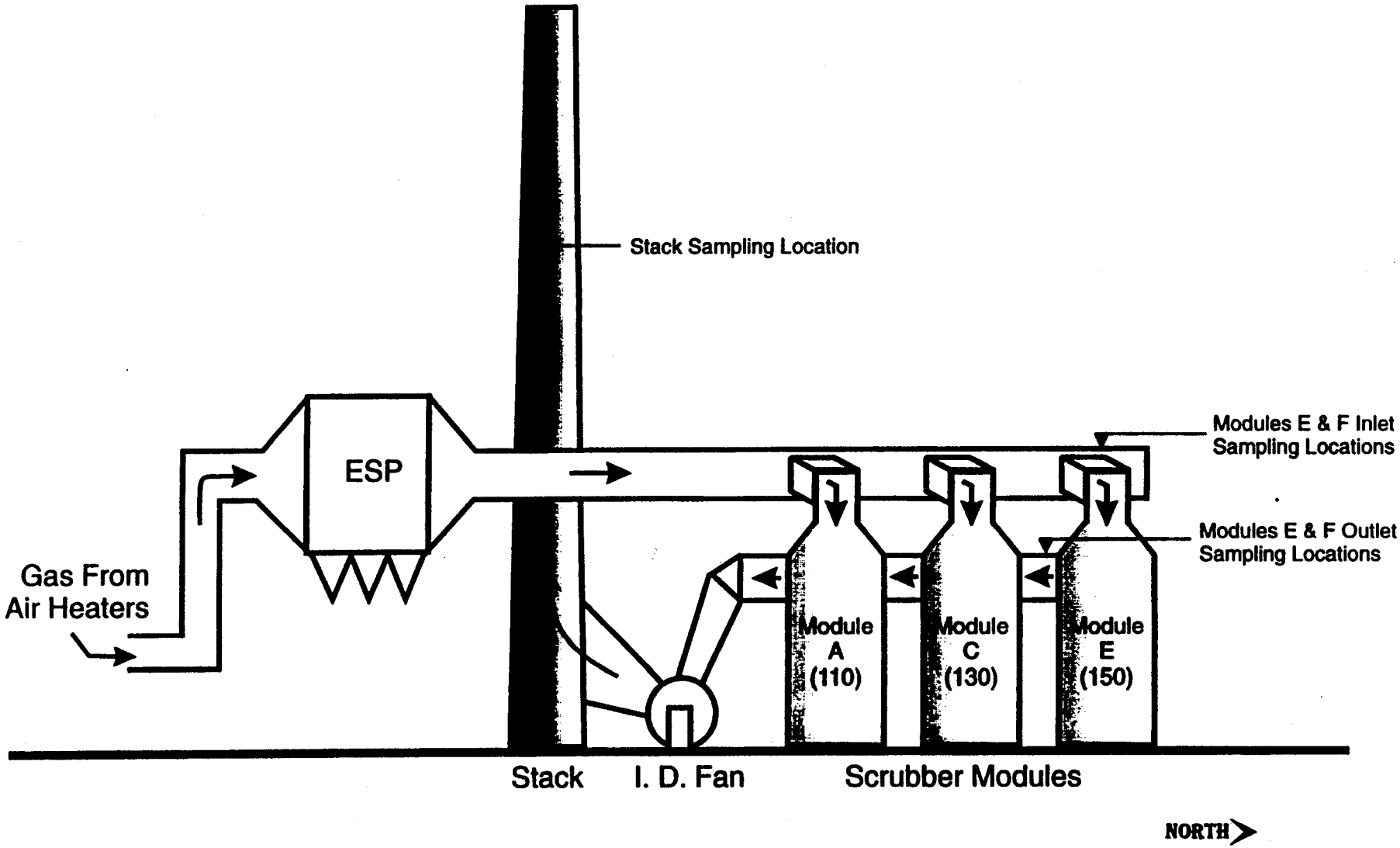


Figure 5-1. Elevation View of the Unit 1 ESP, Scrubber, and Stack

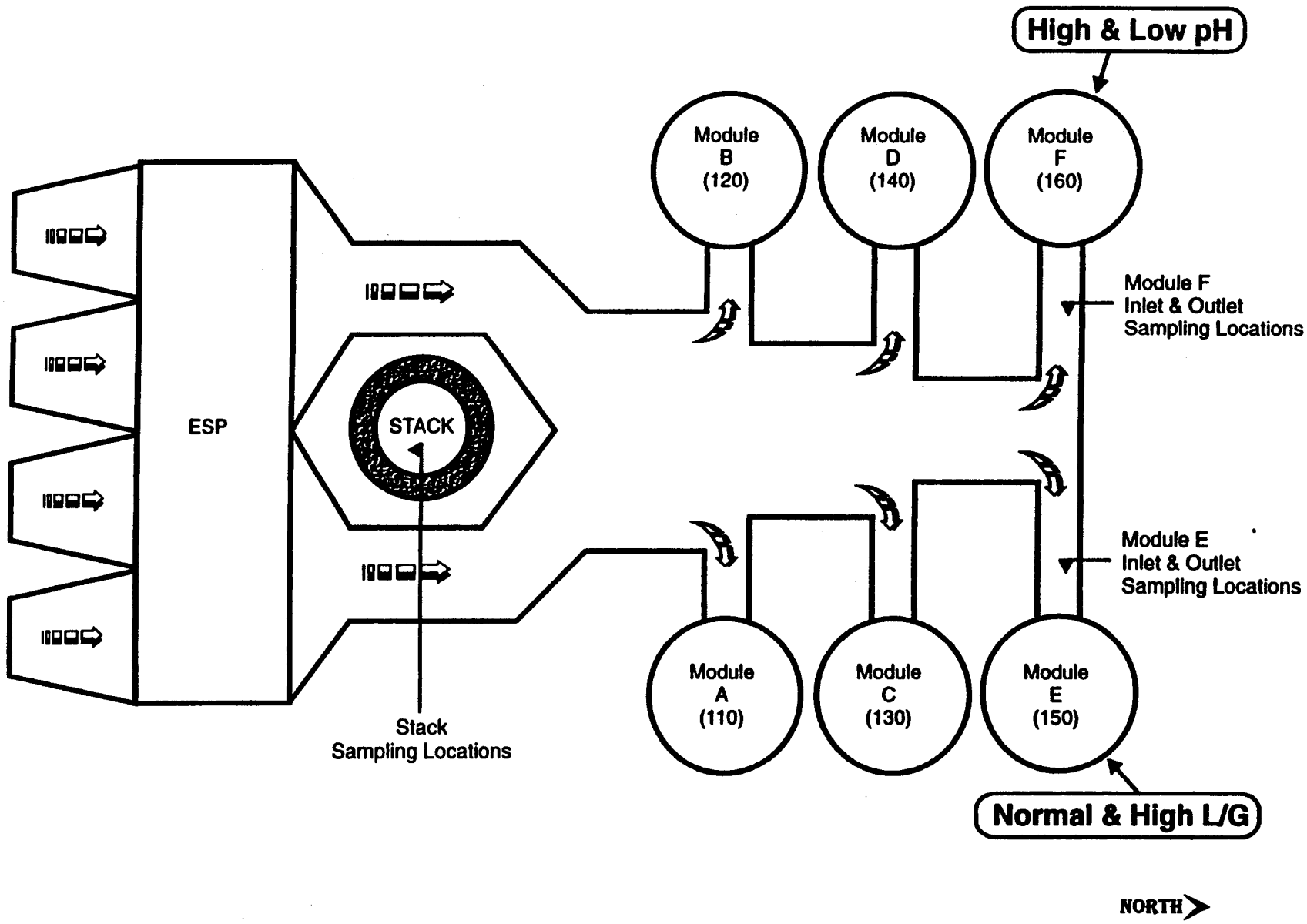


Figure 5-2. Plan View of the Unit 1 ESP, Scrubber, and Stack

Average temperature of flue gases at the inlet of the ESP was measured to be approximately 325 °F. The scrubber, of course, causes a very large cooling effect. There is no reheater for the flue gas beyond the scrubber, but compression from the ID fans between the scrubber and the stack causes some reversal of the cooling that occurs in the scrubber. We measured the temperature of flue gases in the stack to be 132 °F.

The ESP consists of four chambers (A, B, C, and D) of equal size with a total electrode area of 237,760 ft^2. At the total gas flow measured at the ESP inlet during August, 1993 (2,340,000 acfm), the specific collecting area is about 100 ft^2/1000 acfm. Such a low SCA cannot be expected to produce an efficient collection of fly ash. Moreover, the internal mechanical condition of the ESP is said to be poor. Because of the defects and because of the present existence of the scrubber, the ESP is not depended upon for high performance in the removal of particulate matter. The scrubber, added as a retrofit to the original construction, is rated to remove 90% or more of the particulate matter from the flue gas. A test in the summer of 1990 by personnel of Southern showed that the mass collection efficiency of the ESP was about 30%. For operation with the "baseline" coal of that time, presumably similar to the coal used in this study, particulate concentrations at three locations in the gas stream were as follows:

ESP inlet	0.98 gr/dscf (100%)
Scrubber inlet	0.69 gr/dscf (70%)
Stack	0.018 gr/dscf (1.8%)

The combination of ESP and scrubber lowered the particulate concentration by 98.2% of its ESP inlet value according to these measurements.

Two round ducts on either side of the stack carry flue gas from the east and west halves of the ESP to the scrubber; a single round duct carries the gas beyond the union of the two. The latter round duct then feeds into the rectangular trunk line, which has branches that lead to the individual scrubbing modules, as shown in Figure 5-2.

The scrubber was constructed as a retrofit to the original components of the plant. It consists of six venturi modules in an arrangement shown in Figure 5-2. The scrubber was intended to remove 84% or more of the SO_2 and 90% of the fly ash beyond the ESP.

Scrubber sorbent is prepared at the plant by pulverizing limestone in a wet ball mill to produce a slurry that contains about 27.5% solids. Additional water is added to this slurry to maintain a solids concentration in the recycle tanks around 12%. The design feed rate of limestone, set at a time when higher-sulfur coals were in use, was 27 tons/hr. The actual feed rate of limestone is governed by the pH of the recycle tanks. It conforms to a Ca/S mole ratio of about 1.05, or perhaps sometimes as high as 1.10. For a 3.0%-sulfur coal, a Ca/S ratio of 1.05 would correspond to a limestone feed rate of about 24 tons/hr.

Normally, five scrubber modules are in service, and one is in maintenance. Customarily four of the active modules are operated at "high" pH and the fifth is operated at "low" pH. Fresh limestone slurry is supplied only to the high-pH modules; spent slurry from the high-pH modules performs the scrubbing in the low-pH module. The low-pH module is one on the west side of the unit (B, D, or F as seen in Figure 5-2). During this test the high pH was typically 5.7 and the low pH was typically 5.1.

The scrubber is operated with forced oxidation to produce a waste product in which gypsum rather than calcium sulfite is dominant. Waste liquor and solids from the recycle tanks are pumped to an effluent tank and then to an ash pond. At one time there were thickeners for concentrating the slurry prior to disposal, but the thickeners are no longer in use.

5.2 Plant Operation

The main constraint placed on Unit 1 by our test program was the exclusive use of Costain coal. The delivery schedule of the coal prevented the coal washing plant from building up any backlog of this coal. The plant staff were faced with the breakdown of the coal unloader during the test period, which threatened the supply of coal. Through their extra efforts, 31,804 tons of Costain coal were unloaded and 23,335 tons of cleaned Costain coal were fed to the Unit 1 boiler during our test period. This supply was adequate to cover the entire elapsed time of our test.

The gross generating load on Unit 1 was kept at 652 MW ± 3 MW throughout our sampling periods. The record of Unit 1 load is shown in Figure 5-3. In addition to holding the load constant, soot blowing of air heaters was suspended during our sampling times to eliminate the effect of this erratic ash loading from our flue gas measurements. Sootblowers were operated before we began sampling in the morning, and we interrupted our sampling at midday to allow for one hour of sootblowing.

Our test program called for three operating conditions in the scrubber. We wanted to test across a scrubber module at the normal liquid-to-gas ratio (L/G) and at a higher L/G each day of our test. We also wanted to test across another scrubber module operated at low and high pH levels on alternate days. Plant operations staff enabled us to test all of these conditions. The adjustment in L/G was made by reducing the flue gas flow through a scrubber module (Module E) while maintaining the slurry feed rate. The flue gas flow was reduced by closing a louver-type damper at the inlet to the module. This operation typically took less than 15 minutes, and was done at midday. Figure 5-4 shows the venturi plumb bob position for Module E. The plumb bob position changes automatically to maintain a constant differential pressure across the venturi. The change in position corresponds to the change in flow rate through the module.

The change in scrubber pH was made over night on Module F. The module operated at low pH on the first and third test days, and high pH on the second and fourth test days. Figure 5-5 shows the recycle tank pH for Modules E and F.

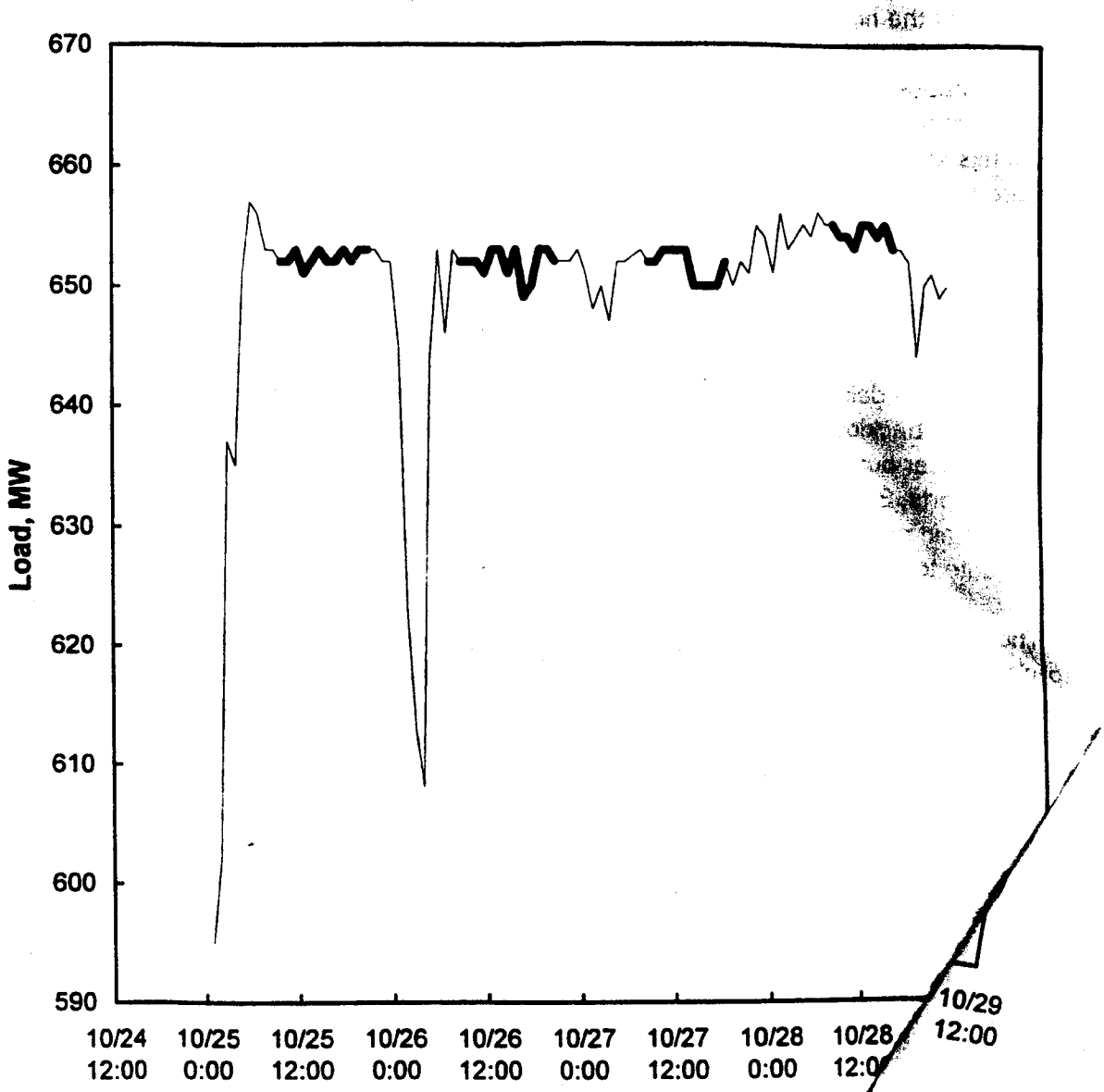


Figure 5-3. The gross generating load for Unit 1 durin[illegible]od. The bold portions of the trace are periods during which w[illegible] gas samples.

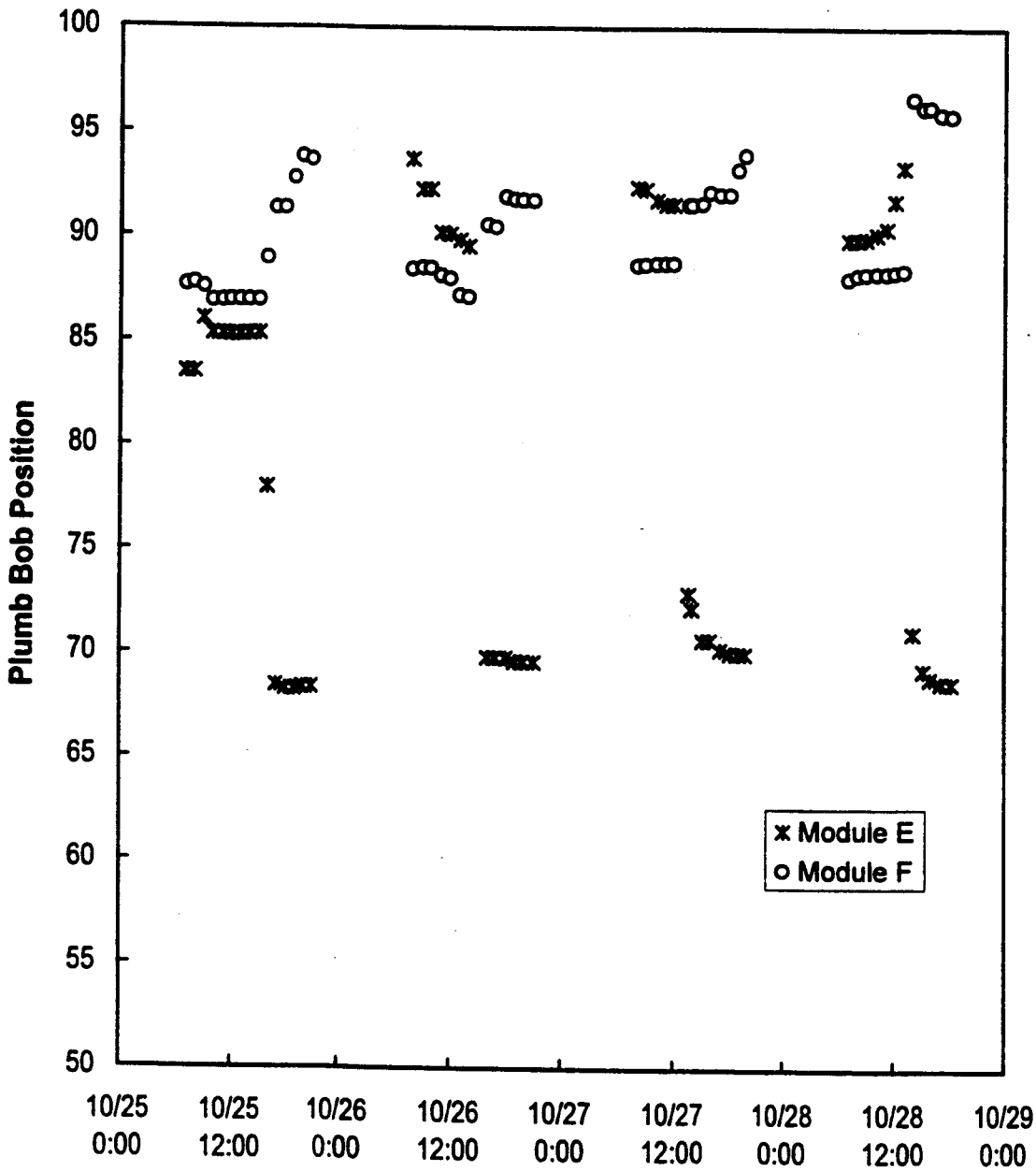


Figure 5-4. The position of the venturi plumb bob for Modules E and F. Daily changes in L/G are seen in the Module E data.

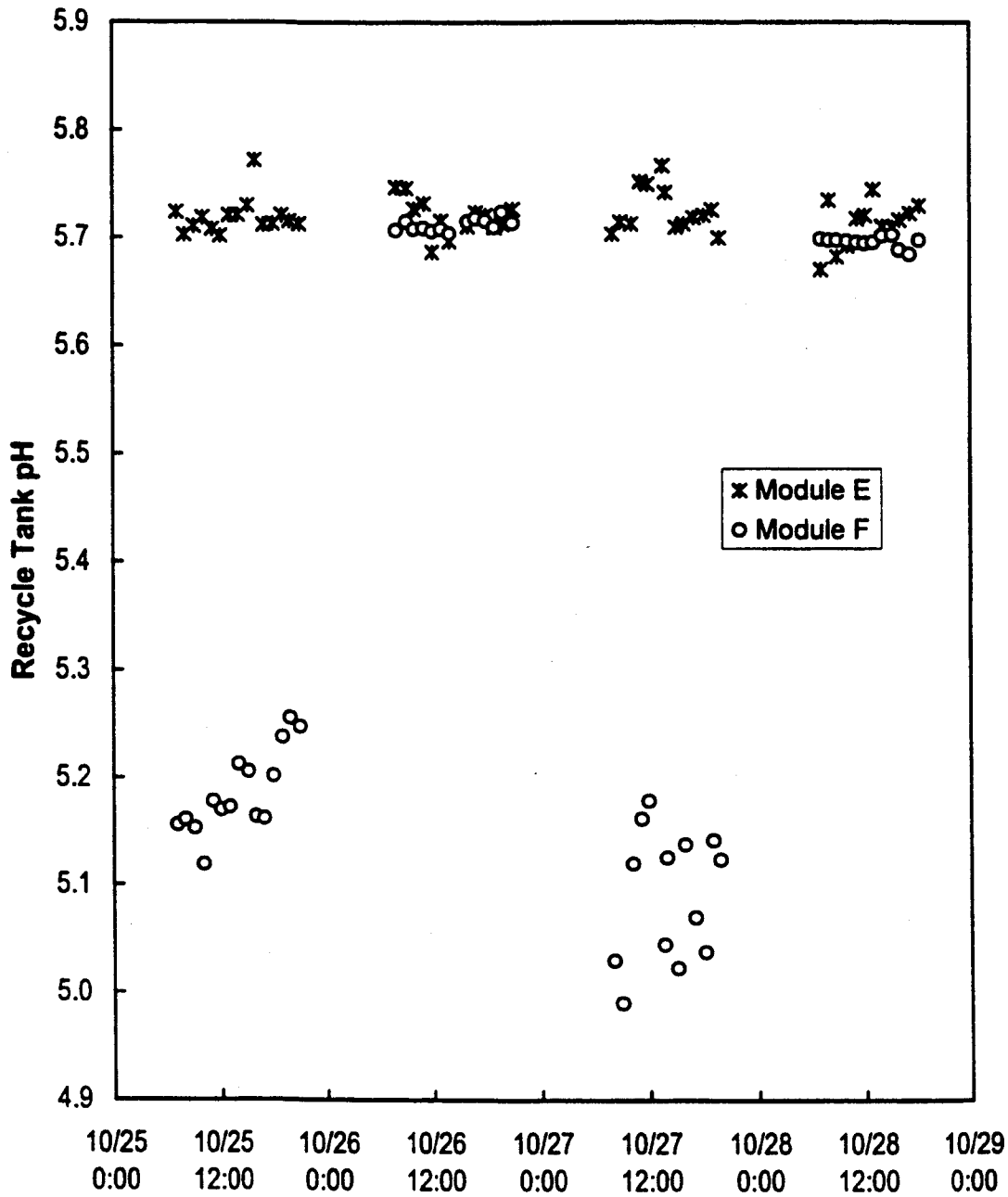


Figure 5-5. Values of pH in the recycle tanks of Modules E and F. These data show the pH in Module F was changed from the normal level of ~5.7 to the low level of ~5.1 on alternate days.

Appendix D contains tables of the boiler, scrubber, and CEM system data recorded during the period of our test. Other than the operational changes in the scrubber modules and the restrictions on sootblowing, Unit 1 boiler and scrubber systems operated during our test program as they would normally operate. The operators maintained very stable conditions during our test periods. Southern used portable computers to acquire the Unit 1 and scrubber operating data from printer ports on the plant data acquisition systems (separate systems for the Unit 1 boiler/turbine/generator and the Unit 1 scrubber). We had printouts of data sheets from the plant systems prepared as a backup to the computer down-link. We also obtained data from the Unit 1 continuous emissions monitoring (CEM) system: this system monitors SO_2 concentration, NO_x concentration, and total flow rate of flue gas in the stack of Unit 1. Data from the CEM instruments are plotted in Figure 5-6.

5.3 Sampling

Samples to be taken during this program were comprised of both flue gas and process liquids and solids. Flue gas samples were taken to characterize the performance of selected scrubber modules with regard to control of particulate matter, acid gases, mercury and other selected metals at two operating pH levels and at two values of L/G. Additional flue gas samples were taken at the stack to characterize the net stack emissions of particulate, acid gases, mercury and selected metals from the unit.

5.3.1 Sampling Locations and Approaches

5.3.1.1 Flue Gases

Four sampling locations used this program were as follows:

1) the inlet to Scrubber Module E,
2) the outlet of Scrubber Module E,
3) the outlet of Scrubber Module F, and
4) the stack.

Sampling at the inlet duct to Module F was eliminated in our plan as its location was symmetrical with Module E and data from the latter could suffice for our analyses. The inlet gas flow to Module F was measured, however.

Scrubber inlet sampling was done through vertical ports at the top of the module inlet duct. The inlet ducts to the scrubber modules are 10 feet wide by 12.5 feet deep. Modules E and F each have six ports (4-inch pipe nipples that are 24 inches long) across the top of the duct. The spacings are 17.1 inches port-to-port while the standard traverse spacings should be 20 inches. Thus, the ports are not quite at the proper locations for a standard traverse but they are close enough that the difference should not be significant.

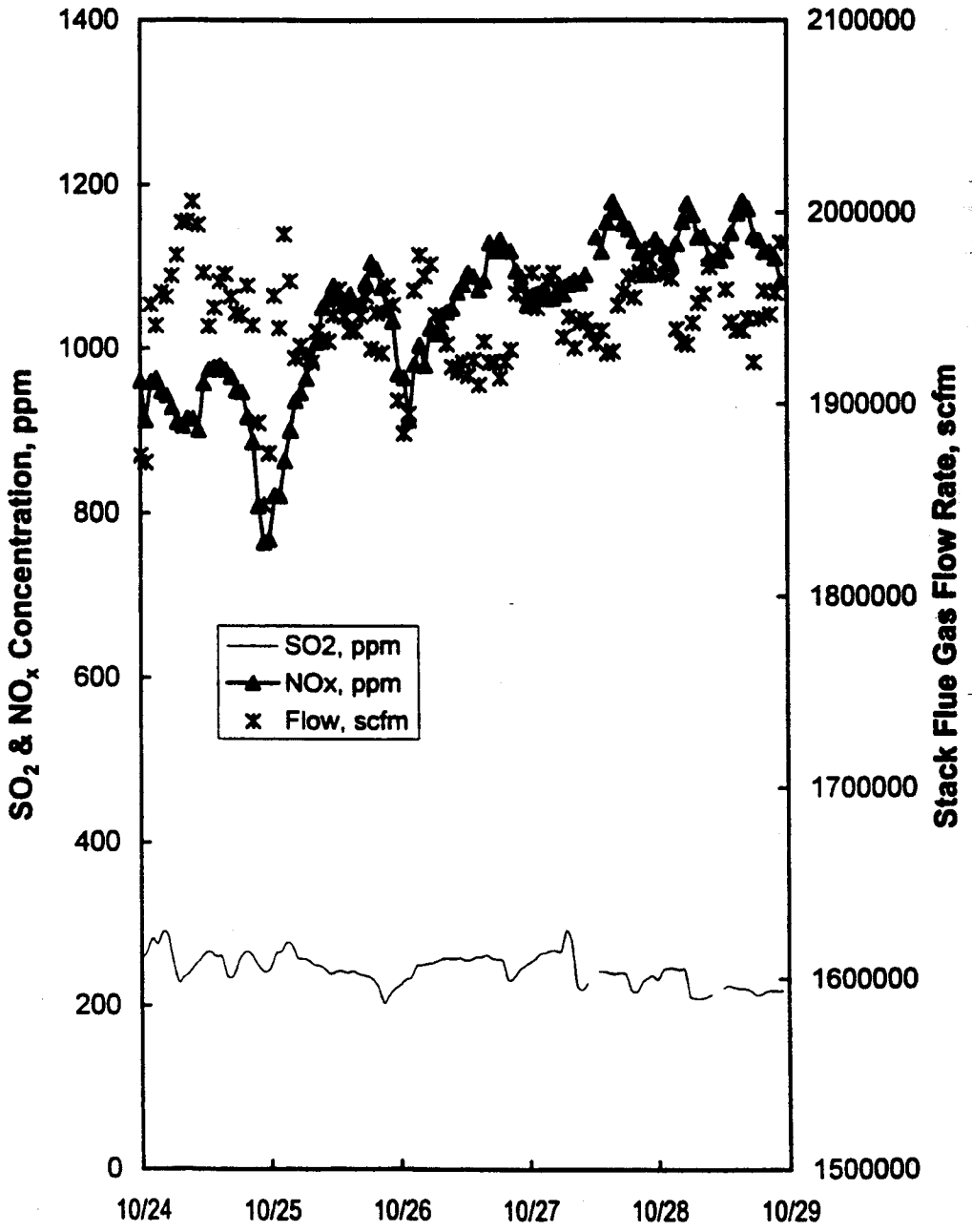


Figure 5-6. Data from the Unit 1 continuous emissions monitoring system for the period including the four days of our flue gas sampling.

Scrubber outlet sampling was done through horizontal ports on the sides of the mist eliminator outlet plenums. These sampling locations are illustrated in Figures 5-1 and 5-2. The scrubber module outlet ducts are 26-feet wide by 16-feet deep. The east side of the ducts on Modules E and F have 12-foot clearances to the outer wall of the adjacent modules. The maximum insertion depth into the duct that we could achieve was about 106 inches because of the limited external clearance and the thickness of the duct walls. The standard traverse pattern for a 40-point traverse (5 ports by 4 points from each side of the duct) calls for the innermost point to be 136.5 inches into the duct with a point-to-point spacing of 39 inches. The host utility put 5 ports in a vertical line on both the north and south walls of the scrubber outlet ducts, and an overhead trolley above each set of ports to support our probes. Sampling on Module E was done from these five horizontal ports in vertical rows on each side of the duct, with half the traverse done from each side. We were not able to reach the point farthest into the duct. In addition, the bottom of the scrubber outlet duct is about 1.5 ft below the grating level. The center-line of the lowest port should be about 19 inches above the bottom of the duct. Since this was rendered inaccessible by the grating, the lowest traverse line was about a foot higher than the standard location to allow room above the grating for the probe and filter assembly.

The stack had four ports at 90° to one another at the 250-foot level which could be used for sampling with those methods that required traversing the duct. However, one of the four was effectively blocked from use by permanently mounted structures adjacent to it that precluded access with probes of the length needed for traverse-type sampling. Additional ports were available at the stack 250-foot level, and were used for the sampling methods that did not require a traverse. The layout of the ports at the stack sampling location is shown in Figure 5-7.

The planned sampling schedule for each day of testing is provided in Figure 5-8. The times shown in Figure 5-8 indicate the overall time frames in which the samples were to be taken, including time for port-to-port moves in traversing. The planned sampling durations were shorter than the times shown in the figure and are provided in Table 5-1. Details of the flue gas sampling activities are provided in Section 5.3.2.

Table 5-1 also lists the manual flue gas sampling methods employed in this test program. All glassware and probes, etc. were cleaned per EPA specification prior to use. Pallflex QAST 2500 pure quartz filters were used as the collection medium for all particulate sampling. The Method 5-type traversing samples were obtained using Pyrex glass and/or quartz nozzles and probes in all cases. Several of the sampling methods we used are not incorporated in the EPA methods published in CFR or SW-846. These methods are described briefly in the paragraphs that follow:

- Method 29, proposed for eventual incorporation in Code of Federal Regulations, for sampling trace metals in both particulate and vapor forms (based on a filter for collecting solids, peroxide-based impingers for vapors of all metals, and permanganate-based impingers for mercury vapor alone that penetrates the peroxide impingers).

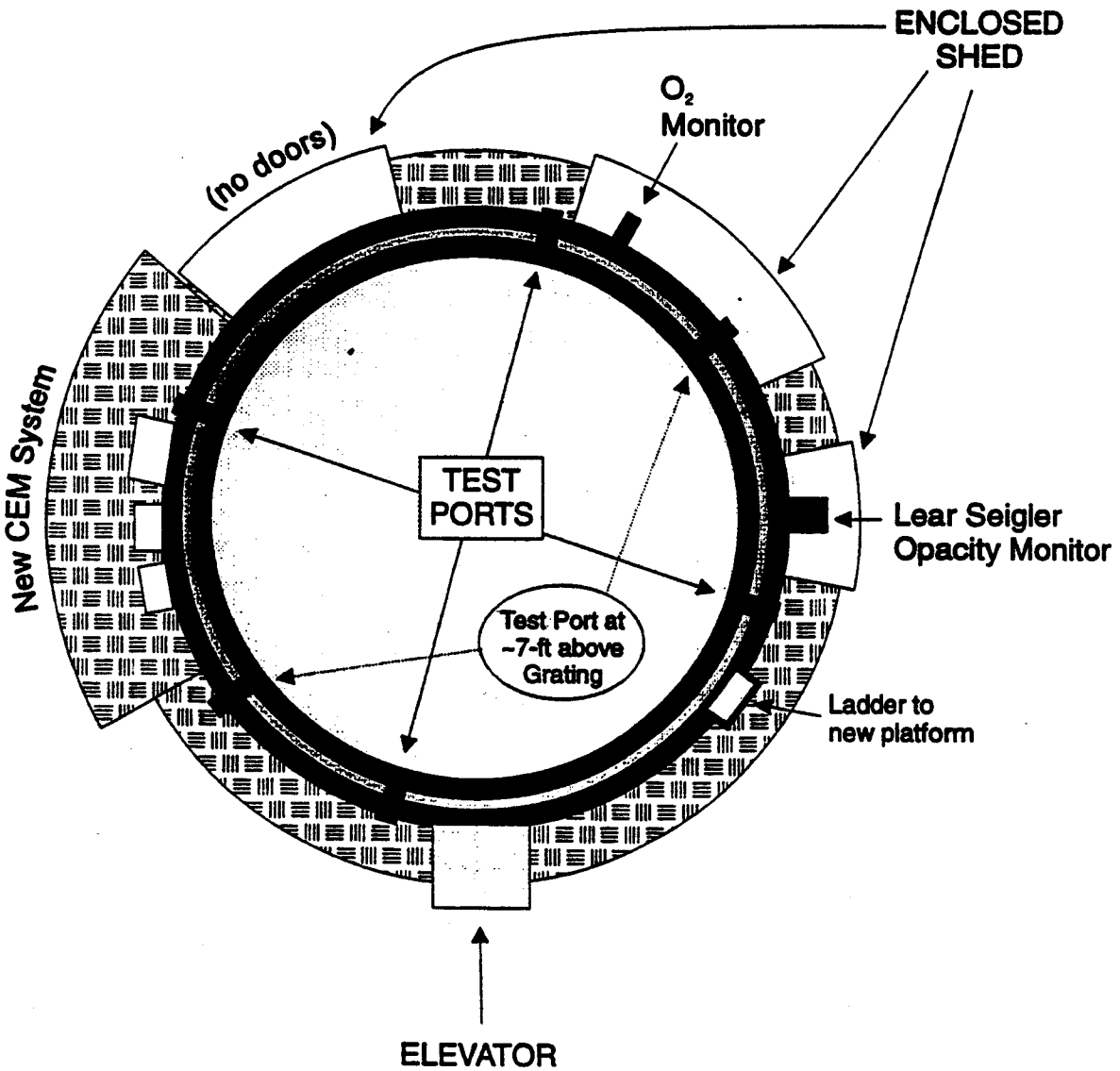


Figure 5-7. Stack Sampling Platform at Unit 1

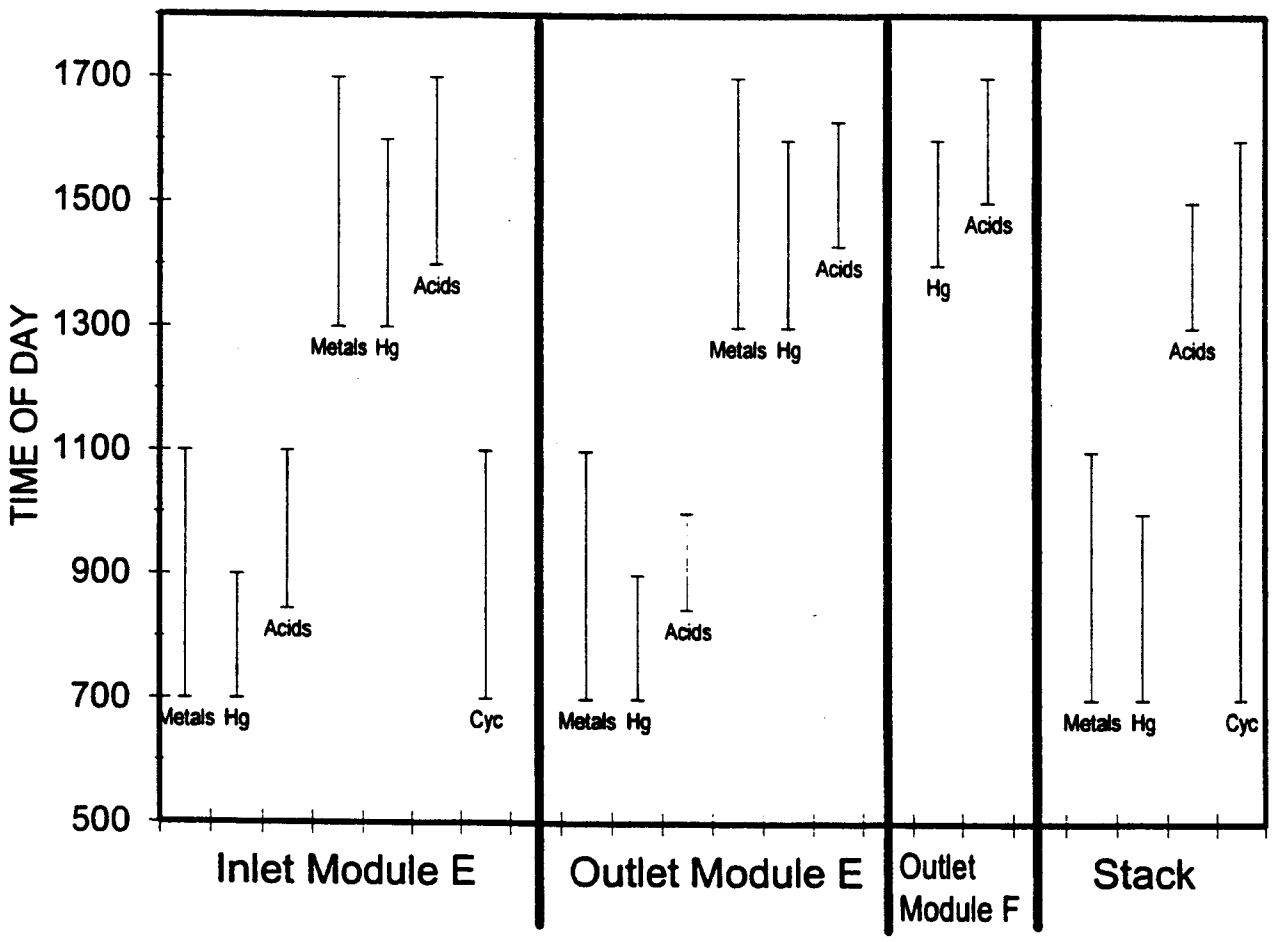


Figure 5-8. Planned Sampling Schedule

Table 5-1. Flue Gas Sampling Methods

Constituent	Method	Traverse/ Single Point	Duration minutes In	Out	Stack
Mornings:					
Module E Inlet & Outlet:					
Metals	M29	T	120[a]	120[a]	
Mercury	Ontario Hydro Train	S	120	120	
Acid gases	M5	S	72	120	
Size fractionated composition	Dual cyclones	S	60		
Stack:					
Metals	M29	T			144
Mercury	Ontario Hydro Train	S			96
Size fractionated composition	Dual cyclones	S[b]			240
Afternoons:					
Module E Inlet & Outlet:					
Metals	M29	T	120[a]	120[a]	
Mercury	Ontario Hydro Train	S	120	120	
Acid gases	M5	S	72	120	
Module F Outlet:					
Mercury	Ontario Hydro Train	S		120	
Acid gases	M5	S		120	
Module F Inlet:					
Gas flow	M2	T			
Stack:					
Acid gases	M5	S			120
Mornings and Afternoons:					
Bulk gas composition	Orsat	T[c]			
Oxygen	Teledyne	T[d]			

Notes:

a. Required greater than normal amounts of H_2O_2 in impingers because of high SO_2 concentrations.

b. Stack cyclone sampling abandoned after first day because 100% of sample passed both cyclones.

c. Taken in conjunction with M29 sampling.

d. Taken at exhaust of each dry gas meter with a Teledyne-Hastings O_2 monitor.

- Mercury was included in the samples collected by Method 29. It was also collected as the single analyte by an impinger train developed by K. Curtis of Ontario Hydro. The Ontario Hydro mercury train is a modification to the EPA Method 101A sampling train, and differs from Method 29 in that it employs a different (proprietary) reagent in the impingers upstream of the permanganate impingers.

- The acid gases were sampled by use of the Method 5 train in which each of two impingers are filled with a solution of 2.5 g of sodium carbonate, 2.5 g of sodium bicarbonate, and 10 mL of 30% hydrogen peroxide. The solids on the filter were retained for analysis as well as the impinger solutions.

- The samples collected for metals analysis in three ranges of particle size were taken using cyclones I and II of the SRI/EPA Five Series Cyclone sampling system. The cyclones and filter holder used for this purpose had been teflon coated to minimize contamination from the materials making up the sampler.

More complete descriptions of sampling methods and trains are given in Appendix B.

5.3.1.2 Process Samples

A limited number of plant process streams were sampled. Since our test program focused on the performance of a scrubber module, we collected samples that were needed to determine the sources and sinks of any of the analytes we sampled in the scrubber inlet and outlet ducts. We therefore required samples of coal, scrubber feed (including limestone, water, and slurry), scrubber recycle slurry, and scrubber waste. Coal sampling was done by host utility staff, who used autosamplers on raw and cleaned coal conveyor belts to obtain samples for each shift during which coal was loaded into the Unit 1 bunkers. The sampling around the scrubber was performed by Southern staff who collected six samples from each of these streams each day. Each of these samples was collected in a 1-liter sample container. Samples were composited in Birmingham prior to analysis. For the scrubber samples, we combined three samples representing the morning flue gas sampling period into one composite sample, and the three samples representing the afternoon flue gas sampling into another composite sample.

5.3.2 Sampling Experience

5.3.2.1 Sampling Schedule

Except at the stack, where limitations in ports, space, and personnel made it impractical, all samples were taken concurrently in-so-far as possible given the differences in sampling times. Figure 5-8 showed our planned sampling schedule for each of the four flue gas sampling locations. Some deviations were made in the flue gas sampling durations because of specific circumstances during some tests. For

instance, filter blinding halted several samples before the planned end of the run. If filter blinding occurred with a large portion of the planned sampling duration remaining, the filter was changed out and the run was continued. However, if a filter blinded late in a run, the run was halted at that point. Figures 5-9 through 5-12 present the actual schedule for flue gas sampling over the four test days. These charts show the time intervals over which flue gas sampling actually took place for each sampling method each day. The indicated intervals include the time required for port-to-port movement during traversing, so they represent the total elapsed times required to acquire the samples and not the actual sampling durations.

With the exception of the coal samples, process solids, liquids, and slurry samples were collected during the time we were sampling flue gases. Coal samples were collected by host utility staff from the autosamplers on raw and clean coal belts for the two shifts during which the washing plant was processing Costain coal. We had samples from the 11 PM to 7 AM and the 7 AM to 3 PM shifts. We were told that the lag time from washing to burning was on the order of 8 hours, so the samples from the 11 to 7 shift had the most overlap with our flue gas sampling. The other process samples were collected six times per day at approximately 2-hour intervals.

5.3.2.2 Samples Collected

The types of samples collected for analysis from solid and liquid streams are listed in Table 5-2. Three of the streams listed under liquids were slurries; both the liquid and solid phases of these slurries were included in the analysis (as separate materials). Although typically six daily samples of the solids and liquids were collected, composites were prepared so that only one sample representing the daily set had to be analyzed. The methods of preparing composites are described in Section 5.4.2.

The types of samples collected from the gas streams for the purpose of analysis are listed in Table 5-3. The samples listed in Table 5-3 were in no case composited. In fact, some samples listed individually consisted of several components that were analyzed separately. One example was the sample of trace metals, which consisted of 1) the filter and solids rinsed from the probe, 2) the peroxide impingers, and 3) the permanganate impingers.

5.3.2.3 Deviations from Standard Techniques

The Method 5-type samples were obtained using Pyrex glass and/or quartz-lined nozzles and probes in all cases. All Method 5-type sampling at the Module E inlet and the stack was done using a small oven mounted at the external end of the probe to contain the filter. A flexible teflon umbilical line was used to convey the filtered sample gases to the condenser/impinger portions of these trains. The impingers were positioned at some convenient location adjacent to the sampling ports. Materials deposited in these umbilicals was recovered as part of the "back-half" catches. The Module E outlet Method 29 sampling was also done in this fashion. The remainder of

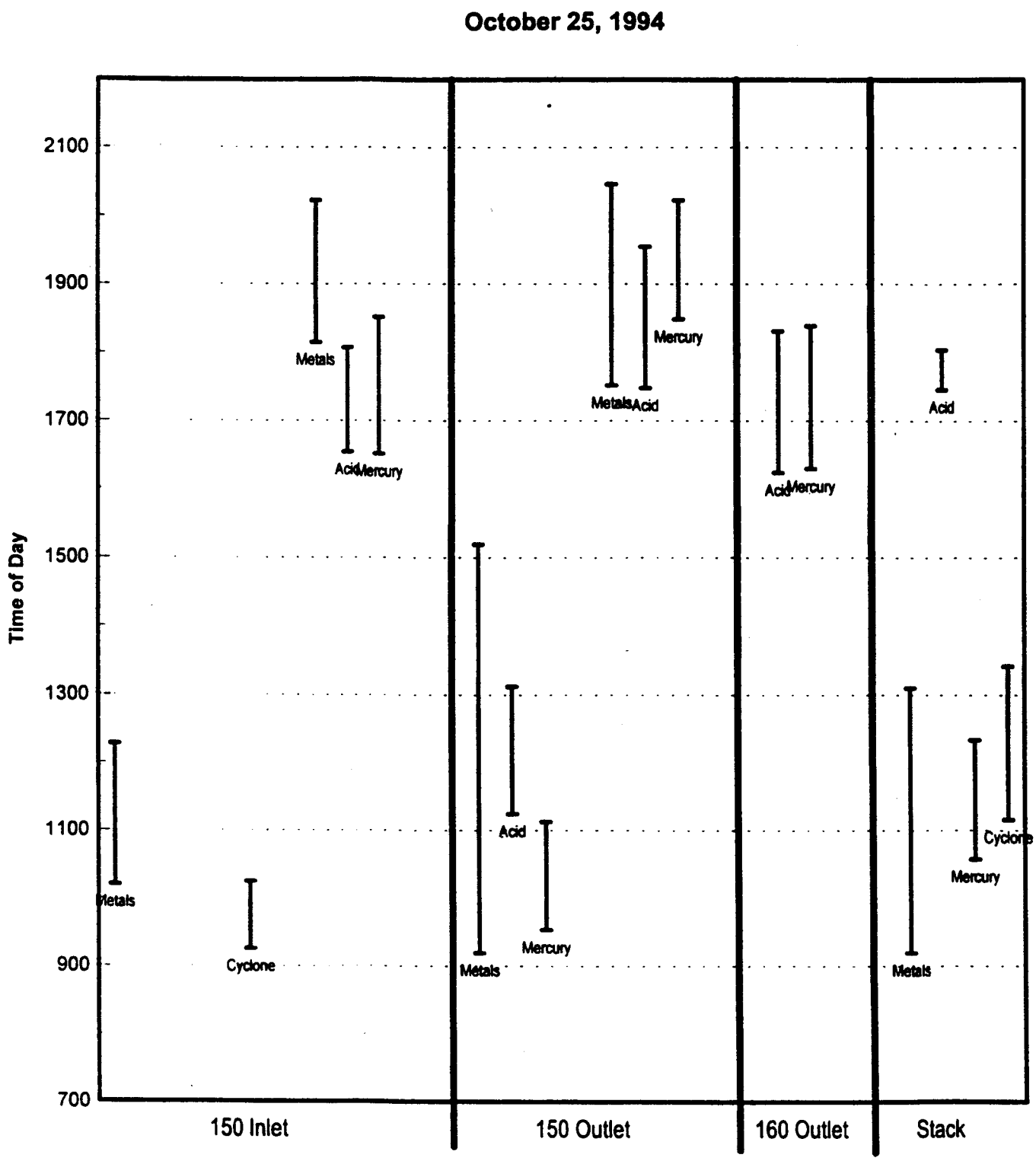


Figure 5-9. Sampling Schedule for October 25, 1994

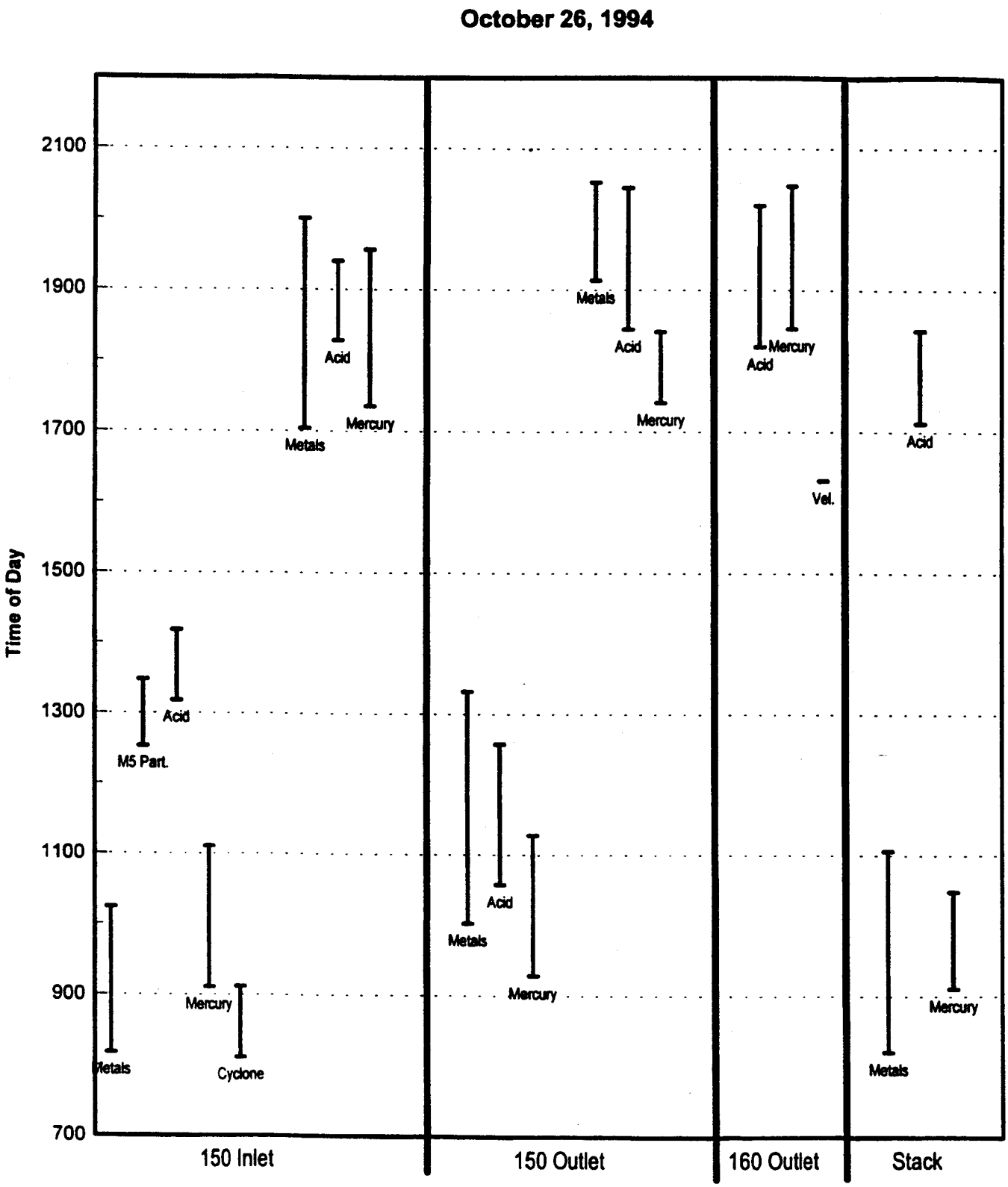


Figure 5-10. Sampling Schedule for October 26, 1994

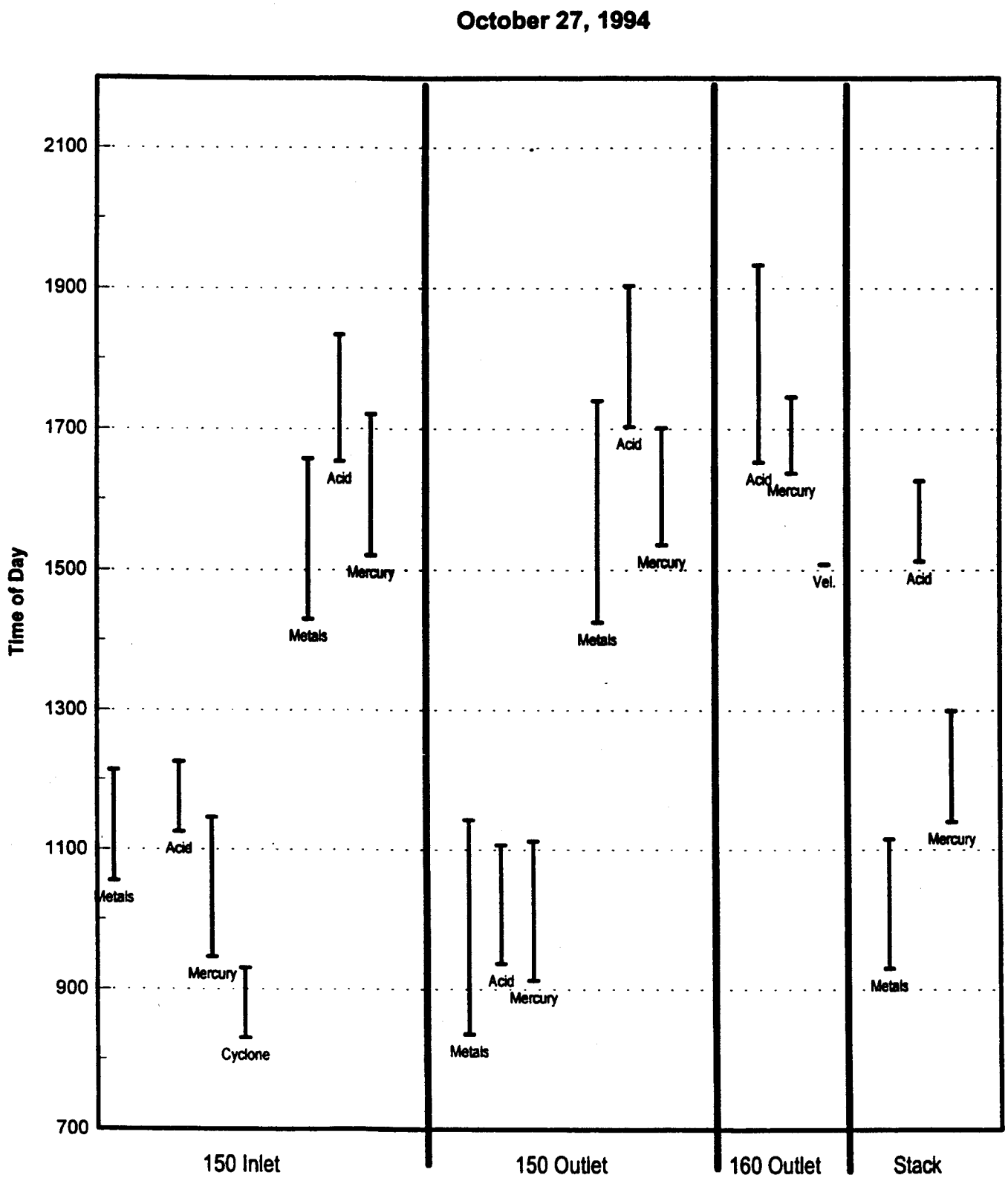


Figure 5-11. Sampling Schedule for October 27, 1994

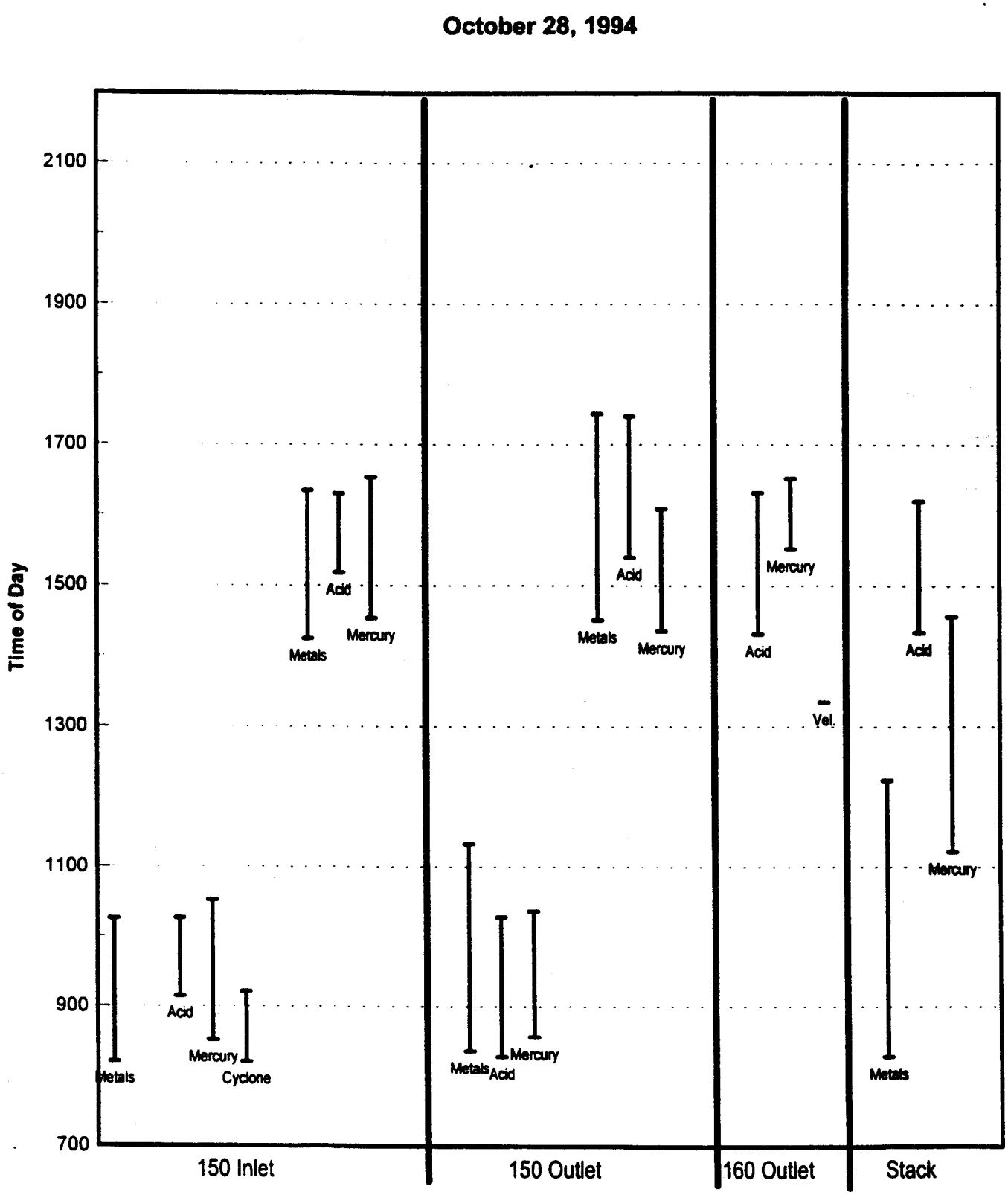


Figure 5-12. Sampling Schedule for October 28, 1994

Table 5-2

Samples Collected for Analysis from Solid, Liquid, and Slurry Streams

	Number of Samples Daily
SOLIDS	
Raw Coal [a]	2
Washed Coal [a]	2
Limestone	6
LIQUIDS	
Scrubber Makeup Water	6
SLURRIES	
Scrubber Limestone Slurry	6
Scrubber Recycle Slurry	6
Scrubber Waste Slurry	6

a. Composite automatically taken with a sampler maintained by the host utility. One sample was taken from the 11 PM to 7 AM shift, and one sample was taken from the 7 AM to 3 PM shift.

Table 5-3

Samples Collected for Analysis from Flue Gas Streams (sum of all test days)

Type of Sample	Module E Inlet	Module E Outlet	Module F Outlet	Stack
Trace Metals	8	8	--	4
Mercury [a]	7	8	4	4
Acid Gases	7	8	4	4
Cyclone Solids [b]	4	--	--	1

NOTES:

a. Using a modification to Method 101A developed by Ontario Hydro Technologies. Mercury was also determined in the Method 29 sampling for trace metals.

b. Only one sample was taken at the stack location because the mass of particles larger than the finest cut point of the series cyclone sampling train was immeasurable.

the sampling at the Module E and F outlets was done using conventional close-coupled Method 5 oven/impinger setups.

All glass-to-glass connections were sealed with DuPont KryTox® sealant, a liquid fluorocarbon of the Teflon family. Southern has used KryTox® on several tests of the type done here, and it has proven satisfactory (non-interfering and low blank levels) for Method 29, Method 5, Method 23, and SW846 Method 0010 and offers superior performance in obtaining leak-free sampling systems.

Teflon check-valves with magnetic closure mechanisms were used immediately downstream of the filters to minimize problems when inserting and removing probes at the scrubber inlets and outlets as the scrubber inlet and outlet ducts were at substantial negative pressures relative to ambient. The impingers contained sufficient volumes of air that backwards flows could occur when the probes were inserted into the ducts, causing impinger solutions to transfer to preceding impingers and/or the filter to be torn or pulled loose from its support. The check valves generally proved easy to use and reliable. The valves were rinsed along with the umbilical or glass connection between the filter and the first impinger.

One sampling port at the stack was inaccessible to the Method 29 train because of space limitations. The port opposite it was traversed twice to compensate for being unable to use it.

The outlet ducts were too wide (26 ft.) to permit full traverses being made, even though sampling was done from both sides of the duct. The points nearest the center of the duct could not be reached because of the proximity of external obstructions that limited the maximum length of the probe that could be used. The innermost points that could be reached were each sampled twice to make up for the point that could not be reached. Further, the standard isokinetic sampling approach at the Module E outlet that was to be used for the Method 29 sampling at that location had to be abandoned. The combination of very low velocity pressures, very negative duct pressure, and high moisture content made it impossible to obtain reliable pitot pressure differential data at that location. Consequently the mean outlet velocity was calculated based on the measured inlet flow rate and the outlet gas conditions, and outlet sampling was done so as to be isokinetic at that mean velocity.

Sampling at all locations was plagued with frequent interruptions. The circuits used to provide electrical power to the systems were all equipped with ground-fault interrupters. Ground faults caused by high static charges on the particles being sampled and/or moisture causing conductive paths from the probe heaters to ground at the duct ends of the probes caused the interrupters to trip rather frequently. In some instances these interruptions resulted in back-flow through the impingers in the trains as pressures tried to equalize. In these cases, we immediately terminated runs, before the intended end times, to preserve the samples. One such interruption resulted in a ruptured filter near the end of an inlet Method 29 traverse. The filter damage was noted and a shorter duration Method 5 particulate traverse was added on that occasion to

provide a valid particulate sample for metals analysis to accompany what at the time was believed to be a valid "back-half" Method 29 sample. However, some particulate matter was later found to have been passed to the impingers when the filter ruptured, confounding the results from the run in question.

The dual cyclones and filter holders used to obtain samples for metals partitioning by particle size were made of teflon-coated stainless steel. Once it had been confirmed that, for practical purposes, all of the particulate matter in the stack gases passed both cyclones, the dual cyclone sampling at the stack was terminated.

Because of the high SO_2 concentrations at the scrubber inlet, we feared that the H_2O_2 and $KMnO_4$ in the impingers of the Method 29 and Modified Method 101A trains would be depleted by the SO_2 in the flue gas. Consequently, greater volumes of the permanganate solutions were used in impingers at the inlet than are normally called for by the method.

Further, we concluded that the sample recovery protocol for the Method 29 permanganate impingers resulted in unnecessary dilution and consequent loss of sensitivity for Hg. The volumes of rinse solutions used were reduced so that a total of 125 mL of solutions were used as compared to 425 mL called for by the method protocol. Finally, the permanganate impinger solutions were preserved and stabilized by titration with hydroxylamine followed by a dichromate solution. (Appendix B provides details of these modifications in the descriptions of the sample recovery procedures.)

All sampling trains, with one exception, passed the required pre-test and post-test leak checks throughout the test program. The mercury train at the stack on 10/27 failed the post-test check by a slight margin (0.025 cfm actual with a 'pass' being less than 0.02). The leakage rate was low enough that a satisfactory correction to the data could be made.

5.4 Analytical Approach

This section of our report briefly describes the sample-preparation techniques and the analytical methods that were used, as well as the identities of the analytes (or species of interest) that were sought during chemical analyses of the various sample types from the test. Also identified are the subcontractors enlisted by Southern to assist in performing the analyses. In addition, this section includes a discussion of the philosophy that prevailed during trace-level analyses with respect to detection limits for trace elements. More detailed descriptions of the analytical methods and sample preparation techniques are provided in Appendix B.

Throughout this section of the report, we use the term "trace metals" to refer to the following elements: antimony, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, lead, manganese, mercury, molybdenum, nickel, selenium, and vanadium. The term "major metals", on the other hand, refers to aluminum, calcium, iron, magnesium, and titanium. It should be pointed out that some of these elements are, at best, only weakly metallic. But our use of the word "metals" to describe them is intended only to differentiate them from elements like sulfur, oxygen, chlorine, and fluorine, which are not commonly determined by optical spectrometric techniques because their resonance absorption and emission lines are in the vacuum-ultraviolet region of the spectrum (i.e., below about 190 nm). Finally, the term "anions" is used here to denote collectively the anions of interest in this project, i.e., chloride, fluoride, and sulfate ions.

5.4.1 Subcontractors for Chemical Analyses

The scope and schedule for the chemical-analysis phase of this project were such that Southern was unable to conduct all of the necessary analyses in-house. Accordingly, Southern obtained major support from the following two primary subcontractors:

Commercial Testing & Engineering Co. (CT&E)
216 Oxmoor Circle
Birmingham, Alabama 35209
Telephone: 205-942-3120
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CT&E specializes in the handling and analyses of coal and related materials. They performed all of the ultimate and proximate analyses, the measurements of calorific value, and the total chlorine and total fluorine determinations. Additionally, they determined sulfate ion in the anionic polymer sample and in the frothing oil sample.

GL analyzed plant-process solids (e.g., coal, limestone, slurry solids, etc.) and Method 29 Multiple-Metals Train (MMT) front-half samples for each of the 21 trace and major metallic (and quasi-metallic) elements of interest in this project. They also determined four of these elements (arsenic, selenium, antimony, and mercury) in plant-process liquids (e.g., water samples and slurry liquids) and in the MMT impinger solutions that contained hydrogen peroxide. In addition, they determined selenium in the Method 5 Acid Train (M5AT) impinger solutions from the afternoon samples at Inlet E and the afternoon samples at Outlet F. (The reasons for conducting the selenium analyses in this way are given elsewhere in this report.)

The back-half MMT impinger media and the back-half Modified Method 101A (MM 101A) impinger media were analyzed for mercury in the laboratories of both GL and Southern. Hence, two complete sets of mercury analysis results were generated for these samples. Southern also carried out the analyses of plant-process liquids and MMT peroxide impinger solutions for the 17 trace and major metallic elements of interest other than arsenic, selenium, antimony, and mercury. Furthermore, Southern performed all determinations of anions (chloride, fluoride, and sulfate ions) other than those few attributed above to CT&E.

Near the end of the chemical-analysis phase of this contract, some questions arose about the elemental analyses of the coal samples. Consequently, we submitted six samples (raw coal, washed coal, clean coal from the conveyor belt, coarse reject, middling reject, and thickener underflow solids) to the University of Missouri, Columbia, for elemental analyses by the neutron-activation analysis (NAA) technique. The elements of interest that were determined by NAA were antimony, arsenic, barium, chromium, cobalt, manganese, mercury, molybdenum, selenium, vanadium, aluminum, calcium, iron, and titanium.

5.4.2 Preliminary Processing and Distribution of Samples

On return of the samples to Southern's corporate facilities, they were promptly prepared for distribution to the subcontractors. Our samples of coal and coal refuse were submitted without prior processing to CT&E for grinding or milling to reduce the particle size and to improve the homogeneity of the samples prior to any chemical analyses. For purposes of distributing them to the subcontractors, aliquots of the various samples were generally packaged in opaque, amber, glass or polyethylene containers that had been precleaned by the vendor (I-CHEM, Inc.) in accordance with EPA specifications. For a few samples, we used colorless (untinted) polyethylene containers that had been washed with 1:1 nitric acid.

Slurry samples were weighed in the jar and allowed to stand until their solids content had settled. Most of the supernatant liquid was then carefully decanted into another container, leaving the wet solids in the bottom of the original container. These solids (and the jar) were dried in an oven at 120 °C, cooled in a desiccator, and weighed. After removing the solids from the jar, the jar was cleaned, dried, and weighed to allow computation of the weight percentage of solids in each slurry. Thereafter, the solid and liquid portions of each slurry were treated like separate samples for purposes of chemical analysis.

The liquid impinger solutions from flue-gas sampling trains were first composited by pouring all redundant impinger solutions for a given sampling train into a large graduated cylinder. For example, the two hydrogen-peroxide-containing impingers (and the 0.1 N HNO_3 back-half wash solution) from each MMT were pooled in this manner to form a single composite sample. Similarly, the two permanganate-containing impingers from each MMT were combined in the field (and were later combined in the laboratory with the rinse of the empty third impinger) to form another composite sample. The same general strategy was invoked for all other back-half train samples. After each successive addition of an impinger solution to the graduated cylinder, the solution volume was read and recorded. The cylinder's contents were then poured into a single large glass or polyethylene container of the type described in the preceding paragraph, and a new composite sample number was assigned and affixed to the container. The composited samples to be analyzed at GL were then split approximately 50:50, and the pertinent portions were transported by automobile to GL. All MMT front-half samples and all cyclone solids were similarly delivered to GL but were not divided or otherwise treated beforehand at Southern.

5.4.3 Philosophy on Detection Limits for Trace Analyses

During other power-plant test programs conducted prior to this test program, we discovered that many of our key samples often yielded analyte concentrations at or near our traditional detection limits. On these occasions, we noted that a "less-than" value for an analyte concentration can cause a major problem in the calculation of mass balance for that analyte at any given location within a power plant. Indeed, a mass balance calculated with the use of a "less-than" value (or some fraction thereof) may not even remotely resemble 100%, even when no fault can be found with the contributing analyses.

For this test program, therefore, we abandoned our conventional estimates of detection limits in favor of a more aggressive (and more risky) decision-making procedure. This procedure was designed to maximize the number of measurement results that could be reported quantitatively (i.e., numerically) rather than as simply "less than" the detection limit. We felt that even an exceptionally inaccurate measurement should be better than a "less than" (or some fraction thereof) for the purpose of computing a mass balance.

Specifically, we chose to report numerical concentration values for all analyte responses lying more than one standard deviation above the average blank response. The "standard deviation" and the "average blank response" that were used for this purpose were computed from a number (usually four or more) of replicate blank measurements for each element. For analyte responses lying less than one standard deviation above the average blank response, we reported the results as "less than" the concentration value that resulted from applying the regression equation to the average-blank-plus-one-standard-deviation response value.

The general idea of defining a detection limit in terms of the average blank plus "n" times the blank standard deviation (where one's choice of n is based on the confidence level desired by the data user) is, to the best of our knowledge, the approach that has been recommended by the International Union of Pure and Applied Chemistry (IUPAC) since 1975. It was also endorsed by the American Chemical Society (ACS) Subcommittee on Environmental Analytical Chemistry in 1980. Thus, we felt justified in pursuing this overall approach for our own purposes. It is only the use of n = 1, rather than the more usual n = 3, in the IUPAC definition that, in our opinion, requires the following further justification.

In a table of normal curve areas, we found that about 14% of blank measurements can be expected to lie at or beyond one standard deviation above the average blank value, assuming that the blank data at least roughly approximate a normal distribution. Likewise, we found that about 2% of blank responses should fall at or above two standard deviations above the average blank value, and about 0.1% of blank responses should fall at or above three standard deviations above the average blank value. Thus, the practice that we adopted, of reporting numerical results for analyte responses falling between one and three standard deviations above the average blank value, clearly leads to a significant risk of mistaking a blank response for an analyte response (or vice versa). Moreover, this statement is even more true if the blank data are not actually distributed normally. Hence, all data points for which the analyte responses fell within one to three standard deviations above the average blank response are identified in our data tables, and we do not recommend their use for any purpose other than that described here, i.e., for mass-balance calculations.

However, even though the error risk described above is significant, we do not feel that it is unacceptably large, as long as the affected data are used only for mass-balance calculations. That is, we feel that 14% is actually a reasonably small minority of the blank responses and that the concomitant level of risk should be acceptable for the limited purpose indicated here. Moreover, it should be noted that the risk of making a mistake in determining the presence or absence of the analyte drops substantially in situations where two or more successive, independent analytical measurements yield essentially the same result. In other words, if the odds of <u>one</u> blank measurement falling more than one standard deviation above the average are about 14%, then the odds of <u>two successive</u> blank measurements falling more than one standard deviation above the average are considerably less than 14%. Thus, we were able to lower our

risk quite a bit in a few situations where two or more replicate analysis results agreed closely with one another.

For response data that are displaced above the average blank response by more than three standard deviations, the risk of a detection error is probably insignificant. But quantitative errors can still be large for results occurring near the lower end of the working concentration range of the analytical method. Hence, the process of establishing the presence or absence of analyte above some meaningful level is almost always a great deal less demanding, in terms of the error requirements, than the process of accurately quantitating any analyte that may be detected near that level.

5.4.4 Analyses of Solids

Table 5-4 lists the principal solid sample types and the analyses that were performed (or the analytes that were sought).

Table 5-4
Analyses of Solids

Sample description	Analyses performed or analytes determined
Coal (all types); thickener underflow solids	Ultimate, proximate Calorific value Total chlorine Total fluorine Trace and major metals
Limestone; magnetite; scrubber slurry solids	Anions (Cl^-, F^-, $SO_4^=$) Trace and major metals

The ultimate analysis is a complete constitutional breakdown of the sample by weight, to include percent moisture, percent carbon, percent hydrogen, percent nitrogen, percent sulfur, percent ash, and percent oxygen. The procedure given in ASTM D3172 was followed in conducting this analysis. The value for percent oxygen is computed by subtracting each of the other measured percentages from 100%, so that the sum of all of the reported parameter values is 100%. The proximate analysis is also a complete breakdown of the sample, but in terms of the following parameters: percent moisture, percent ash, percent volatile material, and percent fixed carbon. Again, the last of these parameters is computed by difference, so that the sum of the reported parameter values is 100%. The parameter referred to in Table 5-4 as "calorific value" is the fuel value of the sample in units of BTUs per pound; it was obtained by ASTM D2015. Total chlorine and total fluorine were determined by ASTM D4208 and D3761 respectively.

For determinations of anions in the solid samples (other than coal), portions of the samples were first fused with solid sodium hydroxide to render them soluble in water. Once the samples were dissolved in water, the anions chloride and sulfate were determined by ion chromatography (IC), whereas fluoride ion was determined by ion-selective electrode (ISE). The IC method was based on EPA Method 300.0 but was tailored to meet the specific requirements of our samples. The ISE method was adapted from EPA Method 340.2, but again, some tailoring of the method was done to meet our needs. Each IC analysis was performed in duplicate, and the two measurement results were averaged.

Table 5-5 summarizes the sample-preparation methods that were used for determining metals in solids. All primary metals determinations in solids, other than the supplemental analyses that followed the initial round of analyses, were performed by GL.

The microwave digestion procedure was, for most solids and most metals, a multi-step process involving the addition of nitric acid, hydrofluoric acid, and (to neutralize excess fluoride ion) boric acid at different steps in the digestion procedure. An aliquot of the digestate was removed prior to the addition of boric acid to the main portion of the sample; this aliquot was used for boron determinations. This particular microwave procedure was closely based on the one recommended for coal digestions by CEM Corporation, vendor of the microwave oven, in their Application Note MS-6. For determinations of trace metals in the magnetite sample, however, a simpler microwave digestion was used. This one was based on a procedure recommended by CEM for digesting iron ore (CEM Application Note OS-21).

Fusion with lithium borate was employed for those samples where there was a concern about the ability of the microwave technique to achieve complete dissolution of the sample material. Occasionally the microwave technique does not quite completely dissolve the sample material, especially if there are silicate minerals present. Nevertheless, the microwave technique ordinarily does a good job of "extracting" the trace metals out of the undissolved sample residue. But this statement may not hold true for the major metals. Therefore, the fusion technique was used primarily to assure accurate determinations of the major metals, although the fused melts of certain sample types (see Table 5-5) were also analyzed for certain trace metals.

For selenium determinations in the solid samples, the samples were decomposed in a Carius furnace. On the other hand, solids were initially prepared and analyzed for mercury by the procedure given in EPA Method 7471, which is a hot-plate (or water bath) digestion. But most solids were later microwave digested by the CEM MS-6 method and then re-analyzed for mercury by Method 7471 because this approach was believed to have provided improved recoveries for mercury.

Table 5-5
Sample-Preparation Methods for Metals Determinations in Solids

Sample description	As	B	Ba	Be	Cd	Co	Cr	Cu	Hg	Mn	Mo	Ni	Pb	Sb	Se	V	Al	Ca	Fe	Mg	Ti
Coals	M	M	F	F	F	F	F	F	M	F	F	F	M	F	C	F	F	F	F	F	F
Thickener underflow solid	M	M	F	F	F	F	F	F	M	F	F	F	M	F	C	F	F	F	F	F	F
Magnetite	M	M	M	M	M	M	M	M	M	M	M	M	M	M	C	M	M	M	M	M	M
Limestone	M	M	M	M	M	M	M	M	M	M	M	M	M	M	C	M	M	M	M	M	M
Scrubber slurry solids	M	M	M	M	M	M	M	M	M	M	M	M	M	M	C	M	M	M	M	M	M
Scrubber effluent slurry solids	M	M	M	M	M	M	M	M	M	M	M	M	M	M	C	M	F	F	F	F	F
Scrubber recycle slurry solids	M	M	M	M	M	M	M	M	M	M	M	M	M	M	C	M	F	F	F	F	F

Key: M = microwave digestion
F = fusion with lithium borate
C = Carius furnace decomposition

The analytical methods that were used for determining metals in the solid samples are tabulated by metal and by sample type in Table 5-6. The digestates of the solid samples were analyzed for all metals except mercury by inductively coupled plasma atomic emission spectrometry (ICPAES) and for mercury by cold-vapor atomic absorption spectrometry (CVAAS). In addition, arsenic, lead, and selenium were re-determined by graphite-furnace atomic absorption spectrometry (GFAAS) to lower the detection limits for these metals below those obtainable by ICPAES. Thus, only the GFAAS results for these metals were reported. The ICPAES analysis conditions and procedures were essentially those given in EPA Method 6010. Similarly, the GFAAS methods were essentially those of EPA Methods 200.9 for arsenic, 239.2 or 7121 for lead, and 7740 or 7741 for selenium. EPA Method 7471, based on CVAAS, was employed for all mercury determinations.

5.4.5 Analyses of Liquids

The major liquid sample types are listed in Table 5-7, along with the pertinent species of interest. These samples were not preserved with nitric acid, as is normally the case for water samples, because the nitric acid would have interfered with the anion analyses by IC.

Anions were determined in the aqueous samples by the IC and ISE methods described above in connection with solid samples. However, the sodium hydroxide fusion step was omitted; that is, the liquids were analyzed directly without any further sample preparation other than filtration, where necessary. The anionic polymer and the frothing oil were analyzed for sulfate ion by ASTM D-2492. They were also analyzed for total chlorine and total fluorine by ASTM D4208 and D3761 respectively.

The sample-preparation procedures that were applied to the analyses of liquid samples for metals are summarized in Table 5-8. Most of the liquid samples were prepared for metals analyses by either of two general microwave-based digestion methods. For determinations of metals other than mercury and selenium, the anionic polymer and the frothing oil were digested by the microwave-based method recommended in EPA Method 29 for digesting metals-train impinger liquids. The remaining liquid samples were digested, for determinations of all metals except mercury, by methods that were derived from EPA Method 3015. All liquid samples were prepared for mercury determinations by EPA Method 7470. In preparation for selenium determinations, the anionic polymer and the frothing oil were decomposed by the Carius furnace technique described above.

The methods used for determining metals in liquid samples are synopsized in Table 5-9. The GFAAS technique was used for all arsenic determinations and for determinations of lead and selenium in the anionic polymer and the frothing oil. Mercury was determined primarily by CVAAS as per EPA Method 7470. But Southern's CVAAS instrument is also equipped for simultaneous determinations by atomic fluorescence spectrometry (AFS), which offers lower detection limits than CVAAS.

Table 5-6
Analysis Methods for Metals Determinations in Solids

Sample description	As	B	Ba	Be	Cd	Co	Cr	Cu	Hg	Mn	Mo	Ni	Pb	Sb	Se	V	Al	Ca	Fe	Mg	Ti
Coals	G	I	I	I	I	I	I	I	C	I	I	I	G	I	G	I	I	I	I	I	I
Thickener underflow solid	G	I	I	I	I	I	I	I	C	I	I	I	G	I	G	I	I	I	I	I	I
Magnetite	G	I	I	I	I	I	I	I	C	I	I	I	G	I	G	I	I	I	I	I	I
Limestone	G	I	I	I	I	I	I	I	C	I	I	I	G	I	G	I	I	I	I	I	I
Scrubber slurry solids	G	I	I	I	I	I	I	I	C	I	I	I	G	I	G	I	I	I	I	I	I
Scrubber effluent slurry solids	G	I	I	I	I	I	I	I	C	I	I	I	G	I	G	I	I	I	I	I	I
Scrubber recycle slurry solids	G	I	I	I	I	I	I	I	C	I	I	I	G	I	G	I	I	I	I	I	I

Key: G = graphite-furnace atomic absorption spectrometry
I = inductively-coupled plasma atomic emission spectrometry
C = cold-vapor atomic absorption spectrometry

Table 5-7
Analyses of Liquids

Sample description	Analyses performed or analytes determined
Thickener underflow liquid Scrubber slurry liquid Scrubber effluent slurry liquid Scrubber recycle slurry liquid Scrubber makeup water Pond return water Pond clarified water Makeup water	Anions (Cl^-, F^-, $SO_4^=$) Trace and major metals
Anionic polymer Frothing oil	Total chlorine, total fluorine, $SO_4^=$ Trace and major metals

Table 5-8
Sample-Preparation Methods for Metals Determinations in Liquids

Sample description	As	B	Ba	Be	Cd	Co	Cr	Cu	Hg	Mn	Mo	Ni	Pb	Sb	Se	V	Al	Ca	Fe	Mg	Ti
Thickener underflow liquid	M	M	M	M	M	M	M	M	W	M	M	M	M	M	M	M	M	M	M	M	M
Scrubber slurry liquids	M	M	M	M	M	M	M	M	W	M	M	M	M	M	M	M	M	M	M	M	M
Scrubber effluent slurry liquids	M	M	M	M	M	M	M	M	W	M	M	M	M	M	M	M	M	M	M	M	M
Scrubber recycle slurry liquids	M	M	M	M	M	M	M	M	W	M	M	M	M	M	M	M	M	M	M	M	M
Scrubber makeup water	M	M	M	M	M	M	M	M	W	M	M	M	M	M	M	M	M	M	M	M	M
Pond return water	M	M	M	M	M	M	M	M	W	M	M	M	M	M	M	M	M	M	M	M	M
Pond clarified water	M	M	M	M	M	M	M	M	W	M	M	M	M	M	M	M	M	M	M	M	M
Makeup water	M	M	M	M	M	M	M	M	W	M	M	M	M	M	M	M	M	M	M	M	M
Anionic polymer	M	M	M	M	M	M	M	M	W	M	M	M	M	M	C	M	M	M	M	M	M
Frothing oil	M	M	M	M	M	M	M	M	W	M	M	M	M	M	C	M	M	M	M	M	M

Key: M = microwave digestion
W = water-bath digestion as per EPA Method 7470
C = Carius furnace decomposition

Anions and acid gases were determined in some of the M5AT front-half and back-half samples. The acid gases HCl, HF, and SO_2 were assumed to exist as the anions Cl^-, F^-, and $SO_4^=$ respectively after entrapment in the M5AT front-half solids and the back-half impinger solutions. Thus, these sample media were analyzed for the anions by the same IC and ISE techniques mentioned previously. All M5AT front-half washes and all back-half samples that were collected were ultimately analyzed for anions in this manner. However, the stack sampling station was the only sampling location for which the M5AT front-half solid sample media were analyzed, and only water extracts of these media were analyzed. This was done mainly to allow an estimate of the amount of condensed sulfuric acid in the stack.

The sample-preparation methods used for metals determinations in the train samples are shown in Table 5-11. Because all metals, including mercury, were determined in the MMT front-half samples, the front-half samples from the M5ATs and the MM101A trains were not analyzed for metals. As discussed elsewhere in this report, the freshly collected train impinger solutions that were to be analyzed only for mercury were stabilized in the field by the addition of an excess of potassium dichromate.

The samples containing entrained solids from the sampled flue gases were microwave-digested according to the method recommended in EPA Method 29 for digesting front-half train samples. Minor portions of all of the resulting digestates were withdrawn and subsequently prepared for mercury determinations by the hot-plate (or water-bath) digestion procedure in EPA Method 7470. Cyclone particulate samples were additionally subjected to lithium borate fusion for major-metals determinations as described above in connection with the analyses of solids.

For determinations of most metals, the peroxide-containing MMT impinger solutions were prepared by the hot-plate digestion procedure of EPA Method 29. The MMT permanganate-containing impinger solutions and both types of MM101A impinger solutions were prepared and analyzed for mercury essentially in accordance with EPA Method 7470.

At Southern, the MMT peroxide-containing impinger solutions were prepared for mercury determinations by a slightly modified version of EPA Method 7470. At the point where potassium permanganate was added to the solutions, we added solid potassium permanganate, after first adding the permanganate solution specified in the method, to minimize the increase in sample volume that is associated with this step. But GL (Galbraith Laboratories) encountered problems in their attempts to follow this protocol for peroxide-containing samples. Specifically, they found that their samples generated too much heat on addition of the solid permanganate. Indeed, the solution temperatures actually reached the boiling point on certain occasions, which raised concerns that certain volatile elements could be lost by evaporation.

It was later discovered that, in an attempt to attain the lowest possible detection limits for mercury, GL had used a lower sample-dilution ratio than we did. Thus, their

Table 5-11
Sample-Preparation Methods for Metals Determinations
in Gases and Entrained Solids

Sample description	As	B	Ba	Be	Cd	Co	Cr	Cu	Hg	Mn	Mo	Ni	Pb	Sb	Se	V	Al	Ca	Fe	Mg	Ti
MMT front-half samples	M	M	M	M	M	M	M	M	C	M	M	M	M	M	M	M	M	M	M	M	M
MMT H_2O_2 impinger solutions	M	H	H	H	H	H	H	H	C	H	H	H	H	M	M	H	H	H	H	H	H
MMT $KMnO_4$ impinger solutions	--	--	--	--	--	--	--	--	W	--	--	--	--	--	--	--	--	--	--	--	--
MM 101A KCl impinger solutions	--	--	--	--	--	--	--	--	W	--	--	--	--	--	--	--	--	--	--	--	--
MM 101A $KMnO_4$ impinger solutions	--	--	--	--	--	--	--	--	W	--	--	--	--	--	--	--	--	--	--	--	--
Cyclone solids (Stages 1 & 2)	M	M	M	M	M	M	M	M	C	M	M	M	M	M	M	M	F	F	F	F	F
Cyclone backup filters	M	M	M	M	M	M	M	M	C	M	M	M	M	M	M	M	M	M	M	M	M
M5AT impinger solutions	--	--	--	--	--	--	--	--	--	--	--	--	--	--	M	--	--	--	--	--	--

Key: M = microwave digestion as per EPA Method 29
F = fusion with lithium borate
W = water-bath digestion as per EPA Method 7470
H = Hot-plate digestion as per EPA Method 29
C = Combined microwave digestion (Method 29) and water-bath digestion (Method 7470)
-- = samples not analyzed for this metal

samples had contained more of the original hydrogen peroxide than ours, and their peroxide-neutralization reactions were thus more intensely exothermic than ours. But in the absence of this knowledge, GL carried out a microwave digestion of these samples (i.e., the EPA Method 29 protocol for MMT impinger liquids) prior to any further preparation or analysis, in hopes of circumventing the problem altogether. Unfortunately, their mercury measurements on these samples correlated poorly with ours; their results were generally much lower and more variable. We can only speculate that they somehow experienced losses of mercury during their microwave sample-preparation step. Note that, if they had decomposed the hydrogen peroxide in the microwave oven, then portions of the ionic mercury could have been reduced to the neutral elemental form, leading to losses of elemental mercury vapor on opening the microwave vessels.

The methods used to analyze train samples for metals are listed in Table 5-12. These methods were essentially the same as those described previously for the analyses of solids and liquids.

The EPA has established maximum holding times for many sample types and many analytes that are of interest to environmental regulators. The only EPA holding times that were exceeded in this project, to the best of our knowledge, were the ones specified for mercury in liquid (back-half) train samples, i.e., 38 days for glass sample bottles and 13 days for plastic sample bottles. Some back-half train samples were stored in glass containers and some were stored in plastic containers. It should be noted that these holding times are new ones that have only recently been issued by the EPA; they were not known to us at the time samples were collected.

All liquid train samples except the MMT peroxide-containing impingers were analyzed for mercury by GL between November 16 and November 20, 1994. Similarly, these same samples were analyzed for mercury by Southern between November 10 and December 2, 1994. Because the samples were collected from October 24 to October 28 of the same year, the 13-day holding time (for samples collected in plastic containers) was exceeded by amounts varying from zero to a maximum of 26 days. But there was very close agreement between the GL results and the Southern results for these particular samples, even though the samples were analyzed in random order at both laboratories. This finding suggests that exceeding the 13-day holding times by up to 26 days had no significant effect on the outcomes of the analyses. It is possible that our deviations from Method 29 sample-recovery procedures in the field, including the addition of potassium dichromate as a stabilizer and the use of hydroxylamine hydrochloride and sodium chloride in place of potassium permanganate and hydrochloric acid, improved the stability of these solutions with respect to mercury.

The treatment history for MMT peroxide-containing impinger samples differed somewhat from that described above. These samples were analyzed by GL on December 7, whereas they were analyzed by Southern on December 1. Because all of these samples were placed into glass bottles, the 38-day holding time applied to them. Thus, the holding time was not exceeded at Southern and was exceeded by a maximum of 6

Table 5-12
Analysis Methods for Metals Determinations
in Gases and Entrained Solids

Sample description	As	B	Ba	Be	Cd	Co	Cr	Cu	Hg	Mn	Mo	Ni	Pb	Sb	Se	V	Al	Ca	Fe	Mg	Ti
MMT front-half samples	G	I	I	I	I	I	I	I	C	I	I	I	G	I	G	I	I	I	I	I	I
MMT H_2O_2 impinger solutions	G	I	I	I	I	I	I	I	C	I	I	I	G	I	G	I	I	I	I	I	I
MMT $KMnO_4$ impinger solutions	--	--	--	--	--	--	--	--	C	--	--	--	--	--	--	--	--	--	--	--	--
MM 101A KCl impinger solutions	--	--	--	--	--	--	--	--	C	--	--	--	--	--	--	--	--	--	--	--	--
MM 101A $KMnO_4$ impinger solutions	--	--	--	--	--	--	--	--	C	--	--	--	--	--	--	--	--	--	--	--	--
Cyclone solids (Stages 1 & 2)	G	I	I	I	I	I	I	I	C	I	I	I	G	I	I	I	I	I	I	I	I
Cyclone backup filters	G	I	I	I	I	I	I	I	C	I	I	I	G	I	I	I	I	I	I	I	I
M5AT impinger solutions	--	--	--	--	--	--	--	--	--	--	--	--	--	--	G	--	--	--	--	--	--

Key: G = graphite-furnace atomic absorption spectrometry
I = inductively-coupled plasma atomic emission spectrometry
C = cold-vapor atomic absorption spectrometry
-- = samples not analyzed for this metal

days at GL. In other words, the samples were held for a total of about 5 weeks at Southern and for about 6 weeks at GL. Unlike the other liquid train samples, these samples were not stabilized with potassium dichromate. As discussed in detail elsewhere in this report, the GL results for several of these samples differed significantly from the corresponding Southern results, and we cannot rule out the possibility that the holding times were a factor in this outcome. But it seems unlikely that samples held for 6 weeks would contain vastly different amounts of available mercury than those held for 5 weeks. Therefore, the discrepancies in the data for MMT peroxide impingers were more likely to have been caused by differences in sample handling in the two laboratories, as discussed previously.

5.5 Analytical Results

5.5.1 Coal

The results of analyses of coal on all five days of the plant visit are presented in Tables 5-13 and 5-14. The composition of the coal during each of the last four days, when the flue gas streams and other process streams were sampled, appears to have been essentially the same as that on the first day, when only the coal processing plant was sampled. It will be noted that Table 5-14 includes the data on the three non-metals of concern (sulfur, chlorine, and fluorine).

Trace metal concentrations in the coal, both raw coal and clean coal, are presented for all five days in Table 5-15. Some of the metals were, on occasion, below the detection limit. To permit calculation of average metal concentrations and standard deviations, the assumption was made that if the concentration was below the detection limit, the concentration was actually one-half the detection limit. The consistency of the metal concentrations from day to day is much poorer than that of the other coal properties listed in the previous two tables. This is readily shown by the relative standard deviations. For boron in the raw coal, for example, the standard deviation is 86% of the average value. The consistency of the data on non-metals, which were previously shown by data in Table 5-14, is better than that for the metals.

The data for mercury in the raw coal are from the Galbraith laboratory. The concentration of mercury in the clean coal on October 24 is also from Galbraith. The concentrations in the clean coal on the other four dates, however, were obtained at Brooks Rand. They are believed to be superior to the earlier results from Galbraith. For the period October 25-28, the concentrations of mercury in the clean coal average 0.0837 μg/g in the analyses at Brooks Rand but only 0.0578 μg/g in the analyses at Galbraith. As will be shown later, only the higher concentrations reported by Brooks Rand could have produced the highly consistent flue-gas concentrations that are reported in Section 5.5.2.1.

Day-by-day reductions in mercury, a metal of particular interest, are listed in Table 5-16. The effects of washing are reported only for the period October 25-28 in order to limit the data for the washed coal to the results from Brooks Rand. The average reduction on the basis of weight alone is 29.6%; that based on calorific values is 39.2%. An unusually low and perhaps erroneous concentration in the raw coal on October 28 is responsible for results on reduction that are less favorable than the others. There is the possibility, of course, that the removals shown are lower than the actual removals, because the data for raw coal from Galbraith may be biased to the low side just as the data for the clean coal from that laboratory appear to be.

Reductions in metal and non-metal concentrations as the result of coal washing are listed in Table 5-17. The reductions are given on the basis of coal mass and on the basis of coal energy value (that is, the reduction in the relative mass concentration of

Table 5-13
Coal Data - Proximate Analysis
Coal Washing Plant - October 24 - 28, 1994

	24-Oct		25-Oct		26-Oct		27-Oct		28-Oct		Average		σ	
As Received	Raw	Clean	Raw	Clean	Raw	Clean	Raw	Clean	Raw	Clean	Raw	Clean	Raw	Clean
% Moisture	2.79	3.22	3.64	5.68	3.21	5.86	3.58	4.55	4.00	5.32	3.44	4.93	0.46	1.08
% Ash	20.15	8.81	22.65	8.15	20.27	7.98	19.10	8.08	19.74	8.20	20.38	8.24	1.35	0.33
% Volatile	34.74	38.71	32.83	38.64	33.39	37.95	34.17	38.97	34.65	38.13	33.96	38.48	0.83	0.42
% Fixed Carbon	42.32	49.26	40.88	47.53	43.13	48.21	43.15	48.40	41.61	48.35	42.22	48.35	0.98	0.62
Btu/lb	11470	13166	10911	12791	11326	12993	11467	13001	11280	13179	11291	13026	228	158
% Sulfur	4.13	3.05	4.86	2.73	4.28	2.80	4.36	2.84	4.63	2.78	4.45	2.84	0.29	0.12
Dry Basis														
% Ash	20.73	9.10	23.51	8.64	20.94	8.48	19.81	8.46	20.56	8.66	21.11	8.67	1.41	0.26
% Volatile	35.74	40.00	34.07	40.97	34.50	40.31	35.44	40.83	36.09	40.27	35.17	40.48	0.85	0.41
% Fixed Carbon	43.53	50.90	42.42	50.39	44.56	51.21	44.75	50.71	43.35	51.07	43.72	50.86	0.95	0.32
Btu/lb	11799	13604	11323	13561	11702	13802	11893	13621	11750	13919	11693	13701	219	153
% Sulfur	4.25	3.15	5.04	2.89	4.42	2.97	4.52	2.98	4.82	2.94	4.61	2.99	0.32	0.10
MAF Btu	14885	14966	14803	14843	14801	15081	14831	14880	14791	15239	14822	15002	38	161

Table 5-14
Coal Data - Ultimate Analysis
Coal Washing Plant - October 24 - 28, 1994

	24-Oct		25-Oct		26-Oct		27-Oct		28-Oct		Average		σ	
As Received	Raw	Clean	Raw	Clean	Raw	Clean	Raw	Clean	Raw	Clean	Raw	Clean	Raw	Clean
% Moisture	2.79	3.22	3.64	5.68	3.21	5.86	3.58	4.55	4.00	5.32	3.44	4.93	0.46	1.08
% Carbon	61.91	71.87	59.32	70.58	61.20	67.91	61.74	71.03	60.96	71.63	61.03	70.60	1.03	1.59
% Hydrogen	4.24	4.87	4.02	4.66	4.23	4.67	4.33	4.78	4.28	4.77	4.22	4.75	0.12	0.09
% Nitrogen	1.25	1.39	1.18	1.35	1.26	1.33	1.23	1.35	1.18	1.38	1.22	1.36	0.04	0.02
% Sulfur	4.13	3.05	4.86	2.73	4.28	2.80	4.36	2.84	4.63	2.78	4.45	2.84	0.29	0.12
% Ash	20.15	8.81	22.65	8.15	20.27	7.98	19.10	8.08	19.74	8.20	20.38	8.24	1.35	0.33
% Oxygen (difference)	5.53	6.79	4.33	6.85	5.55	9.45	5.66	7.37	5.21	5.92	5.26	7.28	0.54	1.32
% Chlorine	0.19	0.21	0.19	0.25	0.18	0.25	0.18	0.21	0.19	0.22	0.19	0.23	0.01	0.02
% Flourine	0.0144	0.0066	0.0130	0.0065	0.0144	0.0065	0.0150	0.0063	0.0152	0.0050	0.0144	0.0062	0.0009	0.0007
Dry Basis														
% Carbon	63.69	74.26	61.56	74.83	63.23	72.14	64.03	74.42	63.50	75.66	63.20	74.26	0.96	1.30
% Hydrogen	4.36	5.03	4.17	4.94	4.37	4.96	4.49	5.01	4.46	5.04	4.37	5.00	0.13	0.04
% Nitrogen	1.29	1.44	1.22	1.43	1.30	1.41	1.28	1.41	1.23	1.46	1.26	1.43	0.04	0.02
% Sulfur	4.25	3.15	5.04	2.89	4.42	2.97	4.52	2.98	4.82	2.94	4.61	2.99	0.32	0.10
% Ash	20.73	9.10	23.51	8.64	20.94	8.48	19.81	8.46	20.56	8.66	21.11	8.67	1.41	0.26
% Oxygen (difference)	5.68	7.02	4.50	7.27	5.74	10.04	5.87	7.72	5.43	6.24	5.44	7.66	0.55	1.44
% Chlorine	0.20	0.22	0.20	0.27	0.19	0.22	0.19	0.23	0.20	0.21	0.20	0.23	0.01	0.02
% Flourine	0.0148	0.0068	0.0134	0.0069	0.0149	0.0066	0.0156	0.0052	0.0157	0.0068	0.0149	0.0065	0.0009	0.0007

Table 5-15
Metal Concentrations in Coal
(Data in µg/g or mg/g)

RAW COAL							
	10/24	10/25	10/26	10/27	10/28	Avg.	Std. Dev.
Trace metals, µg/g							
As	14.1	12.5	22.5	10.8	10.1	14.0	5.0
B	411	94	108	94	105	162	139
Ba	120	144	99	116	115	119	16
Be	1.39	1.29	1.79	2.08	1.72	1.65	0.32
Cd	30.7	21.7	34.3	45.1	35.0	33.4	8.4
Co	5.1	<2.9	<3.1	<3.0	<3.1	<3.0	-
Cr	30.5	32.0	25.0	31.3	27.2	29.2	3.0
Cu	19.9	6.4	10.9	26.2	15.1	15.7	7.7
Hg	0.184	0.108	0.144	0.140	0.096	0.134	0.034
Mn	62.0	62.1	47.2	61.2	53.6	57.2	6.6
Mo	37.8	<24.3	<26.1	41.7	32.3	22.4	20.7
Ni	18.3	12.3	9.5	17.7	22.9	16.1	5.3
Pb	18.2	12.7	19.0	12.3	10.8	14.6	3.7
Sb	51.4	25.4	19.6	13.7	<9.2	22.0	18.9
Se	<1.0	<1.0	<1.1	<0.9	<0.9	<1.0	-
V	95.2	86.8	52.0	72.1	49.9	71.2	20.3
Major metals, mg/g							
Al	20.6	23.8	17.1	16.8	18.8	19.4	2.9
Ca	3.35	2.84	2.03	3.41	2.27	2.78	0.62
Fe	27.9	26.0	25.3	25.9	23.3	25.7	1.6
Mg	1.35	1.67	1.22	1.29	1.3	1.37	0.18
Ti	1.12	1.25	1.01	0.94	1.04	1.07	0.12

Table 5-15 (Concluded)
Metal Concentrations in Coal
(Data in µg/g or mg/g)

CLEAN COAL							
Element	**10/24**	**10/25**	**10/26**	**10/27**	**10/28**	**Avg.**	**Std. Dev.**
Trace metals, µg/g							
As	<1.60	3.79	2.50	3.49	3.80	2.72	1.61
B	88.1	90.8	93.6	103.9	94.8	94.2	6.0
Ba	35.6	40.9	38.0	38.0	37.2	37.9	1.9
Be	2.10	2.38	3.85	2.32	1.48	2.43	0.87
Cd	62.1	72.1	62.9	45.2	30.3	54.5	16.7
Co	<3.0	<2.9	9.3	<1.4	<2.9	<3.0	-
Cr	20.3	16.1	20.8	17.8	14.6	17.9	2.7
Cu	6.8	12.6	53.9	14.5	15.5	20.7	18.9
Hg*	0.0727	0.0781	0.0840	0.0883	0.0844	0.0815	0.0061
Mn	18.0	17.7	15.1	20.1	19.1	18.0	1.9
Mo	64.2	67.4	71.6	50.2	<24.4	53.1	29.4
Ni	11.0	9.5	18.6	9.8	4.2	10.6	5.2
Pb	1.40	1.99	1.25	2.99	<0.29	1.55	1.09
Sb	47.0	17.7	49.2	16.4	<8.8	26.1	21.3
Se	<1.0	<1.2	<1.1	<1.0	<1.1	<3.0	-
V	44.5	31.3	33.8	41.1	66.4	43.4	13.91
Major metals, mg/g							
Al	8.12	8.47	7.80	7.39	8.91	8.14	0.59
Ca	1.00	0.98	0.77	1.26	1.02	1.01	0.17
Fe	8.35	8.45	8.23	8.91	8.80	8.55	0.29
Mg	0.38	0.40	0.49	0.40	0.43	0.42	0.04
Ti	0.47	0.46	0.51	0.41	0.56	0.48	0.05

*Data for 10/24 from Galbraith Laboratories; data for 10/25-10/28 from Brooks Rand.

Table 5-16
Reduction of Mercury in Coal by Washing

	Mercury Concentration, µg/g		Reduction, %	
	Raw Coal	Washed Coal	Mass Basis	Calorific Basis
Oct. 25	0.108	0.0781	27.7	38.3
Oct. 27	0.144	0.0840	41.7	49.2
Oct. 28	0.140	0.0883	36.9	44.4
Oct. 28	0.096	0.0844	12.3	24.9
Average	0.122	0.0837	29.6	39.2
Std. dev.	0.024	0.0042	13.0	10.5

NOTE: Data for 10/24 not included because only Galbraith data are available.

Table 5-17. Reduction of Metals and Non-metals in Coal by Washing (Average concentrations in µg/g or mg/g)

	Raw Coal	Washed Coal	Reduction, %	
			Weight Basis	Calorific Basis
Trace metals, µg/g				
As	14.0	2.7	80.6	83.2
B	162	94	42.0	49.7
Ba	119	38	68.1	72.3
Be	1.7	2.4	-46.7	-27.1
Cd	33.4	54.5	-63.4	-41.6
Co	<3.0	<3.0	a	a
Cr	29.2	17.9	38.6	46.8
Cu	15.7	20.7	-31.6	-14.0
Hg	0.134	0.0837	37.7	46.0
Mn	57.2	18.0	68.5	72.7
Mo	22.4	53.1	-137.5	-105.8
Ni	16.1	10.6	34.2	43.0
Pb	14.6	1.6	89.4	90.8
Sb	22.0	26.9	-22.2	-5.9
Se	<1.0	<1.0	a	a
V	71.2	43.4	39.0	47.2
Major metals, mg/g				
Al	19.4	8.14	58.1	63.7
Ca	2.78	1.01	63.8	68.6
Fe	26	8.55	66.7	71.2
Mg	1.37	0.42	69.2	73.3
Ti	1.07	0.48	55.0	61.0
Non-metals, mg/g				
Cl	1.9	2.2	-15.8	-0.3
F	0.144	0.061	57.6	63.3
S	44.5	28.4	36.2	44.7

a. Not calculated because the element concentration was not measurable in either type of coal.
b. % Reduction on mass basis = 100(1-y/x) where y = concentration in the clean coal and % = concentration in the raw coal.
c. % Reduction on the Btu basis = 100(1-y/1.154x), where 1.154 is the ratio of the Btu/lb value in the clean coal to that in the raw coal. The factor 1.154 is based on average calorific values.

each element or the reduction in the ratio of element mass to calorific value). The reductions on either basis vary widely. It may appear at first sight that the negative reductions are meaningless and are due to erroneous data. Negative reductions are not necessarily without meaning because the waste streams can, in principle, contain a sufficiently low concentration of a given element to cause a real enrichment in the clean coal. On October 24, the combined refuse streams contained 24% of the raw coal. If this refuse had contained none of a given element, the "reduction" on the mass basis would have been 100/(1-[x/0.76]/x) or -32%. The negative figure for the removal of chlorine can be justified in this way. The negative figures for some of the metals — molybdenum, for example — are due to erroneous analytical data.

To provide a background for comparison of contaminant concentrations expected from the coal analysis with the contaminant concentrations actually measured in the flue gas streams, certain calculations were made from the results of coal analysis discussed above. The first task was to calculate the volume of combustion gas to be expected from unit weight of the clean coal. The reference conditions are dry gas at 20 °C and 1 atm, with an O_2 concentration of 3%. The calculation is illustrated in Table 5-18; the results of the calculations for each of the sampling days involving flue-gas streams are listed below:

October 25	0.009399 Nm^3/g
October 26	0.008961 Nm^3/g
October 27	0.009341 Nm^3/g
October 28	0.009403 Nm^3/g

The next step for each metal or non-metal was to divide the concentration in the coal, expressed in $\mu g/g$, by the appropriate gas volume in Nm^3/g. For the metals, the direct results of this calculation — the expected metal concentration in $\mu g/Nm^3$ — were retained. For the non-metals, on the other hand, the equivalent concentration of the expected gas (HCl, HF, or SO_2) in ppmv was calculated in the final step.

It will be understood that these so-called "expected" concentrations were not literally expected for all of the elements, because a loss of ash (as bottom ash or precipitated ash in the ESP, for example) would diminish the value actually expected from those calculated.

The results of the calculation of "expected" concentrations in the flue gas are presented in Table 5-19. As in previous exercises, concentrations below the detection limit were assumed to be equal to one-half of the detection limit.

Table 5-18
Calculation of Combustion Gas Volume from 100 g of Washed Coal
(Data for October 25)

Element	Weight % in Coal	Combustion Product	Product Moles	Required Moles of O_2	Product Moles of Dry Gas
Carbon	71.87	CO_2	5.983682	5.983682	5.983682
Hydrogen	4.66	H_2O	2.311508	1.155754	0
Nitrogen	1.35	N_2	0.04819	0	0.048190
Sulfur	2.73	SO_2	0.085153	0.085153	0.085153
Chlorine	0.25	HCl	0.007052	0	0.007052
Fluorine	0.0065	HF	0.000342	0	0.000342
			sum	7.224588	at 0% O_2
Nitrogen from combustion air			(moles)	27.342820	at 0% O_2
			sum	33.467239	at 0% O_2
			sum	39.076273	at 3% O_2
Gas volume, Nm^3				0.939900	at 3% O_2, 293.15 K, 1 atm
Gas concentrations			vol % CO_2	15.31	at 3% O_2
			ppmv SO_2	2179	at 3% O_2
			ppmv HCl	180	at 3% O_2
			ppmv HF	8.8	at 3% O_2

Table 5-19
Calculated Metal and Non-metal Concentrations in Flue Gas
(Data in µg/Nm³ or mg/Nm³ for metals and in ppmv for non-metals)

	Oct. 25	Oct. 26	Oct. 27	Oct. 28	Avg.	Std. Dev.
Trace metals, µg/Nm³						
As	403	279	374	404	365	59
B	9661	10445	11123	10082	10328	620
Ba	4352	4241	4068	3956	4154	176
Be	253	430	248	157	272	114
Cd	7671	7019	4839	3222	5688	2042
Co	<308	1038	<150	<308	<300	-
Cr	1713	2321	1906	1553	1873	332
Cu	1341	6015	1552	1648	2639	2254
Hg	8.60	10.03	10.71	9.44	9.69	0.90
Mn	1883	1685	2152	2031	1938	201
Mo	7171	7990	5374	<2595	5458	-
Ni	1011	2076	1049	447	1146	678
Pb	212	139	320	<308	206	-
Sb	1883	5490	1756	<936	2399	-
Se	<128	<123	<107	<117	<130	-
V	3330	3772	4400	7062	4641	1672
Major metals, mg/Nm³						
Al	901	870	791	948	878	66
Ca	105	86	135	108	109	20
Fe	899	918	954	936	927	23
Mg	42.9	55.1	42.9	45.6	46.6	5.8
Ti	48.8	57.1	44.1	59.2	52.3	7.1
Acid gases, ppmv						
HCl	180	159	160	144	161	13
HF	8.8	8.8	6.8	9.7	8.5	1.1
SO_2	2179	2344	2281	2218	2256	72

5.5.2 Flue Gas Streams

The data in this section are organized under three analyte types, as listed in the brief outline below. The sources of the samples that were analyzed to obtain these data are included in the outline:

- Mercury, for which samples were obtained by
  - Method 29 (solid- and gas-phase)
  - Ontario Hydro's modification of Method 101A (gas-phase only)
- Other trace metals, consisting of 15 trace metals other than mercury, and 5 major metals (solid- and gas-phase), based on samples from Method 29
- Acid gases (or their associated anions, mainly gas phase but for the stack also solid phase), based on samples from the Method 5 train with peroxide and base in the impingers for collecting acid gases

All of the data for a given analyte at the inlet of the E Module of the scrubber are nominally comparable, for no known significant variation in operating conditions distinguishes one result in the group of eight (two results per day) from any other result. All of the data for a given analyte at the stack are likewise comparable; there is one result per day. Data at the two scrubber module outlets on the other hand fall into two groups each. At the outlet of Module E, the morning run each day was at the normal L/G value, whereas the afternoon run was at an increased L/G. At the outlet of Module F, alternating days yielded data at one scrubber pH, and the other days yielded data at a different pH.

The data presented in this section do not rigorously distinguish between results from different test conditions. Thus, the results from all eight runs at the E Module outlet are averaged, not presented as two averages for different conditions. Supporting data in the appendix are identified with test conditions. The simplifying approach in the body of the report seems justified because the differences in test conditions usually did not produce distinguishable data. The issue of test conditions and their effect on the data is discussed later in Section 5.6.3.

The data on metals were calculated from the original results by applying corrections based on data from four blank trains. Data for reagent blanks were also obtained and considered for use in an alternative approach for correcting the raw data. This alternative approach proved not to be feasible, however, because the amounts of the metals present in the individual reagents were usually below the detection limits and the sums of these amounts could not be assigned realistic values.

The corrections based on blank trains were usually inconsequential for the front half of the sampling train but were usually important for the back half, where generally

the quantities of metals found were much smaller and the blank corrections were relatively larger. The exceptions to these generalities occurred with the metals that were significantly in the vapor state (boron, mercury, and selenium) and thus collected significantly in the back half of the train.

5.5.2.1 Mercury

The results of determinations of the concentration of mercury are presented in Tables 5-20 and 5-21. The first of these tables presents the results for Method 29; it includes data for particulate mercury in the front half of the sampling train. The second table gives the corresponding data for the gas-phase only from the modification of Method 101A that has been developed by Ontario Hydro.

All of the data for the gas phase from both trains in Tables 5-20 and 5-21 were determined in the Southern laboratory. The data for the solids in Method 29 came from Galbraith; the solids were not analyzed at Southern. All of the samples containing mercury from the gas phase were also analyzed by Galbraith. For samples from modified Method 101A, the data from the two laboratories were in excellent agreement. For the peroxide impinger samples from Method 29, the data from Galbraith were unsatisfactory; obviously, the peroxide was not effectively destroyed in the Galbraith procedure and the results for mercury were in error. For the permanganate impingers from Method 29, on the other hand, both laboratories were in agreement. The details of the data on gas-phase mercury from the two laboratories are presented in Tables 5-22 and 5-23.

Table 5-20 implies that the mercury in the particulate state was ionic. Evidently, there is no way to speciate mercury in solid matter; however, it seems plausible that the mercury in this state is ionic (perhaps as the compound HgO), not elemental. The percentage of the total mercury found in the particulate state was 1% or less of the total, confirming the expectation that mercury would occur mainly in the vapor state.

Table 5-20
Mercury, Method 29, Data in µg/Nm³, Southern Analysis

	Oct.25		Oct.26		Oct.27		Oct.28		Avg.	Std. Dev.	%
	AM	PM	AM	PM	AM	PM	AM	PM			
Inlet, E											
Ionized, solid	0.09	0.10	0.23	0.10	0.10	0.06	0.08	0.07	0.10	0.05	1.0
Ionized, gas	8.25	6.79	6.42	6.05	8.29	8.16	7.38	7.80	7.39	0.88	73.5
Elemental, gas	3.39	3.06	2.51	2.61	2.78	2.11	2.12	1.96	2.57	0.50	25.5
Total	11.7	9.95	9.17	8.76	11.2	10.3	9.57	9.83	10.1	0.99	100.0
Outlet, E											
Ionized, solid	0.06	0.05	0.03	0.01	0.02	0.02	0.02	0.01	0.03	0.02	0.5
Ionized, gas	1.05	0.89	1.21	0.63	1.24	1.57	1.44	1.21	1.15	0.30	20.8
Elemental, gas	4.56	4.70	3.81	4.50	4.51	4.10	4.55	4.24	4.37	0.29	78.7
Total	5.66	5.63	5.05	5.14	5.76	5.70	6.00	5.46	5.55	0.32	100.0
Stack											
Ionized, solid		0.06		0.02		0.03		0.02	0.03	0.02	0.5
Ionized, gas		1.22		0.95		1.21		2.05	1.36	0.42	22.6
Elemental, gas		4.81		5.00		4.40		4.31	4.63	0.29	76.9
Total		6.09		5.97		5.63		6.39	6.02	0.27	100.0

Table 5-21
Mercury, Modified Method 101A, Data in µg/Nm³, Southern Analysis

	Oct.25		Oct.26		Oct.27		Oct.28		Avg.	Std. Dev.	%
	AM	PM	AM	PM	AM	PM	AM	PM			
Inlet, E											
Ionized, solid											
Ionized, gas		4.22	4.00	5.84	5.01	4.82	4.42	4.92	4.74	0.61	48.1
Elemental, gas		5.23	5.79	5.41	4.62	4.68	5.44	4.68	5.12	0.46	51.9
Total		9.45	9.78	11.3	9.63	9.50	9.86	9.60	9.87	0.63	100.0
Outlet, E											
Ionized, solid											
Ionized, gas	0.39	0.25	0.67	0.38	0.46	0.83	0.74	0.82	0.57	0.22	9.3
Elemental, gas	5.01	6.05	5.01	6.10	6.18	5.62	6.95	3.62	5.57	1.01	90.7
Total	5.40	6.30	5.68	6.48	6.64	6.45	7.69	4.44	6.14	0.97	100.0
Outlet, F											
Ionized, solid											
Ionized, gas		0.68		0.38		0.51		0.50	0.52	0.12	8.5
Elemental, gas		4.76		6.46		5.71		5.27	5.55	0.72	91.5
Total		5.43		6.83		6.22		5.77	6.06	0.61	100.0
Stack											
Ionized, solid											
Ionized, gas		0.48		0.44		0.96		0.22	0.53	0.31	7.9
Elemental, gas		5.96		7.11		6.01		5.45	6.13	0.70	92.1
Volume, Nm³		6.44		7.55		6.98		5.68	6.66	0.80	100.0

Table 5-22
Comparison of Mercury Determinations by Southern Research and Galbraith Laboratories Using Samples from Method 29

Ionic	Oct.25		Oct.26		Oct.27		Oct.28		Avg.	Std. Dev.
	AM	PM	AM	PM	AM	PM	AM	PM		
Inlet, E										
SRI	8.25	6.79	6.42	6.05	8.29	8.16	7.38	7.80	7.39	0.88
GLI	3.74	3.37	7.31	4.03	8.12	6.68	7.32	6.16	5.84	1.86
Outlet, E										
SRI	1.05	0.89	1.21	0.63	1.24	1.57	1.44	1.21	1.15	0.30
GLI	0.22	0.70	0.01	0.50	0.73	0.94	-*	1.04	0.59	0.37
Stack										
SRI		1.22		0.95		1.21		2.05	1.36	0.42
GLI		1.38		1.59		0.49		1.13	1.15	0.41
Elemental	**Oct.25**		**Oct.26**		**Oct.27**		**Oct.28**		**Avg.**	**Std. Dev.**
	AM	**PM**	**AM**	**PM**	**AM**	**PM**	**AM**	**PM**		
Inlet, E										
SRI	3.39	3.06	2.51	2.61	2.78	2.11	2.12	1.96	2.57	0.50
GLI	3.24	3.16	2.46	2.68	3.45	2.45	2.72	2.66	2.85	0.38
Outlet, E										
SRI	4.56	4.70	3.81	4.50	4.51	4.10	4.55	4.24	4.37	0.29
GLI	4.03	4.38	3.87	4.50	4.42	4.06	4.26	4.08	4.20	0.22
Stack										
SRI		4.81		5.00		4.40		4.31	4.63	0.29
GLI		4.43		4.54		4.25		3.92	4.28	0.24

Table 5-22 (Concluded)
Comparison of Mercury Determinations by Southern Research and Galbraith Laboratories Using Samples from Method 29

Total	Oct.25		Oct.26		Oct.27		Oct.28		Avg.	Std. Dev.
	AM	PM	AM	PM	AM	PM	AM	PM		
Inlet, E										
SRI	11.73	9.95	9.17	8.76	11.17	10.32	9.57	9.83	10.06	0.99
GLI	6.98	6.53	9.77	6.71	11.57	9.14	10.04	8.81	8.69	1.81
Outlet, E										
SRI	5.66	5.63	5.05	5.14	5.76	5.70	6.00	5.46	5.55	0.32
GLI	4.25	5.08	3.88	5.00	5.15	5.00	4.26	5.12	4.72	0.50
Stack										
SRI		6.09		5.97		5.63		6.39	6.02	0.27
GLI		5.81		6.13		4.74		5.05	3.62	2.78

*Note: Outlier of 28.5 µg/Nm^3 deleted data.

Table 5-23
Comparison of Mercury Determinations by Southern Research and Gálbraith Laboratories Using Samples from Modified Method 101A

Ionic	Oct.25		Oct.26		Oct.27		Oct.28		Avg.	Std. Dev.
	AM	PM	AM	PM	AM	PM	AM	PM		
Inlet, E										
SRI		4.22	4.00	5.84	5.01	4.82	4.42	4.92	4.74	0.61
GLI		4.68	4.37	5.02	4.97	4.60	4.49	5.26	4.77	0.32
Outlet, E										
SRI	0.39	0.25	0.67	0.38	0.46	0.83	0.74	0.82	0.57	0.22
GLI	0.38	0.05	0.61	0.44	0.66	0.60	0.85	0.62	0.52	0.24
Outlet, F										
SRI		0.68		0.38		0.51		0.50	0.52	0.12
GLI		0.60		0.52		0.49		0.47	0.52	0.06
Stack										
SRI		0.48		0.44		0.96		0.22	0.53	0.31
GLI		0.50		0.49		0.70		0.27	0.49	0.17
Elemental	**Oct.25**		**Oct.26**		**Oct.27**		**Oct.28**		**Avg.**	**Std. Dev.**
	AM	**PM**	**AM**	**PM**	**AM**	**PM**	**AM**	**PM**		
Inlet, E										
SRI		5.22	5.78	5.41	4.62	4.67	5.44	4.67	5.12	0.46
GLI		4.94	5.86	5.45	5.31	5.78	5.62	5.25	5.46	0.32
Outlet, E										
SRI	5.01	6.05	5.01	6.10	6.18	5.62	6.95	3.62	5.57	1.01
GLI	6.54	6.06	5.29	5.64	5.66	5.49	6.39	3.49	5.57	0.95
Outlet, F										
SRI		4.75		6.45		5.70		5.26	5.54	0.72
GLI		5.43		6.06		5.94		5.58	5.75	0.29
Stack										
SRI		5.96		7.10		6.01		5.45	6.13	0.69
GLI		5.91		6.93		5.77		5.88	6.12	0.54

Table 5-23 (Concluded)
Comparison of Mercury Determinations by Southern Research and Galbraith Laboratories Using Samples from Modified Method 101A

Total	Oct.25		Oct.26		Oct.27		Oct.28		Avg.	Std. Dev.
	AM	PM	AM	PM	AM	PM	AM	PM		
Inlet, E										
SRI		9.45	9.78	11.3	9.63	9.50	9.86	9.60	9.87	0.63
GLI		9.62	10.2	10.4	10.3	10.3	10.1	10.5	10.2	0.30
Outlet, E										
SRI	5.40	6.30	5.68	6.48	6.64	6.45	7.69	4.44	6.14	0.97
GLI	6.91	6.10	5.90	6.08	6.31	6.08	7.23	4.10	6.09	0.92
Outlet, F										
SRI		5.43		6.83		6.21		5.76	6.06	0.60
GLI		6.03		6.58		6.42		6.05	6.27	0.27
Stack										
SRI		6.44		7.55		6.97		5.67	6.66	0.79
GLI		6.41		7.42		6.47		6.15	6.61	0.55

The average mercury concentrations in the vapor state from the two tables are tabulated below for ready comparison. The concentrations are in the units $\mu g/Nm^3$; the percentages of the two forms of mercury are shown in parentheses:

	Method 29 $\mu g/Nm^3$	Modified Method 101A $\mu g/Nm^3$
Inlet, E Module		
Ionic	7.39 (74.3%)	4.74 (48.1%)
Elemental	2.56 (25.7%)	5.12 (51.9%)
Total	9.95	9.86
Outlet, E Module		
Ionic	1.15 (20.8%)	0.56 (9.3%)
Elemental	4.37 (79.2%)	5.56 (90.7%)
Total	5.52	6.13
Outlet, F Module		
Ionic	-	0.51 (8.5%)
Elemental	-	5.54 (91.5%)
Total	-	6.06
Stack		
Ionic	1.35 (22.6%)	0.52 (7.9%)
Elemental	4.63 (77.4%)	6.13 (92.1%)
Total	5.98	6.66

The more important observations from the above tabulation are as follows:

1. The two methods were in good agreement on the total concentration at each location where both methods were used. The differences range only from 0.1 to 0.6 $\mu g/Nm^3$.
2. Both methods indicate that the scrubber removed most of the ionic mercury. Either method shows good agreement between the outlet of Module E and the stack; Method 101A also shows good agreement between the outlets of Modules E and F.
3. The methods differ substantially on the proportions of mercury in the ionic and elemental states. At each sampling location Method 29 gave the higher percentage in the ionic state. Moreover, Method 29 seemed to show that part of the ionic mercury at the scrubber inlet was converted to the elemental form at the outlet.

The difference in speciation cannot be explained unequivocally. It may have to do, however, with the lack of specificity of the peroxide impinger in Method 29 for capturing the ionic form of mercury. This question may be posed: is the observed difference caused by the possibility that the peroxide captures part of the elemental mercury, or by the possibility that the KCl solution (the substitute in modified Method 101A) is unable to retain all the ionic mercury? The first of these explanations seems more likely, because the combination of hydrogen peroxide and nitric acid in the so-

called peroxide impinger surely has the oxidizing potential for converting part of the elemental mercury to the ionic state.

The suggestion that ionic mercury shifts from the ionic state to the elemental state across the scrubber surely must be an illusion. Such a change is contrary to the predictions of thermodynamics. An alternative explanation, however superficial, is that the peroxide impinger captures more of the elemental mercury under scrubber inlet conditions than under scrubber outlet conditions because of the intervention of some other substance that is changed across the scrubber, perhaps that substance is SO_2. There is no apparent mechanism whereby SO_2 could affect mercury capture in peroxide, but certainly the concentration of SO_2 is sharply reduced across the scrubber. The concentration of SO_2 is orders of magnitude higher than that of mercury; thus, there is sufficient SO_2 on a relative scale to affect mercury significantly.

5.5.2.2 Other Metals

The calculated concentrations of the trace metals and major metals derived from the individual experiments with Method 29 are listed in Tables E-1 through E-9 in Appendix E. The data from eight sampling runs at the inlet and eight at the outlet of Module E of the scrubber are presented in separate tables; the tables give the results for the front half of the sampling train, the back half, and the combination. Each table gives also for each metal concentration an average, the standard deviation, and the relative standard deviation (the standard deviation as a percentage of the average concentration). The data tables for the stack are similar, except that they pertain to only four experiments rather than eight. One experiment at the inlet to Module E was eliminated from the averaging (the morning run on October 26), because the filter leaked and caused abnormally high and misleading metal concentrations in the back half.

The key information in Appendix E is summarized in Tables 5-24, 5-25, and 5-26 in the body of this report on the pages immediately following. These tables present the average concentrations of each metal in the front and back halves of the train and present also the total concentration. The averages here are the same as the averages in the appendix, except that blank-corrected values that are negative in the appendix are shown as positive limiting values (that is, they are shown as values below the corresponding blank concentrations). The relative standard deviations in the average concentrations for the complete train are also repeated from the appendix. Finally, the tables give the percentages of the total concentration of each metal that are represented by the front-half value and by the back-half value or, by inference, the solid and the vapor, respectively.

Table 5-24
Summary of Metal Concentration Data for the Inlet of the E Scrubber Module
(Derived from the primary data in Tables E-1,-2,-3; data in µg/Nm³ or mg/Nm³ as indicated; corrected by blank data)

	Average Concentration			Rel. Std. Dev., % in Total	Distribution	
	Solid Phase	Vapor Phase	Total		Solid Phase, %	Vapor Phase, %
Trace metals (µg/Nm³)						
As	198	0	198	14	100	0
B	1123	6175	7522	10	15	85
Ba	768	4	769	11	100	0
Be	29.1	0.3	29.1	11	99.9	0.1
Cd	22.2	0.6	22.5	16	98.7	1.3
Co	58.3	0.4	58.4	7	99.8	0.2
Cr	503	6	503	45	100	0
Cu	259	4	261	13	99	1
Hg	0.08	9.98	10.20	10	0.80	99.2
Mn	400	14	414	13	97	3
Mo	221	6	221	14	100	0
Ni	266	3	267	24	99	1
Pb	229	1	228	11	100	0
Sb	44.7	0.9	45.4	39	98.5	1.5
Se	46.7	16.3	63.8	74	73.2	26.8
V	1331	19	1331	18	100	0
Major metals (mg/Nm³)						
Al	199	0.5	199	12	100	0
Ca	34.9	0.49	35.1	12	99	1
Fe	260	0.8	260	11	100	0
Mg	12.1	0.06	12.2	12	100	0
Ti	16.9	0.07	16.9	12	100	0

Footnote to caption: Only seven of the eight sampling runs are summarized here because of a rupture of the filter in one experiment that contaminated the back half of the train.

Table 5-25
Summary of Metal Concentration Data for the Outlet of Scrubber Module E (Derived from the primary data in Tables E-4,-5,-6; data in µg/Nm³ or mg/Nm³ as indicated; corrected by blank data)

	Average Concentration			Rel. Std. Dev., %, in Total	Distribution	
	Solid	Vapor	Total		Solid Phase, %	Vapor Phase, %
Trace metals (µg/Nm³)						
As	27.9	0.053	28.0	7	99.8	0.2
B	43	397	439	15	9.7	90.3
Ba	42.2	0.540	42.7	6	98.7	1.3
Be	1.09	<0.3	1.0	6	>78	<22
Cd	1.84	0.43	2.3	77	81.0	19.0
Co	<0.7	<5.0	<5.7	-	-	-
Cr	34.0	3.763	37.7	8	90.0	10.0
Cu	13.2	1.679	14.9	14	88.7	11.3
Hg	0.0	5.528	5.6	5	0.4	99.6
Mn	3.4	2.027	5.5	37	62.9	37.1
Mo	46.1	0.247	46.3	2	99.5	0.5
Ni	2.1	1.748	3.9	61	55.1	44.9
Pb	20.1	1.458	21.6	9	93.3	6.7
Sb	<7.8	<5.1	<12.9	-	-	-
Se	32.5	13.095	45.6	40	71.3	28.7
V	98.7	0.462	99.2	35	99.5	0.5
Major metals, mg/Nm³						
Al	1.18	0.00001	1.20	7	99.1	0.9
Ca	1.61	0.036	1.65	39	97.8	2.2
Fe	3.54	<0.07	3.53	6	100.2	<1.9
Mg	0.218	0.0046	0.22	17	97.9	2.1
Ti	0.261	0.00005	0.26	6	100.0	0.0

Table 5-26
Summary of Metal Concentration Data for the Stack
(Derived from primary data in Tables E-7,-8,-9; data in µg/Nm³ or mg/Nm³ as indicated; corrected by blank data)

	Average Concentration			Rel.Std. Dev., % in Total	Distribution	
	Solid	Vapor	Total		Solid Phase, %	Vapor Phase, %
Trace metals (µg/Nm³)						
As	31.4	0.4	31.8	12	98.7	1.3
B	85	372	457	16	18.5	81.5
Ba	40.7	1.3	42.0	6	96.9	3.1
Be	1.05	<0.3	1.20	7	87.5	12.5
Cd	2.80	0.02	2.82	27	99.1	0.9
Co	1.18	<5.0	3.68	-	-	-
Cr	43.4	<0.6	42.6	35	101.8	-1.8
Cu	14.2	1.2	15.4	22	92.2	7.8
Hg	0.03	5.99	6.02	5	0.5	99.5
Mn	6.17	1.35	7.53	38	82.0	18.0
Mo	45.9	1.1	47.0	8	97.8	2.2
Ni	10.3	<1.4	11.3	89	90.8	9.2
Pb	14.3	<1.4	15.0	64	95.3	4.7
Sb	<7.8	<5.1	6.4	-	-	-
Se	29.7	12.2	41.8	24	70.9	29.1
V	106.6	3.4	110.0	4	96.9	3.1
Major metals (mg/Nm³)						
Al	1.22	0.03	1.26	13	97.2	2.8
Ca	0.87	0.12	0.99	3	88.1	11.9
Fe	3.40	0.08	3.48	5	97.8	2.2
Mg	0.185	0.008	0.192	7	95.9	4.1
Ti	0.244	0.005	0.249	6	97.8	2.2

The percentages of vapor of each metal present to a large degree in the vapor state are as follows:

	Inlet, Module E	Outlet, Module E	Stack
Boron	85	91	81
Mercury	99.2	99.6	99.5
Selenium	27	30	29

There is a sharp temperature difference between the inlet and the outlet of the scrubber or between the inlet and the stack — roughly 325 °F at the former and 125 °F at the latter. The data, therefore, show a paradox of nearly invariant vapor percentages between the two temperatures. The paradox seems to exist in actuality for boron and mercury, but it may be illusory for selenium, for which the analytical data lack dependability.

The data that are relatively undependable are those for which the relative standard deviations are high. The specific metals whose concentrations are not well defined are as follows:

- Inlet of Module E. Chromium, mercury, antimony, and selenium were poorly defined in the front half. A number of metals, with boron and mercury as notable exceptions, were poorly defined in the back half. These two metals are volatile and thus captured in relatively large amounts and determined with relatively high dependability in the back half. The data for the remaining metals in the back half cannot be regarded as meaningful indicators of actual gas-phase concentrations, even though the precision of the results for some may be satisfactory, for the occurrence of these metals (except possibly selenium) cannot be expected in the vapor state. As the data relate to the total concentrations present, however, the lack of accuracy in vapor concentrations is usually not important. The poor definition of chromium, antimony, and selenium continues in the totals as well as in the separate halves of the sample collected (see the column of relative standard deviations in Table 5-24).

- Outlet of Module E. Cadmium, cobalt, mercury, manganese, nickel, antimony, selenium, and calcium in the front half all have relative standard deviations that are high (above 40%). The lower concentrations resulting from particulate capture in the scrubber are responsible for the diminished quality of the front-half data at the scrubber outlet. All metals except boron and mercury are poorly defined again in the back half and may be regarded as insignificant components of the vapor phase of flue gas sampled.

- Stack. The quality of the data for the stack is similar to that for the outlet of Module E, but the data in the two locations are similar, indicating that the outlet of one scrubber modules is similar to that of each of the other four operating modules.

The primary discussion of the data on the metals in Tables 5-24, 5-25, and 5-26 is presented later in Sections 5.6.1 and 5.6.2.

Whereas the data tables discussed above employ the concentration units $\mu g/Nm^3$ and mg/Nm^3, three additional tables — Tables 5-27, 5-28, and 5-29 — present concentrations in the units $\mu g/g$ or mg/g. Here, the data express ratios of the component concentration and the total concentration to the total particulate concentration at the location sampled. The significance of these data is discussed later in Section 5.6.5. The only clarification needed at this point has to do with the concentrations in the solid at the outlet of Module E or in the stack; both are believed to be low because of the predominance of sulfate in solids at these locations.

The impingers of the acid gases train were analyzed not just for anions but for selenium. This was done with the idea that selenium in the vapor state as SeO_2 might pass through the filter and react as an acid with the carbonate buffer, making capture likely. One set of carbonate impingers from the inlet of Module E and another set from the outlet of Module F were analyzed for selenium. The results expressed as selenium concentrations in the flue gas ($\mu g/Nm^3$) are as follows:

	Inlet (E)	Outlet (F)
October 25	23.8	7.8
October 26	<7.5	12.9
October 27	<3.8	5.8
October 28	<4.8	13.3

The data seemingly cannot be accepted as valid. If there were to be selenium in the vapor state, the likelihood would be greater at the scrubber inlet, not at the outlet (because of the difference in temperature).

5.5.2.3 Non-metals

The three non-metals under study — fluorine, chlorine, and sulfur — are reported as the corresponding anions — fluoride, chloride, and sulfate — in Table 5-30. The concentrations of the anions are given in the units mg/Nm^3; they are based entirely on analyses of the impinger solutions from the back half of the acid-gases train.

The vapors presumed to have been present in the flue gas were the compounds HF, HCl, and SO_2; the first two compounds are simply captured by acid-base reactions in the alkaline impinger solutions, whereas SO_2 undergoes oxidation and neutralization

Table 5-27
Ratios of Metals to Total Suspended Solids at the Inlet of the E Scrubber Module
(Data in µg/g or mg/g)

	Solid	Vapor	Total
Trace metals (µg/g)			
As	88.7	3.2	92.0
B	540	3029	3569
Ba	376	3	379
Be	14.0	0.3	14.3
Cd	11.6	0.4	12.0
Co	28.8	0.3	29.1
Cr	229	6	235
Cu	126	4	130
Hg	0.06	5.03	5.09
Mn	195	7	202
Mo	102	5	108
Ni	127	2	129
Pb	110	2	112
Sb	18.3	0.5	18.8
Se	20.0	8.1	28.1
V	646	19	665
Major metals (mg/g)			
Al	97.3	0.4	97.7
Ca	16.7	0.4	17.1
Fe	130	1	131
Mg	5.92	0.05	5.97
Ti	8.20	0.07	8.27

Table 5-28
Ratios of Metals to Total Suspended Solid at the Outlet of the E Scrubber Module
(Data in µg/g or mg/g)

	Solid	Vapor	Total
Trace metals (µg/g)			
As	214	0	214
B	325	2676	3002
Ba	324	4	327
Be	8.31	<2.4	9.5
Cd	13.8	3.6	17
Co	<5.4	<39.4	<50
Cr	260	26	287
Cu	101	12	113
Hg	0.2	37.1	37
Mn	27.4	14.6	42
Mo	353	2	355
Ni	16.5	12.3	29
Pb	154	10	164
Sb	0.9	<39.7	<40
Se	249	91	339
V	738	3	741
Major metals (mg/g)			
Al	9.06	0.07	9.13
Ca	12.5	0.2	12.8
Fe	27.1	0.0	27.0
Mg	1.67	0.03	1.70
Ti	1.99	0.00	1.99

Table 5-29
Ratios of Metals to Total Suspended Solid at the Stack
(Data in µg/g or mg/g)

	Solid	Vapor	Total
Trace metals (µg/g)			
As	246	4	250
B	681	2996	3677
Ba	326	13	339
Be	8.33	<3.0	9.8
Cd	22.3	0.3	22.6
Co	8.72	<39.9	<50
Cr	334	<4.5	336
Cu	111	10	121
Hg	0.2	47.9	48.2
Mn	49.8	11.1	60.9
Mo	362	10	373
Ni	75.9	<11.1	<80.4
Pb	117	<40.4	137
Sb	<18.7	1.0	<20
Se	234	101	335
V	846	33	879
Major metals (mg/g)			
Al	9.60	0.34	9.94
Ca	6.92	0.98	7.89
Fe	27.0	0.8	27.8
Mg	1.46	0.07	1.53
Ti	1.93	0.05	1.99

Table 5-30
Concentrations of Anions in the Gas Phase (Acid Gases)
at All Four Gas Sampling Locations
(Data in mg/Nm³ or ppmv)

Module E Inlet						
Run	Sulfate mg/Nm³	SO_2 ppmv	Chloride mg/Nm³	HCl ppmv	Fluoride mg/Nm³	HF ppmv
Oct. 25 AM	-	-	-	-	-	-
PM	8265	2069	182	124	2.0	2.6
Oct. 26 AM	7382	1848	195	132	2.2	2.8
PM	7542	1888	46	31	1.2	1.6
Oct. 27 AM	7537	1887	237	161	2.3	2.9
PM	5663	1418	241	164	1.8	2.2
Oct. 27 AM	7413	1856	238	162	3.2	4.1
PM	7731	1936	245	166	2.5	3.2
Avg.	7362	1843	198	134	2.2	2.8
Std.Dev.	807	202	71	48	0.6	0.8

Module E Outlet						
Run	Sulfate mg/Nm³	SO_2 ppmv	Chloride mg/Nm³	HCl ppmv	Fluoride mg/Nm³	HF ppmv
Oct. 25 AM	1466	367	2.2	1.5	0.10	0.13
PM	1135	284	1.9	1.3	0.08	0.10
Oct. 26 AM	1370	343	2.6	1.8	0.27	0.34
PM	1075	269	1.9	1.3	0.05	0.07
Oct. 27 AM	1426	357	2.5	1.7	0.05	0.07
PM	1994	499	6.8	4.6	0.09	0.11
Oct. 27 AM	1219	305	2.3	1.6	0.06	0.08
PM	963	241	1.8	1.2	0.06	0.08
Avg.	1331	333	2.7	1.9	0.1	0.1
Std.Dev.	321	80	1.7	1.1	0.1	0.1

Table 5-30 (Concluded)
Concentrations of Anions in the Gas Phase (Acid Gases)
at All Four Gas Sampling Locations
(Data in mg/Nm³ or ppmv)

Module F Outlet						
Run	**Sulfate mg/Nm³**	**SO_2 ppmv**	**Chloride mg/Nm³**	**HCl ppmv**	**Fluoride mg/Nm³**	**HF ppmv**
Oct. 25	1992	499	2.8	1.9	0.20	0.25
Oct. 26	1047	262	2.9	2.0	0.09	0.12
Oct. 27	1115	279	2.9	2.0	0.10	0.12
Oct. 28	959	240	2.3	1.6	0.11	0.13
Avg.	1278	320	2.7	1.9	0.1	0.2
Std.Dev.	480	120	0.3	0.2	0.1	0.1
Stack						
Run	**Sulfate mg/Nm³**	**SO^2 ppmv**	**Chloride mg/Nm³**	**HCl ppmv**	**Fluoride mg/Nm³**	**HF ppmv**
Oct. 25	1176	295	2.1	1.4	0.08	0.11
Oct. 26	1386	347	2.2	1.5	0.06	0.08
Oct. 27	1219	305	2.2	1.5	0.08	0.10
Oct. 28	1140	285	2.2	1.5	0.08	0.10
Avg.	1231	308	2.2	1.5	0.1	0.1
Std.Dev.	109	27	0.0	0.0	0.0	0.0

to occur as sulfate. The calculated concentrations of the vapors in the units ppmv are included with the other data on concentrations in Table 5-30.

Only solids from the flue gas in the stack were analyzed for the anions corresponding to the acid gases. The filters from the sampling train were extracted with water and the extracts analyzed. Apparent weight-based concentrations of the anions in the filter solids were as follows:

	Cl^-, μg/g	F^-, μg/g	SO_4^{-2}, %
October 25	140	48	57.1
October 26	160	36	54.3
October 27	170	44	52.4
October 28	-	55	63.8

The concentrations of chloride and fluoride are not high enough to be remarkable; those of sulfate, on the other hand, are quite remarkable. Small concentrations of the anions might be explained as the result of interaction between the acid gases and alkali in the solids; the average sulfate concentration of approximately 60% surely cannot be explained this way.

The probable explanation for the sulfate is the condensation of sulfuric acid vapor during cooling of flue gas in the scrubber, with little capture of the condensed mist occurring in the scrubber. The question to be considered is what concentration of sulfuric acid would be condensed to the amount of sulfate implied by the data above. The average stack particulate concentration was 128 mg/Nm^3. Sixty percent of this figure is 77 mg/Nm^3; this corresponds to a sulfuric acid vapor concentration of 19 ppmv. Such a level of sulfuric acid vapor is easily attainable with a coal containing 2.8% sulfur.

If sulfate accounts for 60% of the solid in the stack, fly ash is not likely to account for the remaining 40%. Sulfate has a formula weight of 96 and anhydrous sulfuric acid has a formula weight of 98; however, the acid as the dihydrate often said to occur as the condensate in a flue-gas environment has a formula weight of 134. Thus, the condensate may weigh 134/96 or 1.4 times as much as the sulfate, leaving perhaps as little as 20% of the stack particulate as the mineral matter that constitutes fly ash.

It is appropriate to calculate the vapor concentrations equivalent to the anion concentrations in the stack solids. The concentrations chosen to be representative of the solids are: chloride, 160 μg/g; fluoride, 45 μg/g; and sulfate, 60%. The average concentration of total stack solids stated above is 128 mg/Nm^3. From these data, the calculated vapor concentrations are: HCl, 0.0139 ppmv; HF, 0.0073 ppmv; and SO_2, 19.2 ppmv (the last value is simply a reiteration of the value expressed above for sulfuric acid vapor). The stack solids thus contain negligible concentrations of the anions compared to the vapor concentrations that were observed. In other words, not much of the vapors is represented by the solids.

5.5.3 Scrubber Solids and Liquid Streams

In addition to the flue gas streams entering and leaving the scrubber, there are the following slurry streams and one make-up water stream. Analysis of the components of these streams included the 16 trace metals, the five major metals, and the three anions produced from non-metals in the coal. Altogether, the analyses included the steps enumerated in the following outline:

- Limestone slurry prepared from make-up water and ball-milled limestone at a concentration of about 30% solids. Analysis was made of
  - the clear make-up water,
  - the dry limestone before ball-milling,
  - the separate liquid and solid phases of the limestone slurry being fed to the scrubber.
- Additional make-up water, without suspended solids, that is supplied to the recycle tank to maintain a solids concentration there of about 12%.
  - the analysis of the clear make-up water listed above was assumed applicable here.
- Waste slurry that is recycled to the scrubber.
  - the separate liquid and solid phases of the recycle slurry were analyzed.
- Waste slurry that is discharged to the sludge pond.
  - the separate liquid and solid phases of the recycle slurry were again analyzed.

The concentration of solids in each of the slurries was determined; the results were as follows:

Limestone slurry	range, 29.6–32.7%
Recycle slurry	range, 11.1–12.1%
Discharge slurry	range, 10.2–10.4%

It is not apparent why there was a consistent difference in the solids concentrations in the recycle and discharge slurries, as indicated above. Perhaps the difference is due to partial loss of water by evaporation from the recycle stream. In any event, as will be shown, the overall concentrations of metals and anions in the two streams were close to the same.

Several months after the samples had been in storage in the laboratory, some of the liquid phases were measured for pH. The values were as follows:

Limestone slurry	pH = ca. 8.0
Recycle slurry	pH = ca. 7.5
Discharge slurry	pH = ca. 6.5

For the limestone slurry, the result is attributable to mild buffering action from slight solubility. For the latter two slurries, the values are in contrast to slurry operating values below pH = 6. Evidently, loss of dissolved CO_2 between the times of collection and pH measurement caused elevation in pH, more so for the recycle slurry than for the discharge slurry.

Very little of the limestone was dissolved when the limestone slurry was made up. Hence, it was possible to compute slurry composition in two ways — 1) by taking a weighted average of the make-up water and dry limestone compositions, and 2) by taking a weighted average of the liquid- and solid-phase compositions of the slurry itself. Neither the liquid phase (water before or after contact with the limestone) nor the solid phase (dry or wet limestone) would have to have the same composition, but the composite developed on either basis should be the same as the other. Computed compositions on the two bases were subsequently compared.

Concentrations in the individual phases of the liquid and solids in the recycle slurry and the discharge slurry were likewise combined to obtain the make-up of either composite. Because the two slurries were expected to be similar, except for differences in water as noted above, the composites were appropriately compared.

5.5.3.1 Mercury

Concentrations of mercury in streams associated with the scrubber are listed in Tables 5-31 and 5-32. It is to be noted that the concentrations in the liquids are in the units ng/mL, whereas those in the solids are in the units μg/g. Thus, there is, practically speaking, a 1000-fold difference in the mercury concentrations in the two phases.

The concentrations in the input water and limestone, whether before or after combination in the slurry, were often below the detection limits. The data can be conservatively summarized by the statements that in the water the value was always below 0.04 ppb and that in the limestone (where the detection limit was much higher) always below 0.02 ppm. As will be shown by other data later, the mercury entering the scrubber in the limestone slurry was far below that entering in the flue gas. In other words, the limestone slurry was responsible for only a small fraction of the total.

The mercury in both liquid and solid phases leaving the scrubber as the recycle slurry or the discharge slurry was much enriched over the level entering in liquid and solid forms. As may be reasonably inferred, the increase was due to the uptake of mercury from the flue gas. There was some variability from sample to sample, but in either slurry composite the calculated mercury concentration was approximately 0.02–0.03 ppm. The composite analyses of the two slurries agree satisfactorily, in general.

Table 5-31
Mercury Concentrations in Liquids and Solids Entering the E Scrubber Module

Sampling Occasion	Make-up Water, ng/mL	Dry Limestone, µg/mL	Limestone Slurry	
			Liquid ng/mL	Solid µg/g
Oct. 25 AM	<0.010	0.0120	<0.010	<0.0079
PM	<0.010	<0.010	0.004	<0.010
Oct. 26 AM	<0.010	<0.0087	0.001	<0.010
PM	0.036	0.0150	0.001	0.0130
Oct. 27 AM	<0.010	0.0100	0.058	<0.010
PM	0.003	<0.00097	0.061	<0.010
Oct. 28 AM	0.005	<0.0066	0.001	0.0180
PM	<0.010	<0.010	<0.010	0.0170

Table 5-32
Mercury Concentrations in Liquids and Solids Leaving the E Scrubber Module

Sampling Occasion	Recycle Slurry			Discharge Slurry		
	Liquid ng/mL	Solid µg/g	Composite µg/g	Liquid ng/mL	Solid µg/g	Composite µg/g
Oct. 25 AM	-	-	-	0.070	0.240	0.0248
PM	0.110	0.260	0.0295	0.070	0.240	0.0248
Oct. 26 AM	0.775	0.069	0.0084	0.326	0.240	0.0248
PM	0.178	0.250	0.0279	0.326	0.240	0.0248
Oct. 27 AM	2.430	0.220	0.0283	0.619	0.230	0.0240
PM	0.126	0.240	0.0289	0.619	0.230	0.0240
Oct. 28 AM	0.152	0.250	0.0303	0.272	0.230	0.0237
PM	0.008	0.270	0.0324	0.272	0.230	0.0237

5.5.3.2 Other Metals

Data illustrating the concentrations of all 16 trace metals and the five major metals of concern in liquids and solids associated with the E scrubber module are presented in Tables 5-33 and 5-34. The first of these tables concerns the input streams; the second is devoted to the output. Mercury is included in these tables, not for the purpose of introducing new information but for the purpose of comparison with the other metals.

Both tables include information on the composites, which were obtained by weight-averaging of the data on the separate phases. For combining data when an analyte was not detected, the concentration was assumed to be one-half of the detection limit. Table 5-33 compares two composites representing the limestone slurry; the one denoted as based on "feed" was derived from analyses of the water and dry limestone before combination, whereas the one denoted as based on "slurry" was derived from analyses of the separate components of the slurry. The final column gives the ratios of concentrations derived the two ways. At times, the ratio is quite far from unity, indicating the lack of reliable data.

Table 5-34 compares not two composites of one type but composites nominally of different slurries — recycle and discharge. The ratio of these values is more nearly consistent at values near unity, showing better reliability of the analytical data (the result of fewer analytes being below the detection limits.

Most of the trace metals were undetectable in the make-up water and the liquid phase of the limestone slurry. There is evidence that only a few metals were extracted from the limestone and thus increased in concentration in the liquid phase. Most of these metals, on the other hand, were sharply enhanced in concentration in the slurry being recycled or discharged. Most were also enhanced in concentration in the waste solids.

There are a few observations that can be made about data integrity, in addition to the inferences derived from internal data consistency (such as the ratios of composite concentrations). Calcium was found at about 38% by weight in either the dry or wet limestone, whereas it is found at 40% in pure calcium carbonate. Calcium was found around 25% in the solids in the waste slurries, in reasonable accord with the expected value of 23% in gypsum. Metals that are akin to calcium — magnesium and barium — showed certain parallels to calcium — for example, appearing at relatively high concentrations in the limestone compared to other metals. Boron was justifiably found at similar concentrations in both phases of each slurry; this is not surprising because of the removal of boric acid from the flue gas and the formation of relatively soluble borate compounds.

Table 5-33
Representative Data on Trace and Major Metals in Liquids and Solids Entering the E Scrubber Module
(Data for samples on the morning of October 27)

	Make-up Water µg/mL	Dry Limestone µg/g	Limestone slurry		Calcd. Composite		Ratio
			Liquid µg/mL	Solid µg/g	Based on feed, µg/g	Based on slurry, µg/g	
Trace metals							
As	0.005	1.060	<0.003	1.000	0.324	0.303	0.94
B	<0.228	0.176	<0.228	2.830	0.133	0.934	7.04
Ba	0.023	39.900	0.074	43.200	12.066	13.098	1.09
Be	0.003	<0.587	0.003	0.264	0.091	0.082	0.90
Cd	<0.001	1.090	<0.001	0.907	0.330	0.274	0.83
Co	<0.005	9.980	<0.005	9.670	3.016	2.922	0.97
Cr	<0.003	5.370	<0.003	5.590	1.623	1.689	1.04
Cu	0.071	232.000	<0.006	3.250	70.113	0.984	0.01
Hg	<0.001	0.010	0.000	0.005	0.003	0.002	0.51
Mn	<0.002	67.700	<0.002	71.300	20.446	21.533	1.05
Mo	<0.005	<3.08	0.038	1.380	0.467	0.444	0.95
Ni	<0.004	3.860	<0.004	2.720	1.167	0.823	0.70
Pb	<0.061	18.800	<0.061	0.460	5.699	0.166	0.03
Sb	<0.050	<6.020	<0.050	2.710	0.108	0.992	9.16
Se	<0.527	<0.930	<0.527	0.500	0.326	0.335	1.03
V	<0.004	2.520	<0.003	2.720	0.764	0.822	1.08
Major metals							
Al	<0.123	700	<0.123	744	211	225	1.06
Ca	38	386000	62	374000	116599	112991	0.97
Fe	<0.143	1010	<0.143	1240	305	375	1.23
Mg	7.220	14600	19	12700	4414	3848	0.87
Ti	<0.002	2	<0.002	3.10	0.73	0.94	1.28

Table 5-34
Representative Data on Trace and Major Metals in Liquids and Solids Leaving the E Scrubber Module
(Data from the morning of October 27)

	Recycle Slurry		Calcd. Composite µg/g	Discharge Slurry		Calcd. Composite µg/g	Ratio of Compos-ites
	Liquid µg/mL	Solid µg/g		Liquid µg/mL	Solid µg/g		
Trace metals							
As	0.028	17.200	2.072	0.032	18.300	1.93	0.93
B	56.900	68.100	58.233	56.200	84.600	59.15	1.02
Ba	0.345	40.000	5.064	0.105	53.900	5.70	1.13
Be	0.004	0.390	0.050	0.004	<0.690	0.04	0.79
Cd	0.077	1.010	0.188	0.086	1.680	0.25	1.34
Co	0.042	5.540	0.697	0.028	<2.15	0.19	0.27
Cr	0.003	23.700	2.823	<0.003	34.300	3.58	1.27
Cu	0.038	12.400	1.509	0.026	16.200	1.71	1.13
Hg	0.002	0.220	0.028	0.001	0.230	0.02	0.86
Mn	4.470	22.100	6.568	2.160	38.700	5.96	0.91
Mo	1.190	13.500	2.655	0.415	18.700	2.32	0.87
Ni	0.184	6.640	0.952	0.204	11.100	1.34	1.40
Pb	<0.061	7.960	0.974	<0.061	11.400	1.21	1.25
Sb	0.008	<5.60	0.340	0.023	7.400	0.79	2.33
Se	<0.527	<0.95	0.289	<0.527	<0.95	0.29	0.99
V	0.008	52.500	6.255	0.009	72.000	7.50	1.20
Major metals							
Al	2.110	20200	2406	6.080	21500	2241	0.93
Ca	1560	225000	28149	1139	255000	27541	0.98
Fe	<0.143	30200	3594	<0.143	32600	3390	0.94
Mg	235	6970	1036	634	3670	950	0.92
Ti	<0.002	1770	211	<0.002	1790	186	0.88

5.5.3.3 Anions

Table 5-35 gives information for the anions chloride, fluoride, and sulfate in the same format as the preceding data in Table 5-33 and 5-34 for metals.

Absorption of the acid gases HCl, HF, and SO_2, with forced oxidation of SO_2, produced very large enhancements in the fluoride, chloride, and sulfate concentrations in aqueous solution. Chloride, being more soluble in the presence of calcium than sulfate, and being present at a higher concentration than fluorine in the flue gas, reached the highest concentration in the liquid phase — somewhat over 2000 ppm.

Sulfate, on the other hand, experienced the greatest enhancement in the solid phase. It was found at 42% in the solid phase of the recycle slurry or 51% in the solid phase of the discharge slurry. The latter is the more plausible value; sulfate is 56% of gypsum.

Table 5-35
Representative Data on Anions in Liquids and Solids Associated with Scrubber Module E
(Data for samples on the morning of October 27)

	Make-up Water µg/mL	Dry Limestone µg/g	Limestone slurry		Calcd. Composite		Ratio
			Liquid µg/mL	Solid µg/g	Based on feed, µg/g	Based on slurry, µg/g	
Cl^-	11	198	48	511	67	188	2.80
F^-	0.120	395	1.800	374	119	114	0.96
SO_4^{-2}	25	1760	141	4420	549	1433	2.61

	Recycle Slurry		Calcd. Composite µg/g	Discharge Slurry		Calcd. Composite µg/g	Ratio of Compos-ites
	Liquid µg/mL	Solid µg/g		Liquid µg/mL	Solid µg/g		
Cl^-	2266	492	2055	2324	937	2180	1.06
F^-	18	492	74	20	478	68	0.91
SO_4^{-2}	1218	416000	50577	1782	506000	54221	1.07

5.6 Data Analysis and Interpretation

5.6.1 Material Balances

5.6.1.1 Upstream from the Scrubber

The data obtained in this investigation do not permit material balance calculations to be performed for the streams ahead of the scrubber. The plan of the investigation did not include collection of samples of bottom ash or ESP ash. Moreover, the plan did not include measurement of the proportions of ash leaving the boiler as bottom ash and fly ash or the measurement of ash removal in the ESP. The only task relevant to these general considerations that can be undertaken is a comparison of the concentrations of substances flowing in the duct leading to the E Module against the concentrations that would have been observed if all of these substances originally in the coal had been entrained uniformly in the inlets to all five operating modules.

The average metal concentrations based on the coal analysis are compared with the averages found at the E Module inlet in Table 5-36. The wide range of values makes inescapable the conclusion that there are some very poor data underlying the recovery data. For a discussion, it is appropriate to focus initially on the data for the major metals, for which recoveries range approximately from 23-32%. For fly ash at the inlet of the E Module, the recovery might be expected to fall somewhere within this range. This statement is based in part on the idea that the major metals are matrix components of the ash, whether in the coal or the gas stream. It is also consistent with what was learned in earlier studies performed by Southern at Unit 1. First, the distribution of ash between bottom ash and fly ash was determined in 1993 and found to make the latter about 30% of the total. In 1993, the efficiency of the ESP was found to be negligible, whereas in 1990 it was measured at about 40%. If 30% of the coal ash were fly ash and 40% or less of the fly ash were collected in the ESP, the recovery at the inlet of Module E would be 18% or more.

Reasons thus need to be found to explain recoveries of trace metals that differ a great deal from values in the range 20-30%. There cannot be any justification for values such as 0.4% for cadmium or other values below 10%. Footnotes in the table denote metals in the coal whose concentrations were below detection limits or were suspect for other reasons. Unfortunately, if these metals are deleted from consideration, implausible results still remain. Faulty coal analysis is suspected as the more probable source of erroneous data than the flue-gas analysis, but this is an opinion that cannot be rigorously supported.

The recovery of mercury is listed as 105%. The result for this metal is highly gratifying. (As discussed in the presentation of the analytical results for mercury in the coal in Section 5.5.1, this favorable result came about by substituting a new set of results for the clean coal for those originally in hand.)

Table 5-36
Comparison of Metal Concentrations at the E Module Inlet with Concentrations Calculated from the Coal Analysis

	Average Based on Coal	Average Found by Analysis	Recovery, %
Concn, µg/Nm³			
As	365	198	54.2
B	10328	7522	72.8
Ba	4154	769	18.5
Be	272	29	10.7
Cd	5688	23	0.4
Co	<300	58	
Cr	1873	503	26.8
Cu	2639	261	9.9
Hg	9.69	10.20	105.3
Mn	1938	414	21.4
Mo	5458	221	4.1
Ni	1146	267	23.3
Pb	206	228	110.6
Sb	2399	45	1.9
Se	<130	64	
V	4641	1331	28.7
Concn, mg/Nm³			
Al	878	199	22.7
Ca	109	35	32.3
Fe	927	260	28.1
Mg	46.6	12	26.1
Ti	52.3	17	32.3

NOTE: the Hg value in the flue gas is from Method 29 (GL).
NOTE: the values for Co and Se in the coal are shown as limits because three of four of the daily results were indeterminate.
NOTE: for Mo, Pb, and Sb one of the four daily results was indeterminate.

A few metals other than mercury can be explained at recoveries above the range given for the major metals. One is boron, which is volatile as boric acid; the recovery of 73% is plausible. The recovery of selenium is not given because the concentration in the coal was below the detection limit. The recovery of 54% for arsenic can be justified because this metal is probably too volatile at boiler temperatures to be discharged in the bottom ash. The value 111% for lead, on the other hand, cannot be justified.

The following tabulation gives an overall assessment of the data validity:

Recovery range	Metals	Comment
<10%	Cd, Cu, Mo, Sb	Not plausible
10-20%	Ba, Be	Probably lower than actual, but perhaps indicative of selective discharge in bottom ash
20-35%	Cr, Mn, Ni, V Al, Ca, Fe, Mg, Ti	Probably not grossly in error
>35%	As, B, Hg, and Pb	Only Pb not believable

The recovery data for acid gases appear in Table 5-37. The average recoveries are about 82% for HCl and SO_2 but only 34% for HF. The recoveries calculated from individual sampling experiments vary widely: for HCl, 20-115%; for HF, 18-47%, for SO_2, 62-95%. Low recoveries might be explained by reaction of the gases with solids entrained in the gas stream. No data bearing on this possibility was obtained in this investigation; earlier studies in other test sites, however, suggest that loss from the gas phase in this manner is not an important process.

5.6.1.2 Across the E Module of the Scrubber

Material balance calculations at this location require assignment of concentrations and flow rates pertinent to each of the following streams:

1) Entering the scrubber
   -— Flue gas at the E Module inlet
   -— Limestone slurry
   -— Make-up water apart from that in the limestone scrubber
2) Leaving the scrubber
   -— Flue gas at the E Module outlet
   -— Waste slurry being discharged

Table 5-37
Comparison of Acid Gas Concentrations at the E Module Inlet with Concentrations Calculated from the Coal Analysis

	Average Based on Coal	Average Found by Analysis	Recovery, %
Concn, ppmv			
HCl	161	134	83
HF	8.3	2.8	34
SO_2	2256	1843	82

In actuality, the compositions of all five streams were determined but flow rates of only the inlet gas stream could be determined reliably. The duct geometry at the outlet prevented a reliable traverse and calculation of gas flow rate; consequently, it was necessary to assume that the outlet flow rate (corrected for moisture and oxygen changes) was the same as the inlet flow rate. There was no way to obtain any direct data whatsoever regarding the flow rates of the limestone slurry and the make-up water. Also, the available data from the scrubber control room on the flow rate of waste slurry were deemed to be unreliable. On consecutive sampling days, average recorded flow rates at hourly intervals and the standard deviations of the rates were as follows:

October 25	1529 ± 532 gal/min
October 26	1297 ± 633 gal/min
October 27	1180 ± 675 gal/min
October 28	976 ± 599 gal/min

The wide hourly variation each day and the significant downward trend from day to day makes it very doubtful that the data were dependable.

Certain assumptions about the flow rates of the water and slurries were thus necessary, as described below:

- Sulfur from the inlet gas stream (occurring as SO_2) was said to be conserved in the outlet gas stream (again as SO_2) and as sulfate in the waste slurry. Because the flow rates of SO_2 into and out of the scrubber were known, and because the sulfate concentration in the waste slurry was known, the flow rate of the waste slurry was thus fixed.

- Calcium was assumed to be the same in the limestone slurry as in the waste slurry. This assumption was nearly equivalent to assuming conservation of calcium in all input and output streams because very little calcium was present elsewhere. This assumption, of course, fixed the rate of flow of the limestone slurry, inasmuch as the concentration of calcium in the limestone slurry was known. It is gratifying that the calculated mole ratio of calcium in the limestone to SO_2 in the inlet flue gas was near unity, for such a value is said to be a typical operating parameter for the scrubber.

- Water flow was assumed to be conserved. This means that the make-up water flowing to the recycle tank was calculated to be about eight times that of the water entering the scrubber in the limestone slurry. The practice is to feed water to the recycle tank to keep the solids near 12% by weight, whereas limestone is transported to the scrubber at 30%. Much of the water associated with material balance in the scrubber, of course, was in the form of water vapor in the inlet and outlet gas streams — typically around 6.5% by volume at the inlet or about 13% at the outlet.

Every other compositional parameter that was measured was tested for balance on the basis that the three conditions listed above were satisfied. Still another factor that was tested was heat balance, which is concerned with the heat exchange that occurs when hot flue gas is adiabatically cooled and saturated in the scrubber. Water entering the scrubber absorbs heat when the temperature is elevated approximately from 75 to 125 °F and the evaporation of a substantial fraction (roughly 25%) occurs, while the entering flue gas gives up the same amount of heat as it cools approximately from 325 to 125 °F.

The results of material balance calculations based on data for the morning of October 27 are presented in Table 5-38. The flow-rate data that are based on analytical results below detection limits are shown in parentheses (as usual, the undetected analytes were assumed to be present at one-half the detection limit). The data for all parameters of interest are combined in the one table (trace and major metals, anions, water, and heat). The first four data columns pertain to input streams, the next three deal with output, and the final gives the "closure" — defined as the total output as a percentage of the total input.

Attention naturally falls early on the column of closure values. Inspection of these data should begin with the values that are 100% — for calcium, sulfate, and water, for reasons already discussed (values fixed at the outset of calculations). Aside from these values, the closure of 99% for heat is, to a degree, independent of the assumed closure for water; the result is highly gratifying. Beyond these four results, the balance can be classified as follows:

	Number of closures		
	<75%	75-125%	>125%
Trace metals	7	7	2
Major metals	0	3	1
Anions	0	2	1

The value for mercury, 91%, can justifiably be singled out as quite good. All of the mercury data in the table having to do with flue gas, it must be said, are based on Method 29.

A question of some importance is whether concentrations arbitrarily set at one-half of detection limits were responsible for three closures below 50% and two above 125%. The low closure of 7% for cobalt cannot be attributed to this factor since this metal was undetected in samples related to output, not input (in other words, the convention respecting detection limits made the closure higher than it would have been otherwise).

Table 5-38. Material Balance at the E Scrubber Module (Data from the morning of October 28)

October 28 AM

T in gas 324	Water g/s 19037	Limestone g/s 766.4	Flue Gas E Inlet Nm^3/s 102	Total Input mg/s	Slurry g/s 11890.16	Flue Gas E Outlet Nm^3/s 102	Total Output mg/s	
T out gas 125		Ca, mol/s 7.324			SO_4, 5.2979%			Matl Balance Closure, % (Output/ Input)
T in water 75		Ca, mol/s 0.933	S, mol/s 8	Total			Total	
Trace metals, mg/s								
As	0.057	0.820	22.714	23.591	20.440	3.202	23.642	100
B	(2.170)	(0.050)	788.255	790.475	676.087	46.966	723.053	91
Ba	0.527	33.262	79.506	113.295	69.559	4.270	73.829	65
Be	0.066	(0.258)	2.937	3.261	0.861	0.098	0.959	29
Cd	0.012	0.812	2.058	2.882	2.717	0.114	2.830	98
Co	0.051	7.894	6.242	14.186	(1.518)	(-0.591)	0.927	7
Cr	(0.032)	2.368	42.372	44.772	43.254	3.930	47.185	105
Cu	1.057	106.530	26.525	134.111	20.814	1.462	22.277	17
Hg	0.000	(0.003)	0.976	0.979	0.282	0.610	0.892	91
Mn	0.021	50.046	40.816	90.882	82.388	0.317	82.705	91
Mo	(0.045)	(1.357)	21.142	22.543	26.987	4.664	31.652	140
Ni	0.050	2.958	24.303	27.311	14.721	0.201	14.922	55
Pb	(0.581)	7.817	23.076	31.474	(12.696)	2.667	15.363	49
Sb	(0.474)	(2.652)	4.190	7.316	12.241	-0.397	11.844	162
Se	5.007	(0.422)	2.631	8.059	(3.390)	1.187	4.577	57
V	(0.025)	1.625	126.250	127.899	89.331	11.391	100.722	79
Major metals, g/s								
Al	0.002	0.392	21.216	21.610	25.259	0.126	25.384	117
Ca	0.822	293.531	3.540	297.894	297.061	0.210	297.271	100
Fe	0.005	0.714	26.620	27.340	37.113	0.362	37.475	137
Mg	0.139	10.806	1.271	12.216	11.364	0.025	11.388	93
Ti	(0.001)	0.002	1.806	1.807	2.122	0.028	2.150	119
Anions, mg/s								
Cl^-	0.179	0.198	24.205	24.582	26.930	0.234	27.164	111
F^-	0.002	0.244	0.325	0.572	0.930	0.006	0.936	164
SO_4^{-2}	0.445	1.265	753.902	755.612	629.938	123.972	753.910	100
H_2O, kg/s	19037	0	6677	25714	13408	12306	25714	100
Heat, kcal/s				3839			3814	99

The value of 17% for copper cannot be explained as the result of this factor, since this metal was always assigned a concentration value above the detection limit. The value of 49% for lead does not have this explanation either. Similarly, the two high closures, for antimony and fluoride, would have to be explained otherwise.

Some of the overall aspects of the individual flow rates are these:

1) The inlet flue gas dominates input in every aspect except for calcium, where the limestone is dominant. Another way to make this point is that neither the make-up water nor the limestone is the dominant source of any objectionable element.

2) The discharge slurry dominates output for every element. The quantitative impact of this statement will be shown later by data revealing scrubber efficiencies.

The results of material balance calculations for all eight test occasions are summarized in Table 5-39. The data for the entire set of experiments are very similar to those for the one experiment already discussed.

5.6.2 Removal Efficiencies Across the Scrubber

Measurements at the inlet and outlet of the E Module provided data at two L/G ratios: the customary value around 85 gal/kacf and an increased value of about 100 gal/kacf. For most of the substances measured, the efficiency of removal in the scrubber was not greatly affected by the change in L/G; indeed, only for SO_2 was the efficiency clearly increased at the higher L/G. Accordingly, the data are first presented here without regard to L/G; later, in Section 5.6.3.1, the data are presented separately for the two different conditions.

Removal efficiencies were calculated from flow rates of the substances of interest by use of the mass flow rates that were evaluated in the calculations of material balance. These efficiencies, of course, are identical to those that would have been derived from concentrations, because of the assumed identity of inlet and outlet flow rates.

The removal efficiencies in the E Module are summarized in Table 5-40. Data are given in the table for all eight combinations of inlet and outlet sampling experiments; they pertain to all 21 metals and 3 non-metals that were under study. The data for some of the metals are spurious and need not be given serious consideration. The positive results for cobalt are obviously meaningless; they are due to blank corrections that gave the outlet apparently negative concentrations. The wide variability of the data for selenium, both positive and negative, means, in effect that reliable information as to the removal of selenium were not obtained. Antimony seems to have a plausible average value, but the wide range in individual results undermines confidence in the result.

Table 5-39. Summary of Material Balances Across the E Scrubber Module (Data on Closures in %)

	Oct. 25		Oct.26		Oct. 27		Oct. 28		Avg.	Std. Dev.
	AM	PM	AM	PM	AM	PM	AM	PM		
Trace metals										
As	160	135	175	118	127	103	100	120	130	26
B	111	114	121	112	102	49	91	101	100	23
Ba	66	51	66	62	59	46	65	66	60	8
Be	36	32	28	23	16	14	29	32	26	8
Cd	145	67	81	96	83	83	98	105	95	23
Co	30	31	6	6	11	8	7	8	13	11
Cr	105	45	92	83	75	78	105	119	88	23
Cu	19	18	12	12	10	14	17	15	15	3
Hg	73	88	85	92	76	71	91	86	83	8
Mn	88	82	73	64	69	60	91	94	78	13
Mo	144	134	146	132	117	112	140	153	135	14
Ni	68	45	59	51	44	43	55	62	53	9
Pb	51	47	48	47	39	42	49	46	46	4
Sb	65	41	183	75	194	145	162	165	129	59
Se	78	85	118	95	51	44	57	65	74	25
V	61	54	67	58	66	57	79	97	67	14
Major metals										
Al	165	133	134	115	115	90	117	134	125	22
Ca	100	100	100	100	100	100	100	100	100	0
Fe	186	155	142	139	131	108	137	152	144	22
Mg	97	103	92	96	82	83	93	110	95	9
Ti	191	154	135	114	116	90	119	136	132	31
Anions										
Cl^-	86	90	111	473	103	63	111	116	144	134
F^-	195	238	179	229	141	122	164	168	179	40
SO_4^{-2}	100	100	100	100	100	100	100	100	100	0
H_2O	100	100	100	100	100	100	100	100	100	0
Heat	120	106	85	102	109	94	99	110	103	11

Table 5-40. Summary of E Module Scrubber Efficiencies (Data in %)

	Oct. 25		Oct. 26		Oct. 27		Oct. 28		Avg. Dev.	Std. Dev.
	AM	PM	AM	PM	AM	PM	AM	PM		
Trace metals										
As	85	88	80	89	84	80	86	86	85	3
B	93	93	95	93	93	96	94	95	94	1
Ba	94	94	93	95	95	94	95	94	94	1
Be	96	97	96	97	97	96	97	97	96	1
Cd	74	84	90	94	97	93	94	96	90	8
Co	110	106	108	111	108	108	109	107	108	2
Cr	90	97	90	92	94	87	91	90	91	3
Cu	93	95	93	94	95	93	94	95	94	1
Hg	52	44	45	41	48	45	37	44	45	4
Mn	98	99	97	99	99	99	99	98	99	1
Mo	80	82	74	79	81	73	78	78	78	3
Ni	98	99	96	99	99	99	99	99	98	1
Pb	91	92	90	91	92	88	88	91	90	2
Sb	105	102	63	103	97	72	109	103	94	17
Se	23	-43	-135	-68	54	55	55	28	-4	71
V	99	93	91	93	92	89	91	92	92	3
Major metals										
Al	99	99	99	99	99	99	99	99	99	0
Ca	90	97	94	97	95	96	94	97	95	2
Fe	98	99	99	99	99	98	99	99	99	0
Mg	97	98	98	99	98	98	98	99	98	0
Ti	98	99	98	98	99	98	98	99	98	0
Anions										
Cl^-	99	99	99	96	99	97	99	99	98	1
F^-	95	96	88	96	98	95	98	98	95	3
SO_4^{-2}	82	86	81	86	81	65	84	88	84	2

NOTE: Average for SO_4 does not count the value 65.

The computation of individual removal values for selenium, rather than the computation of a single value based on the averages of inlet and outlet concentrations, gives a far more realistic understanding of the analytical problems with this element. The averages in Tables 5-26 and 5-29 indicate that the removal was a plausible 27%. If it were not for the wide range in individual values, this might be viewed as an indication of absorption of SeO_2 vapor in the scrubber. The average front- and back-half values of the selenium concentration at the scrubber inlet indicate that 27% of the element was in the vapor state. The credibility of this result, however, is destroyed by data indicating similar vapor percentages at the scrubber outlet and the stack.

Despite the difficulties pointed out above, there are realistic data in Table 5-40. For the anions, the data appear to be credible — on the average, 84% removal for sulfur and 95-98% for chlorine and fluorine. The stronger acidities of HCl and HCl (compared to SO_2) make higher removals for the two halogen compounds believable. The average removal of mercury is 45%; this is the result for data from Method 29, but the result would be about the same for data from modified Method 101A. For the five major metals, the range is 95-98%. An efficiency in this range, it may be imagined, should match the efficiency for removal of total particulate matter, inasmuch as there is likely to be a 1:1 correspondence between the five major metals and total particulate. In actuality, the measured efficiency for total particulate averaged 93%. Among the 13 trace metals that remain when cobalt, mercury, and selenium are not counted, 11 have removal efficiencies in the range 90-99%.

5.6.3 Effects of Scrubber Variables

5.6.3.1 L/G Variations

The efficiencies of the E Module of the scrubber for removing metals and acid gases are presented in Table 5-41 with groupings as to the L/G ratio. Allowances must be made, as suggested earlier in Section 5.6.2, for the fact that the cobalt, antimony, and selenium data are too unreliable to justify conclusions. Otherwise, however, the data seem to indicate that only the removal of SO_2 was significantly enhanced at the higher L/G ratio. At the higher ratio, 87% of the SO_2 was removed; at the lower ratio, 82% was removed. Each of these two removals is outside the range of the other plus or minus two standard deviations. This statement cannot be made for any other element except those three excepted in the earlier remark.

The data on mercury in Table 5-41 are based on Method 29. It is clear from the data given for mercury in Section 5.5.2.1 that the data based on the modification of Method 101A lead to the same conclusion — that mercury removal in the scrubber is not altered by changing L/G.

Table 5-41
Scrubber Efficiencies Separated as to L/G Values
(Data in %)

	Low L/G				High L/G			
	25th	26th	27th	28th	25th	26th	27th	28th
Trace metals								
As	85	80	84	86	88	89	80	86
B	93	95	93	94	93	93	96	95
Ba	94	93	95	95	94	95	94	94
Be	96	96	97	97	97	97	96	97
Cd	74	90	97	94	84	94	93	96
Co	110	108	108	109	106	111	108	107
Cr	90	90	94	91	97	92	87	90
Cu	93	93	95	94	95	94	93	95
Hg	52	45	48	37	44	41	45	44
Mn	98	97	99	99	99	99	99	98
Mo	80	74	81	78	82	79	73	78
Ni	98	96	99	99	99	99	99	99
Pb	91	90	92	88	92	91	88	91
Sb	105	63	97	109	102	103	72	103
Se	23	-135	54	55	-43	-68	55	28
V	99	91	92	91	93	93	89	92
Major metals								
Al	99	99	99	99	99	99	99	99
Ca	90	94	95	94	97	97	96	97
Fe	98	99	99	99	99	99	98	99
Mg	97	98	98	98	98	99	98	99
Ti	98	98	99	98	99	98	98	99
Anions								
Cl^-	99	99	99	99	99	96	97	99
F^-	95	88	98	98	96	96	95	98
SO_4^{-2}	82	81	81	84	86	86	65	88

Table 5-41 (Concluded)
Scrubber Efficiencies Separated as to L/G Values
(Data in %)

	Low L/G		High L/G		Hi/lo ratio
	Avg.	Std.	Avg.	Std.	
Trace metals					
As	84	3	86	4	1.02
B	94	1	94	1	1.00
Ba	94	1	94	1	1.00
Be	96	1	97	1	1.00
Cd	89	10	92	5	1.04
Co	109	1	108	2	0.99
Cr	91	2	91	4	1.00
Cu	94	1	94	1	1.01
Hg	46	6	44	2	0.95
Mn	98	1	99	0	1.00
Mo	78	3	78	4	1.00
Ni	98	2	99	0	1.01
Pb	90	1	90	2	1.00
Sb	94	21	95	15	1.02
Se	-1	91	-7	58	8.87
V	93	4	92	2	0.98
Major metals					
Al	99	0	99	0	1.00
Ca	93	2	97	1	1.04
Fe	99	0	99	0	1.00
Mg	98	0	98	0	1.01
Ti	98	0	98	0	1.00
Anions					
Cl^-	99	0	98	2	0.99
F^-	95	5	96	1	1.02
SO_4^{-2}	82	1	87	1	1.05

5.6.3.2 pH Variations

In a previous section, concentrations of HCl, HF, and SO_2 were shown at the outlet of the F Module when scrubbing occurred at recycle pH values of 5.7 and 5.1. The pair of outlet concentrations observed for each gas at either pH are again listed below in the units ppmv:

	Higher pH	Lower pH
HCl	1.9, 2.0	1.6, 2.0
HF	0.12, 0.25	0.12, 0.13
SO_2	279, 499	240, 262

The poor reproducibility revealed by just one pair of results makes it impossible to say that the removal of any of the gases was affected by a change in pH.

A tabulation like the one above is given below for mercury (except that the concentrations are in $\mu g/Nm^3$):

	Higher pH	Lower pH
Ionic	0.67, 0.50	0.37, 0.50
Elemental	4.75, 5.70	6.45, 5.26

Again, the data are not decisive enough to show any difference due to pH.

5.6.4 Stack Emissions

The emission factors of the substances discussed in this report were calculated from the concentrations listed for the stack in Table E-9. The calculation was based on the following equation, in which actual data on October 25 for arsenic in the stack and for properties of the coal (from Section 5.5.1) are employed:

Emission factor (g/J) = stack concentration (30.4 μg As/Nm^3)

x 1 x 10^{-6} g/μg

x gas volume per coal unit weight (0.009399 Nm^3/g coal)

x coal mass per calorific unit (1/29752 g coal/J)

= 9.61 x 10^{-12} g As/J

Table 5-43
Metal Concentrations in Cyclone-Fractionated Solids at the E Module Inlet (Data in µg/g or mg/g)

October 25	Coarse (1.134 g)	Medium (0.523 g)	Fine (0.210 g)	Composite (calcd.)
Trace metals, µg/g				
As	92.1	164	267	132
B	458	882	1952	745
Ba	413	449	581	442
Be	16.2	21.8	22.9	18.5
Cd	6.36	12.6	7.1	8.2
Co	41.6	57.4	42.4	46.1
Cr	151	341	548	249
Cu	111	176	236	143
Hg	0.0144	0.199	0.441	0.114
Mn	231	271	3048	559
Mo	305	409	605	368
Ni	141	235	211	175
Pb	92.8	184	299	142
Sb	20.0	22.6	18.1	20.5
Se	69	163	254	116
V	545	947	1548	770
Major metals, mg/g				
Al	111	100	76	104
Ca	15.8	14.1	18.1	15.6
Fe	157	178	157	163
Mg	5.43	5.72	6.29	5.61
Ti	7.09	8.75	10.10	7.89

Table 5-43. (Continued)
Metal Concentrations in Cyclone-Fractionated Solids at the E Module Inlet (Data in µg/g or mg/g)

October 26	Coarse (1.021 g)	Medium (0.613 g)	Fine (0.265 g)	Composite (calcd.)
Trace metals, µg/g				
As	74.4	153	246	124
B	407	783	1426	671
Ba	408	494	615	465
Be	13.4	19.4	24.2	16.8
Cd	4.57	8.92	9.3	6.6
Co	37.1	53.0	52.8	44.4
Cr	127	304	600	250
Cu	86	149	227	126
Hg	0.037	3.83	<0.00002	1.26
Mn	213	265	320	245
Mo	276	397	581	358
Ni	111	196	218	153
Pb	70.3	162	275	128
Sb	14.9	29.9	46.8	24.2
Se	72	161	248	125
V	495	937	1577	789
Major metals, mg/g				
Al	99.5	97.2	84.2	96.6
Ca	16.2	14.4	19.7	16.1
Fe	131	156	165	144
Mg	5.56	5.89	6.72	5.83
Ti	7.15	8.84	11.62	8.32

Table 5-43. (Continued)
Metal Concentrations in Cyclone-Fractionated Solids at the E Module Inlet (Data in µg/g or mg/g)

October 27	Coarse (1.011 g)	Medium (0.552 g)	Fine (0.231 g)	Composite (calcd.)
Trace metals, µg/g				
As	88.6	158	288	136
B	438	881	1481	709
Ba	403	471	597	449
Be	14.6	20.8	26.0	18.0
Cd	4.9	10.4	13.3	7.6
Co	39.8	59.1	48.1	46.8
Cr	148	334	628	267
Cu	93.5	164	255	136
Hg	0.0633	<0.003	0.00002	0.036
Mn	219	268	325	248
Mo	293	410	628	372
Ni	125	200	216	160
Pb	88.8	194	311	150
Sb	16.9	31.3	62.3	27.2
Se	77.1	161	253	126
V	525	973	1636	806
Major metals, mg/g				
Al	103	97	84	99
Ca	15.2	14.9	20.7	15.8
Fe	130	149	157	139
Mg	5.41	5.90	6.84	5.74
Ti	7.30	9.18	11.73	8.45

Table 5-43. (Concluded)
Metal Concentrations in Cyclone-Fractionated Solids at the E Module Inlet (Data in µg/g or mg/g)

October 28	Coarse (1.031 g)	Medium (0.583 g)	Fine (0.226 g)	Composite (calcd.)
Trace metals, µg/g				
As	90	158	365	145
B	416	765	1575	669
Ba	405	420	562	429
Be	14.5	18.2	24.8	16.9
Cd	5.46	8.39	7.79	6.67
Co	36.3	53.5	47.3	43.1
Cr	145	290	588	245
Cu	93.3	143	243	127
Hg	<0.0019	<0.0034	0.000016	-
Mn	210	239	300	230
Mo	293	365	597	353
Ni	120	169	197	145
Pb	81.9	158	281	131
Sb	10.7	35.0	52.2	23.5
Se	88	123	243	118
V	475	802	1469	701
Major metals, mg/g				
Al	105	97	81	99
Ca	14.2	14.5	19.3	14.9
Fe	130	149	149	138
Mg	5.39	5.82	6.55	5.67
Ti	7.46	9.39	11.55	8.57

Table 5-44
Comparison of Calculated Compositions of Cyclone Composites and Observed Compositions of Front-Half Solids in Method 29
(Data in µg/g or mg/g)

	Composites				Avg.	Std. Dev.
	Oct. 25	Oct. 26	Oct. 27	Oct. 28		
Trace metals, µg/g						
As	132	124	136	145	134	9
B	745	671	709	669	698	36
Ba	442	465	449	429	446	15
Be	18.5	16.8	18.0	16.9	17.6	0.8
Cd	8.2	6.6	7.6	6.7	7.3	0.8
Co	46.1	44.4	46.8	43.1	45.1	1.7
Cr	249	250	267	245	253	10
Cu	143	126	136	127	133	8
Hg	0.144	1.26	0.036	-	-	-
Mn	559	245	248	230	320	159
Mo	368	358	372	353	363	9
Ni	175	153	160	145	158	13
Pb	142	128	150	131	138	10
Sb	20.5	24.2	27.2	23.5	23.8	2.7
Se	116	125	126	118	121	5
V	770	789	806	701	766	46
Major metals, mg/g						
Al	103.9	96.6	98.6	99.4	99.6	3.1
Ca	15.6	16.1	15.8	14.9	15.6	0.5
Fe	163	144	139	138	146	11
Mg	5.61	5.83	5.74	5.67	5.71	0.10
Ti	7.89	8.32	8.45	8.57	8.31	0.30

Table 5-44. (Concluded)
Comparison of Calculated Compositions of Cyclone Composites and Observed Compositions of Front-Half Solids in Method 29
(Data in µg/g or mg/g)

	Cyclone Composite		Front-half Solids	
	Avg.	Std.Dev.	Avg.	Std.Dev.
Trace metals, µg/g				
As	134	9	90	14
B	698	36	545	150
Ba	446	15	378	122
Be	17.6	0.8	14.1	4.0
Cd	7.3	0.8	11.7	5.5
Co	45.1	1.7	29.2	9.8
Cr	253	10	233	85
Cu	133	8	130	40
Hg	-	-	0.073	0.074
Mn	320	159	198	62
Mo	363	9	106	25
Ni	158	13	130	41
Pb	138	10	111	32
Sb	23.8	2.7	19.7	6.3
Se	121	5	25	22
V	766	46	647	207
Major metals, mg/g				
Al	99.6	3.1	97.4	31.3
Ca	15.6	0.5	16.8	4.7
Fe	146	11	130	48
Mg	5.71	0.10	5.93	1.90
Ti	8.31	0.30	8.21	2.50

NOTE: The variability of mercury in the cyclone composites prevents calculation of a meaningful average.

Table 5-45 lists further data where a dependence on particle size is to be expected; it gives the compositions of fly ash in the three locations where flue gas was sampled. The data are from Tables 5-27, 5-28, and 5-29; they are for solids collected in the front half of the Method 29 train. This table also lists values for the coal ash, which are hypothetical; they were calculated by dividing concentrations in the clean coal (Table 5-15) by the weight fraction of ash in each coal sample.

The concentrations listed for the coal ash and the Module E inlet ash would be the same if the fly ash and bottom ash leaving the boiler were identical in composition and if none of the metals occurred in the vapor state. Comparison of these two ashes shows some expected agreements and some expected disagreements. The lower concentrations of boron and mercury in the inlet ash are to be expected since most of the mercury in the coal was in the vapor state at the flue-gas sampling location. Higher concentrations of some of the metals in the inlet ash, such as arsenic, are plausible for they are consistent with the metal leaving the boiler completely in the vapor state (little or none in the bottom ash) but undergoing deposition on the ash before the gas stream reached the sampling location. Some of the concentrations that are lower in the inlet ash than in the coal ash, unlike those of mercury, do not signify occurrence in the vapor state but conceivably could mean selective partitioning toward the bottom ash. Cadmium, copper, and molybdenum might be explained this way, but it seems more likely that some of the data are erroneous.

The major metals do not differ greatly in the coal ash and in the inlet ash. This is in accord with the argument that these are matrix elements, which are partitioned neither between bottom ash and fly ash nor between fly ash particles of different sizes.

Ash at the outlet of the scrubber or in the stack should consist of finer particles than that entering the scrubber (the coarser particles are more efficiently captured in the scrubber). Thus, it is unexpected to see the absence of increases in concentrations over those in the inlet ash, or to see the pronounced decreases for major metals from those in the inlet ash. One factor, however, that would alter the data listed for the outlet ash or the stack ash is the predominance of sulfate in these ashes. Section 5.5.2.3 pointed out that roughly 60% of the ash in the stack was sulfate or perhaps 80% was hydrated sulfuric acid; the same is likely true for ash at the outlet of the scrubber. Alternatively expressed, only 20% of the outlet or stack ash may be truly fly ash. These possibilities mean that to make the concentrations in the last three columns of Table 5-45 comparable, the concentrations in the last two columns should be multiplied by some factor. The factor would be five if it were true that 80% of the material collected is actually sulfuric acid. Such a multiplication of the outlet and stack concentrations would give a more plausible data set.

Table 5-45
Comparison of Metal Concentrations in Coal Ash with Those in Size-Dependent Fly Ash

	Coal Ash	Module E Inlet Ash	Module E Outlet Ash	Stack Ash
Trace metals (µg/g)				
As	42	89	214	246
B	1182	540	325	681
Ba	475	376	324	326
Be	31.1	14.0	8.3	8.3
Cd	650	11.6	13.8	22.3
Co	-	28.8	<5.4	8.72
Cr	214	229	260	334
Cu	300	126	101	111
Hg	1.110	0.060	0.168	0.240
Mn	222	195	27	50
Mo	782	102	353	362
Ni	131	127	16.5	75.9
Pb	26	110	154	117
Sb	346	18.3	0.9	<18.7
Se	-	20	249	234
V	532	646	738	846
Major metals (mg/g)				
Al	100	97.3	9.06	9.60
Ca	12.4	16.7	12.5	6.9
Fe	106	130	27.1	27.0
Mg	5.33	5.92	1.67	1.46
Ti	5.98	8.20	1.99	1.93

5.6.6 Comparison of Mercury Sampling Methods

The more important observations from the tabulations of data on mercury in the three flue-gas locations are as follows:

1. The two methods were in good agreement on the total concentration at each location where both methods were used. The differences range only from 0.1 to 0.6 $\mu g/Nm^3$.

2. Both methods indicate that the scrubber removed most of the ionic mercury. Either method shows good agreement between the outlet of Module E and the stack; Method 101A also shows good agreement between the outlets of Modules E and F and between the two outlets and the stack.

3. The methods differ substantially on the proportions of mercury in the ionic and elemental states. At each sampling location Method 29 gave the higher percentage in the ionic state. Moreover, Method 29 seemed to show that part of the ionic mercury at the scrubber inlet was converted to the elemental form at the outlet.

The difference in speciation cannot be explained unequivocally. It may have to do, however, with the lack of specificity of the peroxide impinger in Method 29 for capturing the ionic form of mercury. This question may be posed: is the observed difference caused by the possibility that the peroxide captures part of the elemental mercury, or by the possibility that the KCl solution (the substitute in modified Method 101A) is unable to retain all the ionic mercury? The first of these explanations seems more likely, because the combination of hydrogen peroxide and nitric acid in the so-called peroxide impinger surely has the oxidizing potential for converting part of the elemental mercury to the ionic state.

The suggestion that ionic mercury shifts from the ionic state to the elemental state across the scrubber surely must be an illusion. Such a change is contrary to the predictions of thermodynamics. An alternative explanation, however superficial, is that the peroxide impinger captures more of the elemental mercury under scrubber inlet conditions than under scrubber outlet conditions because of the intervention of some other substance that is changed across the scrubber, perhaps that substance is SO_2. There is no apparent mechanism whereby SO_2 could affect mercury capture in peroxide, but certainly the concentration of SO_2 is sharply reduced across the scrubber. The concentration of SO_2 is orders of magnitude higher than that of mercury; thus, there is sufficient SO_2 on a relative scale to affect mercury significantly.

If the results on speciation by the modification of Method 101A are indeed superior to those by Method 29, then the preferred ratio of ionic vapor to elemental vapor at the scrubber inlet is 48/52 rather than 74/26. It is surprising to reach the conclusion that the split between the two states is about 50:50 when the coal burned contained over 0.2%

chlorine. The past work by this and other organizations suggests that a much higher proportion of ionic mercury should have been found at this comparatively high chlorine level. This suggestion depends upon the availability of a higher concentration of HCl in the flue gas and the resulting higher degree of conversion of elemental mercury or the oxide of mercury (HgO) to the volatile compound $HgCl_2$. All the past work we know about, however, employed Method 29 or the Bloom method (based on solid media for collecting mercury vapor) for speciation. The present results that seem preferable but also exceptional in terms of past experience are based on a different medium entirely for collecting ionic mercury. If the present results from Method 29 were deemed more acceptable, they would be consistent with past experience.

Obviously, it is premature to judge the modification of Method 101A to be a superior method for general use in speciating mercury. Nevertheless, it will be of interest to compare the conclusion from this investigation with the results of ongoing experimentation and to decide at a later time, on the basis of additional data, whether the new method provides a means of obtaining improved knowledge on the species of mercury.