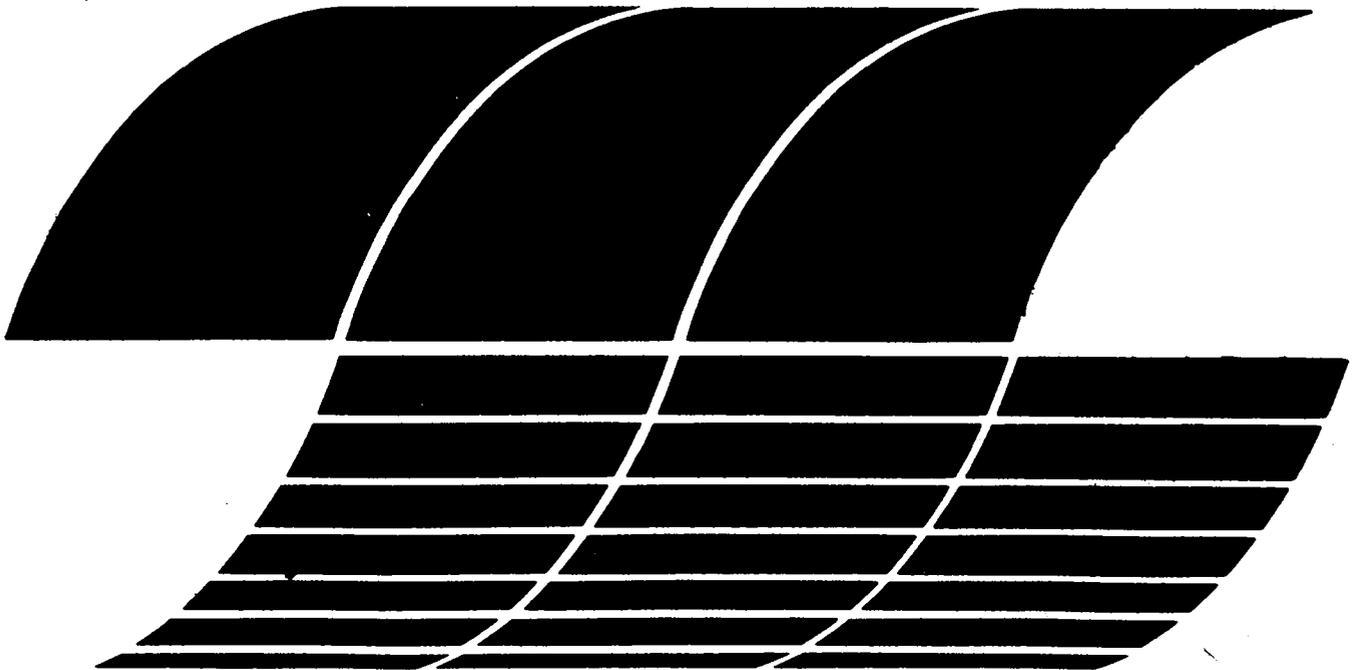




# Application of Combustion Modifications to Industrial Combustion Equipment

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# Application of Combustion Modifications to Industrial Combustion Equipment

by

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## LIMITATIONS ON APPLICATION OF DATA REPORTED

The pollutant emission data cited in this report represent a small sample of industrial combustion equipment. The data are intended to present the general emission characteristics of each type of equipment tested and the response of that equipment to combustion modifications. Because of the small sample size, application of the data to estimate mean emissions from a class of similar equipment, or to predict emissions from any other single piece of equipment, or for use in establishing emissions standards would be a misapplication.

## CONTENTS

<u>Section</u>	<u>Page</u>
ACKNOWLEDGMENTS	ii
FIGURES	v
TABLES	viii
1.0 INTRODUCTION AND SUMMARY	1
1.1 Objective and Scope	1
1.2 Results of Combustion Modifications	2
1.3 Trace Species and Organic Emissions	7
1.4 MATE Value Comparison	15
1.5 Conclusions	16
2.0 TEST UNIT SELECTION	18
2.1 Objective	18
2.2 Approach	18
2.3 Results	19
3.0 INSTRUMENTATION AND TEST PROCEDURES	27
3.1 Gas Sampling and Conditioning System	28
3.2 Gaseous Emissions	28
3.3 Particulate Emissions	29
3.4 Trace Element and Organic Emissions	29
3.5 Unit Operational Data	30
3.6 Test Procedures	30
4.0 TEST RESULTS	31
4.1 Petroleum Process Heaters	31
4.2 Mineral Kilns	68
4.3 Metal Processing	100
4.4 Boilers	139
4.5 Internal Combustion Engines	184
4.6 Gas Turbines	207
5.0 RECOMMENDATIONS	216
5.1 Areas Requiring Additional Work	216
5.2 Recommended Program Objectives	218
5.3 Proposed Program Scope	218
5.4 Technical Approach	220
5.5 Support and Discussion of Program Elements	222
6.0 REFERENCES	224
7.0 CONVERSION FACTORS	225

CONTENTS (continued)

<u>Section</u>	<u>Page</u>
APPENDICES:	
A. EQUIPMENT SURVEY	227
B. GASEOUS AND PARTICULATE EMISSIONS TEST METHODS AND INSTRUMENTATION	353
C. TRACE SPECIES AND ORGANICS SAMPLING AND ANALYSIS PROCEDURES	387
D. EFFICIENCY MEASUREMENTS	427
E. DATA RECORDING FORMATS	433
F. TRACE SPECIES AND ORGANIC EMISSIONS DATA	449
G. SASS TRAIN EVALUATION TEST	527

## FIGURES

<u>Number</u>		<u>Page</u>
4-1	Vertical fired heater, Location 4.	32
4-2	Burner patterns for refinery heater burner out of service (BOOS) tests (Location 4 tests).	37
4-3	Schematic of Location 5 process heaters.	39
4-4	NO <sub>x</sub> emissions from refinery process heater 5/1 as a function of process rate.	43
4-5	NO <sub>x</sub> emissions from refinery process heater 5/2 as a function of process rate.	44
4-6	NO <sub>x</sub> emissions from refinery process heater 5/1 as a function of excess oxygen.	45
4-7	Burner patterns tested on No. 1 petroleum refinery heater at Location 5.	46
4-8	NO <sub>x</sub> emissions from a refinery process heater as a function of excess oxygen.	48
4-9	Schematic of Location 12/1 process heater.	55
4-10	NO emission as a function of excess oxygen, Location 12/1 refinery heater with air preheat.	58
4-11	Schematic of dehexanizer reboiler (Unit 12/2).	61
4-12	NO <sub>x</sub> emission as a function of excess oxygen, Location 12/2 refinery heater without air preheat.	64
4-13	Schematic plan view of ceramic linear tunnel kiln.	69
4-14	Schematic of a dry process cement kiln system, Location 3.	76
4-15	Sintered sampling probe filter, Location 3.	77
4-16	Particle size distribution for a cement kiln.	80
4-17	Schematic of wet process rotary kiln.	81
4-18	Cement kiln particulate size distribution, Location 9.	85
4-19	Cement kiln particulate size distribution, Location 9.	86
4-20	The effect of combustion air temperature on cement kiln NO emissions.	87
4-21	The effect of cement kiln temperature on NO emissions.	88
4-22	Rotary cement kiln - sample port locations, Location 9.	90
4-23	Trace species Test 9-3 at cement kiln precipitator inlet.	93
4-24	Trace species Test 9-4 at cement kiln precipitator outlet.	93
4-25	Trace species Test 9-5 at cement kiln precipitator outlet.	95
4-26	Trace species Test 9-6 at cement kiln precipitator outlet.	95

FIGURES (continued)

<u>Number</u>		<u>Page</u>
4-27	Schematic of an open hearth furnace.	101
4-28	NO emissions as a function of time for an open hearth furnace, Test No. 14-1.	103
4-29	CO emission and flue gas O <sub>2</sub> as a function of time for an open hearth furnace, Test No. 14-1.	104
4-30	NO emissions as a function of flue gas excess O <sub>2</sub> , Test No. 14-1.	105
4-31	NO emissions as a function of time for an open hearth furnace at baseline conditions.	108
4-32	CO emissions and flue gas O <sub>2</sub> as a function of time for an open hearth furnace at baseline conditions, measured between the waste heat boiler and the precipitator.	109
4-33	Combustible emissions and flue gas O <sub>2</sub> as a function of time at open hearth furnace bridge wall at baseline conditions.	110
4-34	Combustible emissions and flue gas as a function of time at open hearth furnace bridge wall at low O <sub>2</sub> condition.	111
4-35	CO emissions and flue gas O <sub>2</sub> as a function of time for an open hearth furnace at low O <sub>2</sub> conditions.	112
4-36	NO emissions as a function of time for an open hearth furnace at low O <sub>2</sub> conditions.	113
4-37	NO emissions as a function of time for an open hearth furnace, Test No. 14-2.	116
4-38	Schematic section of reheat furnace at Location 16.	121
4-39	NO <sub>x</sub> emissions and O <sub>2</sub> as a function of load at baseline conditions for a reheat furnace.	124
4-40	NO <sub>x</sub> as a function of O <sub>2</sub> at various loads for a reheat furnace in baseline configurations.	125
4-41	Schematic cross-section through a steel ingot soaking pit building.	129
4-42	Method of heat application in a steel ingot soaking pit.	129
4-43	NO <sub>x</sub> emissions and O <sub>2</sub> as a function of load at baseline conditions for a soaking pit.	132
4-44	NO <sub>x</sub> as a function of O <sub>2</sub> at 2 MW load for a soaking pit at Location 16.	133
4-45	Plan view of aluminum melting furnace.	135
4-46	Particle size distribution for a wood/bark boiler, Test No. 13-8.	143

FIGURES (continued)

<u>Number</u>		<u>Page</u>
4-47	NO <sub>x</sub> emissions as a function of excess oxygen for a wood/bark boiler.	145
4-48	Particle size distribution for a wood/bark boiler, Test No. 13-20.	147
4-49	Particle size distribution for the wood/bark boiler at Location 10/1.	155
4-50	NO <sub>x</sub> emissions as a function of excess oxygen for the wood/bark boiler at Location 10/1.	157
4-51	Black liquor recovery boiler schematic.	160
4-52	Trace species test 10/2-10 boiler conditions.	169
4-53	Trace species test 10/2-12 boiler conditions.	171
4-54	Trace species test 10/2-14 (Part 1) boiler conditions.	172
4-55	Trace species Test 10/2-14 (Part 2).	173
4-56	Trace species test 10/2-16 boiler conditions.	175
4-57	Schematic of fluid catalytic cracking unit (FCCU) with CO boiler.	179
4-58	NO <sub>x</sub> versus excess oxygen for a carbon monoxide boiler.	181
4-59	CO as a function of excess oxygen for a CO boiler.	182
4-60	Schematic of the natural gas engine at Location 2.	185
4-61	Effect of load on NO emissions from the internal combustion engine at Location 2.	188
4-62	Effect of speed on hydrocarbon emissions from an internal combustion engine.	190
4-63	Effect of RPM on efficiency at constant load for the natural gas engine at Location 2.	193
4-64	Effect of load on efficiency at constant RPM for the natural gas engine at Location 2.	194
4-65	Block diagram of large diesel engine system at Location 15.	196
4-66	The effect of unit load on NO emissions for a diesel engine.	200
4-67	The effect of inlet air temperature on NO emissions from a diesel engine.	201
4-68	Particulate size distribution for a diesel engine firing No. 2 diesel fuel.	202
4-69	Schematic of Location 8 combined cycle unit.	212

## TABLES

<u>Number</u>		<u>Page</u>
1-1	Industrial Combustion Test Units Selected and Summary of Results Obtained	4
1-2	Trace Species and Organic Emissions From Industrial Combustion Equipment	9
1-3	Trace Species and Organics Particulates, Emission in Particulate Less Than 3 $\mu\text{m}$	10
2-1	Test Units Initially Selected	21
4-1	Summary of Fuel Gas Analyses for Location 4 Tests, % by Volume	33
4-2	Ultimate Analysis fo Fuel Oil Sample From Location 4 Tests	34
4-3	Summary of Gaseous Emissions Data, Location 4 - Petroleum Refinery Heater	36
4-4	Summary of Fuel Gas Analyses for Location 5 Tests	40
4-5	Summary of Gaseous Emissions Data, Location 5 - Petroleum Refinery Heaters	42
4-6	Summary of Fuel Gas Chromatographic Analyses	49
4-7	Summary of Gaseous Emissions Data, Location 7 - Petroleum Refinery Heater	51
4-8	Summary of Natural Draft Process Heater Efficiencies	53
4-9	Summary of Field Measurements, Location 12/1 Process Heater With Air Preheat	57
4-10	Fuel Analyses, Location 12	59
4-11	Summary of Emissions Data, Location 12/2 - Process Heater Without Air Preheat	62
4-12	Trace Species and Organics Sampling Conditions, Petroleum Process Heater - Location 12/2	65
4-13	Trace Species and Organic Emissions, Petroleum Process Heater, Location 12/2	67
4-14	Summary of Emissions Data, Location 1 - Linear Ceramic Tunnel Kiln	71
4-15	Natural Gas Fuel Analysis, Location 1 Ceramic Kiln	72
4-16	Gas Burner Oxygen Measurements in a Linear Ceramic Tunnel Kiln	73
4-17	Cement Kiln Solid Coke Fuel Analysis, Location 3	77
4-18	Rotary Cement Kiln Emission Data Summary	78
4-19	Analysis of Fuel Gas at Location 9	82
4-20	Summary of Emissions from Wet Process Rotary Kiln, Location 9	84

TABLES (continued)

<u>Number</u>		<u>Page</u>
4-21	Trace Species and Organics Sampling Conditions, Location 9 - Rotary Cement Kiln	92
4-22	Trace Species and Organic Emissions, Cement Kiln, Location 9	97
4-23	Trace Species and Organics Overall Mass Balance, Averages of Four Tests, Tests 9-3, 9-4, 9-5, and 9-6, Cement Kiln	98
4-24	Location 14 Fuel Analyses, Open Hearth Furnace	100
4-25	Trace Species and Organics Sampling Conditions, Open Hearth Furnace - Location 14	114
4-26	Trace Species and Lorganic Emissions, Open Hearth Furnace, Location 14.	117
4-27	Comparison of KVB SASS Train Results with Previous Data for the Open Hearth Furnace at Location 14	118
4-28	Natural Gas Analysis - Location 16/1	120
4-29	Summary of Tests for 10" Reheat Furnace at Location 16/1 - Natural Gas Fuel	123
4-30	Natural Gas Analysis - Location 16/2	128
4-31	Summary of Test Data at Location 16/2, Steel Soaking Pit - Natural Gas Fuel	131
4-32	Fuel Analysis, Location 6	137
4-33	Summary of Gaseous Emissions Data, Location 6 - Aluminum Melting Furnace	138
4-34	Summary of Emissions from Location 13 Wood/Bark Boiler	141
4-35	Location 13 Fuel Analyses	142
4-36	Trace Species and Organics Sampling Conditions, Location 13 - Wood/Bark Boiler	148
4-37	Trace Species and Organic Emissions, Wood/Bark Boiler, Location 13	150
4-38	Design Characteristics of Location 10/1 Wood/Bark Boiler	151
4-39	Summary of Emissions from Location 10/1 Wood/Bark Boiler Field Tests	153
4-40	Fuel Analysis, Wood Fuel, Location 10/1	154
4-41	Design Characteristics of Location 10/2 Black Liquor Boiler	159
4-42	Black Liquor Recovery Boiler, Liquor and Smelt Analysis, Location 10/2	161
4-43	Combustion of Black Liquor, Test 10/2-10	162

TABLES (continued)

<u>Number</u>		<u>Page</u>
4-44	Flue Gas Composition Based on Black Liquor Analysis, Test 10/2-10	164
4-45	Summary of Emissions from Location 10/2 Black Liquor Recovery Boiler	165
4-46	Trace Species and Organics Sampling Conditions, Location 10 - Black Liquor Recovery Boiler	167
4-47	Black Liquor Recovery Boiler Process Flow Rates for SASS Tests	168
4-48	Trace Species and Organic Emissions, Black Liquor Recovery Boiler Location 10/2	176
4-49	CO Boiler Fuel Composition	177
4-50	Summary of Field Measurements, Location 11 - CO Boiler	180
4-51	Natural Gas Composition, Location 2	184
4-52	Summary of Test Results, Location 2 - Internal Combustion Engine	187
4-53	Summary of Test Data at Location 15 - Diesel Engine	197
4-54	Location 15 Fuel Analysis	198
4-55	Trace Species and Organics Sampling Conditions - Location 15 Diesel Engine	204
4-56	Trace Species and Organic Emissions Diesel Engine, Location 15	205
4-57	Trace Species Mass Balances, Diesel Engine, Location 15	206
4-58	Summary of Gaseous Emissions Data - Location 7, Petroleum Refinery Combined Cycle Gas Turbine	209
4-59	Summary of Fuel Gas Chromatographic Analyses for Combined Cycle at Location 7	210
4-60	Summary of Emissions for Location 8 Combined Cycle Gas Turbine	214
4-61	Fuel Gas Analysis - Location 8	215

## SECTION 1.0

### INTRODUCTION AND SUMMARY

#### 1.1 OBJECTIVE AND SCOPE

The objective of the program is to investigate the effectiveness of combustion modifications and operating variable changes as a means of improvement in thermal efficiency and for emissions control in industrial combustion equipment. These techniques have previously been shown to be effective on industrial boilers (Refs. 1, 2) and the purpose of this program is to investigate the basic feasibility and/or limitations for application of this technology to other industrial combustion devices.

The program included a survey of equipment in use, and tests of selected representative devices including evaluation of combustion modifications.

The program scope provided for tests on 22 industrial combustion devices representative of kilns, process furnaces, boilers, stationary engines and gas turbines in industrial use. Emissions measured included NO, NO<sub>x</sub>, SO<sub>2</sub>, SO<sub>3</sub>, CO, CO<sub>2</sub>, O<sub>2</sub>, gaseous hydrocarbons, and where possible, particulates, particle size distribution, smoke number, and opacity. Combustion modifications evaluated, where possible, included lowered excess air, staged combustion, reduced air preheat, and burner register adjustments.

On six of the devices tested, samples were collected for analysis of trace species and selected organics emissions.

Two industrial boilers with extensive combustion modifications were also tested as an addition to this contract. Results of those tests were reported in a separate final report (Refs. 3 and 4).

This is a final report documenting the results of the program, including selection of the test units, preparation of a mobile laboratory, a summary of the test data acquired, and a discussion of the data in relation to each type of unit design and operation. The discussions and conclusions presented are based on tests of a limited number of devices. The test units were selected as representative of typical devices. However, because of the wide diversity of designs in use the results cannot be interpreted as truly representative of the entire national population of such devices. Also included are recommendations based on testing regarding the most promising directions for future research on industrial combustion devices to reduce air pollutant emissions and increase unit efficiency.

## 1.2 RESULTS OF COMBUSTION MODIFICATIONS

The initial task of the study consisted of a survey of each type of industrial combustion equipment. Existing data were collected and equipment manufacturers, operators and associations were contacted. Industries were defined for which emissions reduction or efficiency increase through combustion improvement would be of significance on a national basis. These industries were petroleum refining, minerals, paper and metals. The characteristics of specific combustion equipment of most importance in those industries were defined within the limitations of available data. These characteristics were used as guides in selection of test units that would be most nearly representative of the total population.

Together, several thousand devices were considered and relatively little information was available on many device types. Therefore, the selected test units could not be established as a statistically representative sample. The test results cannot, therefore, be interpreted as representative, in a firm statistical sense, of emission levels or efficiency of the various device groups. Rather, the results are intended to serve the prime program objective: investigation of the feasibility and effectiveness of combustion modifications by definition of those modifications that offer the most promise for further investigation and application.

The device types that were tested and a brief summary of NO<sub>x</sub> emissions, reductions and control methods are shown in Table 1-1. In general the results indicate that combustion modifications can be applied to industrial combustion equipment but reductions achievable vary significantly for different types of devices. Reductions in NO<sub>x</sub> of up to 69% were observed but on many devices reductions were less than 10%.

A government-owned mobile laboratory was used for measuring air pollutant emissions and unit efficiency parameters. The mobile laboratory contains analytical instrumentation for continuous measurement of NO, NO<sub>x</sub>, SO<sub>2</sub>, CO, CO<sub>2</sub>, O<sub>2</sub>, and hydrocarbons. Sulfur oxides (SO<sub>2</sub> and SO<sub>3</sub>), total particulate and particle size distribution were measured and analyzed by grab sample techniques. Six units were sampled for trace species and organics emissions. In addition to the effect of operational changes on air pollutant emissions, the effect on unit efficiency was also evaluated. Section 3.0 discusses instrumentation and test procedures.

Most petroleum refinery heaters are natural draft vertically fired box type designs firing refinery fuel gas. Five units tested were of this type, but some also were fired with oil fuel. The number of burners ranges widely from one up to 100, but typical units have 10 to 30 burners. Modifications evaluated included process rate, excess air, air register adjustment, and two-stage combustion. In general, the natural draft design was found to be very limited in the degree of adjustments. As a result, emissions and efficiency were fairly unresponsive to combustion modifications. There was a general absence of exhaust heat recovery, and excess air levels were high. This indicates a large potential for efficiency improvement but more extensive modifications are required that were possible in this program.

Three mineral kilns were tested. A stationary ceramic tunnel kiln exhibited low NO<sub>x</sub> emissions and extensive heat recovery was employed. Programmed temperatures along the length of the kiln must be maintained within  $\pm 3$  K (5 °F) so that, although the unit had 70 burners, no significant combustion adjustments were possible. Rotary cement kilns are of either wet or dry

TABLE 1-1. INDUSTRIAL COMBUSTION TEST UNITS SELECTED AND SUMMARY OF RESULTS OBTAINED

Device Type	Test Site No.	Rated Heat Input, MW	Fuel	Average Baseline NO <sub>x</sub>		Maximum Percent Reduction in NO <sub>x</sub>	Combustion Modification <sup>b</sup>
				ng/J <sup>a</sup>	ppm at 3% O <sub>2</sub>		
Natural Draft Process Heater	4	25.0	Ref. Gas	59	116	18	4 of 32 BOOS
Natural Draft Process Heater	5/1	15.9	Ref. Gas	50	97	22	Air Register Adjust
Natural Draft Process Heater	5/2	10.1	Ref. Gas	39	76	21	High Load, Low O <sub>2</sub>
Natural Draft Process Heater	7/1	15.5	Ref. Gas	52	103	8	2 of 16 BOOS
Natural Draft Process Heater	7/2	11.0	Ref. Gas	49	98	27	Air Register Adjust
Forced Draft Heater, Air Preheat	12/1	27.5	Ref. Gas	163	320	0	Baseline is Lowest NO <sub>x</sub>
	12/1		No. 6 Oil	113	222	0	Baseline is Lowest NO <sub>x</sub>
Forced Draft Heater, No Air Preheat	12/2	13.6	Ref. Gas	109	214	67	Low O <sub>2</sub>
	12/2		No. 6 Oil	97	172	15	Low O <sub>2</sub>
Clay Tunnel Kiln	1	9.4	Nat. Gas	46	90	41	Low O <sub>2</sub>
Rotary Cement Kiln (Dry Process)	3	70.3	Nat. Gas NG + Coke	903	1460	27	Fuel Switch, Gas to Coke
Rotary Cement Kiln (Wet Process)	9	59.0	Nat. Gas	1319	2250	14	Low O <sub>2</sub> , High Air Temperature
Steel Open Hearth Furnace	14	57.0	NG + No. 6 Oil	1094	2070 (Avg)	40	Low O <sub>2</sub>
Steel Reheat Furnace	16/1	35.0	Nat. Gas	56	110	43	3 of 27 BOOS
Steel Soaking Pit	16/2	2.9	Nat. Gas	52	101	69	Low O <sub>2</sub>
Aluminum Melter	6	10.6	Nat. Gas	49	96	0	Low O <sub>2</sub> (NO <sub>x</sub> Increased) <sup>x</sup>
	6		No. 2 Oil	104	185	0	Low O <sub>2</sub> (NO <sub>x</sub> Increased) <sup>x</sup>
Wood Bark Boiler	13	34.0	Wood+Coal	188	300	15	Low O <sub>2</sub>
Wood Bark Boiler	10/1	69.0	Wood+NG	124	229	23	1 of 4 BOOS
Black Liquor Recovery Boiler	10/2	117.0	Liquor	35	52	30	Secondary Air Adjust
CO Boiler	11	135.0	CO Gas	147	126	12	Air Register Adjust
Natural Gas Engine	2	3.2	Nat. Gas	1020	1990	20	Fuel, Air Adjust
Diesel Engine	15	1.8	No. 2 Oil	904	1611	19	Low Inlet Air Temperature
Gas Turbine Combined Cycle	7/3	230.0	Ref. Gas	59	118	14	1 of 8 BOOS
Gas Turbine Combined Cycle	8	728.0	Ref. Gas	52	103	38	4 of 16 BOOS

<sup>a</sup> 1 lb/10<sup>6</sup> Btu = 430 ng/J

<sup>b</sup> BOOS = Burners Out of Service

process types and have a single burner. A dry process kiln was tested to evaluate the effect of fuel type. This kiln had previously been tested firing gas and oil (Ref. 3) and, in contrast to most other combustion devices,  $\text{NO}_x$  emissions firing gas were nearly double the emissions when firing oil. The current test involved coke firing and the results indicate  $\text{NO}_x$  is equal to that for oil fuel. Many kilns are being converted from gas to solid fuel and 50% reduction in  $\text{NO}_x$  emissions is expected.

A wet process cement kiln was tested while firing natural gas to evaluate the effect of variation of excess air and combustion air temperature. The two variables had to be changed simultaneously to maintain process temperature. Reduction of excess air and increase in air preheat reduced  $\text{NO}_x$  by 14% at design temperature.

Three steel processing furnaces were tested. An open hearth furnace, firing natural gas and No. 6 oil, produced large fluctuations in  $\text{NO}_x$  emissions, from near zero to over 3000 ppm. By reducing excess air it was possible to reduce the average  $\text{NO}_x$  emissions by 40%. A steel billet reheat furnace firing natural gas was tested to evaluate removal of burners from service and reduced excess air. With 3 of 13 burners out of service,  $\text{NO}_x$  was reduced by 43%. A steel ingot soaking pit firing natural gas with a single burner was tested with reduced excess air.  $\text{NO}_x$  was reduced by 69%--the largest reduction achieved on the devices tested.

One aluminum furnace was tested to evaluate the effect of excess air. The unit was a batch type scrap aluminum melter with two burners. Emissions were measured for both natural gas and distillate oil firing. This unit exhibited the unusual but not unique characteristic of an increase in  $\text{NO}_x$  as excess air was reduced. Stack temperatures were very high, 1200 K (1700 °F) indicating a good potential for efficiency improvement through combustion air preheat.

Four boilers were tested, firing unconventional fuels: two with wood, one with papermill black liquor, and one with carbon monoxide gas from an oil refinery catalytic cracking unit. Tests on the two wood-fired boilers were complicated by fluctuations in wood flow. On one of these boilers, reduction

of air preheat and burner adjustments did not reduce  $\text{NO}_x$  but removing one of the four burners from service reduced  $\text{NO}_x$  by 20%. The second boiler fired wood and coal.  $\text{NO}_x$  on coal alone was 38% higher than with wood and coal together. Lowered excess air and shutting overfire air ports reduced  $\text{NO}_x$  by about 18%.

The boiler firing black liquor (by product from wood digestion to make pulp) required very close control of operation to ensure complete recovery of sodium from the liquor.  $\text{NO}_x$  emissions were low; adjustment of secondary air registers reduced  $\text{NO}_x$  by 33% but increased HC by 200%. The boiler firing carbon monoxide gas was tested with reduced excess air,  $\text{NO}_x$  port adjustment, and burners out of service.  $\text{NO}_x$  was variable and did not respond well to the modifications. This was attributed to ammonia in the CO gas; conversion of ammonia to  $\text{NO}_x$  is relatively insensitive to flame conditions.

One natural gas fired internal combustion engine was tested and modifications were made to the operation to evaluate the effect on emissions and efficiency. Modified operation included the effect of load, RPM, and air/fuel ratio on emissions and efficiency. Load had a pronounced effect on  $\text{NO}_x$  emissions and efficiency while engine speed influenced HC emissions and efficiency to a large extent. Reductions of up to 23% in  $\text{NO}_x$  and 42% in CO were obtained but consistent repeatability is questionable.

A 600 kW diesel powered electric generator was tested to evaluate the effect of load and inlet air temperature. Reduction of load to 200 kW did not reduce  $\text{NO}_x$  but at 100 kW,  $\text{NO}_x$  was reduced by 14%. Reduction of inlet air manifold temperature reduced  $\text{NO}_x$  by 7% at full load.

Two gas turbine/boiler combined cycles were tested. Both units fired refinery gas. Adjustment of the boiler air registers and removing one of eight burners from service reduced  $\text{NO}_x$  by 14% on the first unit. Similar tests in the second unit (4 of 16 burners out of service) reduced  $\text{NO}_x$  by 38%.

Results for all tests are discussed in detail in Section 4.0.

As a result of tests and observations, recommendations have been formulated to define objectives for future research. These recommendations are contained in Section 5.0.

### 1.3 TRACE SPECIES AND ORGANIC EMISSIONS

Samples were collected from six of the units with the Source Assessment Sampling System (SASS Train) to determine trace, minor and major species and organics emissions. Fuel and process samples were also collected so that mass balances could be evaluated. On two of the units, SASS samples were taken upstream and downstream of electrostatic precipitator dust collectors. Atomic absorption was used for analyzing 20 elements, wet chemistry was used for chloride, fluoride, nitrates, and sulfates, and chromatography was used for total POM and total PCB. Samples from the SASS train organic module were also analyzed by gas chromatography-mass spectrometry to identify eight specific POM compounds that are considered to be the most carcinogenic.

A total of fifteen SASS sample runs were made. Except for one unit (test 14), all runs were repeated. The SASS train used was one of the original prototype designs. The unit was sized to operate at 4 actual cubic feet per minute ( $0.113 \text{ am}^3/\text{m}$ ) at the cyclone particle collectors (478 K, 400 °F). Later trains were resized for 4 standard cfm. Sampling runs were made for 5 hours or until two filters were loaded to capacity. The design goal for the SASS train was to sample a total volume of 30 dry normal cubic meters ( $\text{dNm}^3$ ). This goal was primarily for sampling on coal-fired utility boilers. For the industrial units tested downstream of dust collectors, the sample time of 5 hours typically resulted in a total sample volume of 10 to 18  $\text{dNm}^3$  (depending on stack gas moisture content). When sampling upstream of collectors, the sample volumes were much less, 1.3 to 2.9  $\text{dNm}^3$  based on the restriction to two filters. Based partly on KVB experience in this program, the SASS train has been redesigned for a higher flow rate and the filter has been enlarged to increase the time between filter changes. Also the size of the 1  $\mu\text{m}$  cyclone collection cup was increased.

Minor mechanical problems in train operation were encountered, involving breakage of glass impingers, cyclone oven heater shorts and sample probe heating element failure. These failures did not cause any significant delay in testing. However, operation of the SASS train was considerably more time consuming than a standard EPA Method 5 particulate train. Total elapsed time to make one run was about 16-24 hours; this included training precleaning, assembly, set up, sample collection, sample recovery, and train clean up.

Results of the sample analysis represent a massive amount of data as seen in the 76 tables contained in Appendix F. Appendix F presents sample concentrations, emission rates, and mass balances. A brief summary of the emission rates is presented in Table 1-2. EPA MATE values (Ref. 10) are shown in Table 1-2 for comparison with emissions. Table 1-3 shows the particulate emissions less than 3  $\mu\text{m}$  (as percent of total particulate emissions). Results for each unit tested are discussed in the sections of this report that present individual test unit results. A summary of the overall perspective of the results for each specie is presented below.

#### Antimony--

Antimony was detected in the exhaust of three units at 120 to 230  $\mu\text{g}/\text{m}^3$ . Mass balances were very poor, mainly because fuel and process sample concentrations were frequently below detection limits. In the fine particulate ( $< 3 \mu\text{m}$ ), antimony was either not detected or samples were too small to analyze.

#### Arsenic--

Arsenic was detected on four of the units at 0.4 to 370  $\mu\text{g}/\text{m}^3$ . Mass balances ranged from 0.43 to 360. In general the arsenic was collected in the solid particulate (52 to 95%) rather than the impinger section indicating condensation at over 477 K (400 °F).

#### Barium--

Barium emission was 31 to 830  $\mu\text{g}/\text{m}^3$  and was detected on all units. Barium was detected in the fine particulate on only one unit, the open hearth furnace, for which 50% of the barium was in the fine particulate. Barium is one of the elements that usually produces good mass balances. However, for these tests mass balances varied from 0.29 to 5.3.

#### Beryllium--

Beryllium was detected on four units at 0.24 to 5.1  $\mu\text{g}/\text{m}^3$ . Mass balances ranged from 0.25 to 2.0. Beryllium was detected in fine particulate on only one test, the cement kiln, for which 100% was in fine particulate.

TABLE 1-2. SUMMARY OF TRACE SPECIES AND ORGANIC EMISSIONS  
FROM INDUSTRIAL COMBUSTION EQUIPMENT

micrograms per normal cubic meter

Fuel - Test Number	Forced Draft Process Heater		Rotary Cement Kiln		Open Hearth Steel Furnace		Wood/Bark Boiler		Black Liquor Recovery Boiler		Diesel Engine		EPA* MATE Value
	Ref. Gas - 12/2		Natural Gas - 9		Nat. Gas, No. 6 Oil - 14		Wood - 13		Black Liquor - 10/2		Diesel Oil - 15		
	Emission	Mass Balance	Emission	Mass Balance	Emission	Mass Balance	Emission	Mass Balance	Emission	Mass Balance	Emission	Mass Balance	
Units	µg/m <sup>3</sup>	--	µg/m <sup>3</sup>	--	µg/m <sup>3</sup>	--	µg/m <sup>3</sup>	--	µg/m <sup>3</sup>	--	µg/m <sup>3</sup>	--	µg/m <sup>3</sup>
Antimony	< 850	Mass	230	> 0.009	120	0.5 - 5	140	< DL	< 160	< 0.93	< 360	< DL	500
Arsenic	< 47	Balance	0.4	0.43	150	360	370	> 1.6	< 16	< 0.15	47	> 0.51	2
Barium	140	Not	280	> 0.16	38	5.3	31	3.2	150	0.29	830	> 3.7	500
Beryllium	< 10	Possible	0.24	0.88	0.37	> 0.72	< 8.6	0.25	5.1	2.0	3.9	> 0.3	2
Cadmium	7.7	With	15	1.8	570	> 1.8	1.9	1.5	18	0.3	3.6	> 0.26	10
Calcium	280000	Gas	480000	1.1	53000	185	24000	0.81	440	2.7	1000	0.73	*
Chromium	170	Fuel	120	1.5	2400	550	270	0.85	150	> 2.5	140	> 0.62	1
Cobalt	< 390		170	0.84	120	340	< 55	< DL	300	2.2	6	< DL	50
Copper	29		78	0.79	2700	75	59	0.82	3.3	0.7	9.7	> 0.07	200
Iron	2500		2900	1.0	530000	1.5 < 1700	2600	0.62	1700	2.9	510	> 2	*
Lead	28		20	< DL	44000	95	9.8	0.65	63	0.3	< 32	< DL	150
Manganese	320		80	10.0	3000	7.3 < 1000	250	0.57	32	1.1	30	0.65	5000
Mercury	< 10		< 24	< DL	< 10	< DL	0.11	< DL	< 9.9	< 0.22	< 1.8	< DL	50
Nickel	180		110	0.79	2100	23	260	1.5	69	1.4	120	> 2.7	15
Selenium	< 73		< DL	< DL	62	> 7.5	< 67	> 0.52	1.9	1.8	22	> 0.5	200
Tellurium	< 3100		< DL	< DL	590	> 2.8	< 2700	< DL	< 2700	< 0.3	< 300	< DL	100
Tin	< 4200		< DL	< DL	< 4400	> 25	< 3600	< DL	< 2800	< 0.3	< 740	< DL	*
Titanium	2700		1300	0.2	1300	11 < 160	470	0.96	1900	> 3.0	< 1500	< DL	6000
Vanadium	112		9	1.1	110	0.8	< 110	0.65 < 0.71	< 130	< 0.8	< 110	< DL	500/1
Zinc	150		73	1.1	200000	8000	110	0.61	84	> 0.8	74	0.17	4000
Chloride	44		15000	0.95	3100	2.9	1200	0.12	13000	6.5	1100	2.4	†
Fluoride	860		490	1.1	15000	1.1	2700	0.47	330	0.7	68	0.12	†
Nitrates	10		1700	1.5	1600	--	190	0.10	9.1	--	480	5.4	†
Sulfates	19000		2900	0.06	45000	--	21000	0.97	46000	--	1300	0.38	†
Total POM	0.6		0.17	--	230	--	350	--	5000	1.5	< 0.9	--	†
Total PCB	< 15		< 85	--	2.4	--	< 14	--	< 130	< 0.37	< 9	--	500
Benz(a)pyrene	DL		0.000038	--	< DL	--	0.000040	--	0.18	--	0.000023	--	0.2
Benzo(c)phenanthrene	< DL		< DL	--	< DL	--	< DL	--	0.0092	--	0.000023	--	27300
Dibenzo(a,h)anthracene	< DL		< DL	--	< DL	--	< DL	--	0.017	--	DL	--	0.093

< DL = Less than detection limit.

\*MATE = Minimum Acute Toxicity Effluent, values shown are based on health effects, except vanadium with health/ecological values shown. Elements indicated \* have no MATE value established.

†MATE values vary depending on specific compounds.

TABLE 1-3. SUMMARY OF TRACE SPECIES AND ORGANICS PARTICULATES, EMISSION IN PARTICULATE LESS THAN 3  $\mu\text{m}$

Species	Test No.	Percent of Total Emissions					
		Forced Draft Process Heater	Rotary Cement Kiln	Open Hearth Steel Furnace	Wood/Bark Boiler	Black Liquor Recovery Boiler	Diesel Engine
		12/2	9-6	14	13	10/2	15
Antimony		NES	< DL	< DL	NES	< DL	NES
Arsenic		NES	79	52	95	< DL	NES
Barium		NES	< DL	50	NES	NES	NES
Beryllium		NES	100	< DL	NES	< DL	NES
Cadmium		NES	3	68	NES	NES	NES
Calcium		NES	5	42	NES	NES	NES
Chromium		NES	13	14	NES	NES	NES
Cobalt		NES	14	< DL	NES	NES	NES
Copper		NES	4	59	NES	NES	NES
Iron		NES	91	51	NES	NES	NES
Lead		NES	< DL	73	NES	0.7	NES
Manganese		NES	37	70	NES	NES	NES
Mercury		0	< DL	< DL	72	< DL	NES
Nickel		NES	11	6	NES	NES	NES
Selenium		NES	< DL	< DL	NES	3	NES
Tellurium		NES	< DL	88	NES	NES	NES
Tin		NES	< DL	< DL	NES	NES	NES
Titanium		NES	100	50	NES	NES	NES
Vanadium		NES	99	52	NES	NES	NES
Zinc		NES	15	65	NES	NES	NES
Chloride		0.055	7	35	NES	9	NES
Fluoride		NES	< DL	2	34	15	NES
Nitrates		NES	100	29	NES	< DL	NES
Sulfates		1.0	< DL	55	NES	8	NES
Total POM		NES	NES	27	2	NES	NES
Total PCB		NES	NES	< DL	< DL	NES	NES

NES = Small sample, not enough for complete analysis.  
 < DL = Less than detection limit.

#### Cadmium--

Emissions ranged from 1.9 to 18  $\mu\text{g}/\text{m}^3$  with mass balances from 0.3 to 1.9. The amount in fine particulate was 3% and 68% for two tests.

#### Calcium--

Emissions ranged from 440 to 480,000  $\mu\text{g}/\text{m}^3$  with very good mass balances on four units (0.73 to 2.7). For the open hearth furnace the mass balance was 185 relative to the fuel input. On that unit additional material was picked up from the molten steel bath; there was no way to determine an overall mass balance that included the steel. The amount of calcium in fine particulate was 5% and 42% for two tests, very nearly the same as for cadmium.

#### Chromium--

Emissions ranged from 140 to 2,400  $\mu\text{g}/\text{m}^3$ , with mass balances of 0.62 to 1.5, except for 550 on the open hearth furnace. Fine particulate contained 13 and 14% for two tests.

#### Cobalt--

Cobalt was detected for five units, emissions ranged from 6 to 300  $\mu\text{g}/\text{m}^3$  with mass balances of 0.84 to 2.2 (340 on the open hearth). Fine particulate contained 14%, detected on only one unit.

#### Copper--

Copper was detected on all six units at 3.3 to 2700  $\mu\text{g}/\text{m}^3$ , with mass balances of 0.7 to 0.82 on three units (75 on open hearth). For two tests, the fine particulate contained 4% and 59% of the copper.

#### Iron--

Iron was detected on all units at 510 to 530,000  $\mu\text{g}/\text{m}^3$ , with mass balances of 0.62 to 2.9 (1.5 to < 1700 on open hearth). Fine particulate contained 91% and 51% of the iron on two units.

#### Lead--

Lead was detected on five units, with emissions of 20 to 44,000  $\mu\text{g}/\text{m}^3$  and mass balances of 0.3 to 0.65 (95 on open hearth). The fine particulate contained 0.7% and 73% of the lead for two units.

#### Manganese--

Manganese was detected on all units, with emissions of 30 to 3000  $\mu\text{g}/\text{m}^3$  and mass balances of 0.57 to 10 (< 1000 on open hearth). The fine particulate contained 37% and 70% of the manganese on two tests.

#### Mercury--

Mercury was below detection on five units. Based on the detection limits, emissions could be as high as 1.8 to 24  $\mu\text{g}/\text{m}^3$  on these five units. Mercury was detected on the wood/bark boiler at 0.11  $\mu\text{g}/\text{m}^3$  but mercury could not be detected in the fuel so no mass balance could be made. The fine particulate from the wood/bark boiler contained 72% of the mercury.

#### Nickel--

Nickel was detected on all units at 69 to 2100  $\mu\text{g}/\text{m}^3$  with mass balances of 0.79 to 2.7 (23 on the open hearth furnace). The fine particulate contained 11% and 6% of the nickel for two tests.

#### Selenium--

Selenium was detected on three units at 1.9 to 62  $\mu\text{g}/\text{m}^3$  with mass balances of 0.5 to 1.8 (> 7.5 on open hearth). Selenium in the fine particulate was 3% for the black liquor boiler but was undetected on other units.

#### Tellurium--

Tellurium was detected only on the open hearth furnace at 590  $\mu\text{g}/\text{m}^3$ . The mass balance was > 2.8 based on the fuel input detection limit (tellurium was below detection in the fuel). The fine particulate contained 88% of the tellurium. Tellurium was not detected on other units. The detection limits for tellurium are relatively high compared with the other elements.

#### Tin--

Tin was below detection for all tests.

#### Titanium--

Titanium was detected for five units but not for the diesel engine. Emissions ranged from 470 to 2700  $\mu\text{g}/\text{m}^3$ , with mass balances of 0.2 to 3.0 (< 160 for the open hearth). The fine particulate contained 100% and 50% for two units.

#### Vanadium--

Vanadium was detected on three units at 9 to 112  $\mu\text{g}/\text{m}^3$ . Mass balances were 0.8 and 1.1 for two tests, and for those tests the fine particulate contained 15% and 65% of the vanadium.

#### Zinc--

Zinc was detected on all tests at 73 to 200,000  $\mu\text{g}/\text{m}^3$ , with mass balances of 0.17 to 1.1 (8000 for the open hearth). For two tests, the fine particulate contained 15% and 65% of the zinc.

#### Chloride--

Chloride was detected in all tests at 44 to 15,000  $\mu\text{g}/\text{m}^3$ , with mass balances of 0.12 to 6.5 (29 for the open hearth). The fine particulate contained 0.055, 7, 35 and 9% of the chloride for four tests.

#### Fluoride--

Fluoride was detected in all tests at 68 to 15,000  $\mu\text{g}/\text{m}^3$  with mass balances of 0.12 to 1.1. The fine particulate contained 2, 34 and 15% of the fluoride in three of the tests.

#### Nitrates--

Nitrates were detected for all tests at 9.1 to 1700  $\mu\text{g}/\text{m}^3$  with mass balances of 0.1, 1.5 and 5.4 on three of the tests. The fine particulate contained 100% and 29% of the nitrates on two tests.

#### Sulfates--

Sulfates were detected on all tests at 1300 to 45,000  $\mu\text{g}/\text{m}^3$ . Mass balances for three tests were 0.06, 0.38 and 0.97. Complete mass balance is not expected because sulfur in the fuel can form sulfates during combustion.

Sulfate was detected in fine particulate on three tests at 1, 55 and 8% of the total sulfates. Sulfate reported was that collected in the cyclones, filter and XAD-2. The impinger values were not reported because SO<sub>2</sub> is trapped and cannot be distinguished from sulfates.

#### Total POM--

POM was detected on all units except the diesel engine. Total POM emissions ranged from 0.6 to 5000 µg/m<sup>3</sup> by gas chromatographic analysis. The highest value, 5000 µg/m<sup>3</sup> on the black liquor recovery boiler, was 14 times higher than the next highest unit, the wood boiler. Mass balance for POM was not established because POM is not expected to be conserved in combustion. However, it was noted that POM emission on the black liquor boiler was 1.5 times the POM content of the black liquor fuel. Most of the POM was collected in the organic module. For two tests, sufficient particulate was obtained for POM analysis. In those two tests, 27% and 2% of the total POM was in the fine particulate.

#### POM Compounds--

Organic module samples were analyzed by GC/MS for eight specific POM compounds. As shown in Table 1-2, only three of these compounds were detected on four tests:

Benz(a)pyrene

Benzo(c)phenanthrene (detected in one test only)

Dibenzo(a,h)anthracene (detected in one test only)

All three of these compounds were detected on the black liquor recovery boiler. The B(a)P concentration was 0.18 µg/m<sup>3</sup>. This was about 4500 times the B(a)P concentration for the other units. B(a)P from other units ranged from 0.000023 to 0.000040 µg/m<sup>3</sup> (23 to 40 pg/m<sup>3</sup>). However, the value of 0.18 µg/m<sup>3</sup> is similar to the range of 0.07 to 1.4 µg/m<sup>3</sup> reported for coal-fired steam power plants (Ref. 8, 20-400 µg/10<sup>6</sup> Btu ÷ 283 m<sup>3</sup>/10<sup>6</sup> Btu). The other two compounds above were not detected on the other three units.

Five other compounds, to be analyzed, were not detected in any samples:

7,12-Dimethylbenz(a)anthracene

3-Methylcholanthrene

Dibenzo(a,h)carbazole

Dibenz(ai)pyrene

Dibenz(ah)pyrene

The detection limit for each specific POM compounds was 0.1 ng in the total sample. As reported in Appendix F a number of other POM compounds were detected. However, these compounds are not considered to be highly carcinogenic.

#### Polychlorinated biphenyls (PCB)--

PCB was detected for only one test, the open hearth steel furnace. The concentration was  $2.4 \mu\text{g}/\text{m}^3$  and was reported to be almost entirely Aeroclor 1248, a commercial PCB compound. Aeroclor 1248 was used as the standard for quantifying the measured PCB. It is possible that the sample became contaminated with the standard although the reporting laboratory indicates that did not occur. If the PCB was in fact emitted from the open hearth furnace, the source was most probably scrap metal added to the melt. The scrap may have included a container that had been in contact with PCB. The plant operator did not have any information on the source of the scrap.

#### 1.4 MATE VALUE COMPARISON

EPA Minimum Acute Toxicity Effluent (MATE) values shown in Table 1-2 are "approximate concentrations in source emissions to air which will not evoke significant harmful or irreversible responses in exposed humans, when those exposures are limited to short duration (less than 8 hours per day)" (Ref. 10). MATE values are exceeded for one or more elements in all the six units tested. Elements and the "Degree of Hazard" (Emission/MATE) are:

- . Process Heater: nickel (12)
- . Rotary Cement Kiln: cadmium (1.5), chromium (120), cobalt (3.4), nickel (7.3)
- . Open Hearth Steel Furnace: arsenic (75), cadmium (57), chromium (2400), cobalt (2.4), copper (13.5), lead (290), nickel (140), tellurium (5.9), zinc (50)

- . Wood/Bark Boiler: arsenic (185), chromium (270), nickel (17)
- . Black Liquor Recovery Boiler: beryllium (2.6), cadmium (1.8), chromium (150), cobalt (6), nickel (5), benz(a)pyrene (9)
- . Diesel Engine: arsenic (24), barium (1.7), beryllium (2), chromium (140), nickel (8)

## 1.5 CONCLUSIONS

1. Selection of representative industrial combustion devices was difficult because of the limited amount of information available. Effort should be directed to the further study of all types of devices. In particular, no data were found on petroleum refinery heater size and populations.
2. Natural draft petroleum process heaters appear to be low emitters on an individual device basis. However, as a total group, they apparently constitute a large fraction of industrial NO<sub>x</sub> emissions. Conventional combustion adjustments were found to be of limited effectiveness for NO<sub>x</sub> emissions reduction or efficiency improvement. There is a need for development of specific techniques for these particular devices.
3. Forced draft process heaters tested produced higher NO<sub>x</sub> emissions than did natural draft heaters, particularly with combustion air preheat. Reduction of excess air reduced NO<sub>x</sub> on a heater without air preheat but there was no reduction on the heater that had air preheat.
4. Rotary cement kilns produce high levels of NO<sub>x</sub> emissions and appear to have a good potential for NO<sub>x</sub> reduction by fuel switching and adjustment of operating temperatures. The single burner employed in most units has little provision for adjustment other than excess air levels or burner redesign.
5. Three steel processing furnaces showed good potential for NO<sub>x</sub> reduction by reducing excess air; 40 to 69% reductions were obtained. Removing burners from service on a reheat furnace reduced NO<sub>x</sub> by 43%.
6. Tests of one aluminum melting furnace indicated premixed burning characteristics, i.e., NO<sub>x</sub> increased with decreased excess air. NO<sub>x</sub> emissions were found to be relatively low in spite of hot refractory. The unit tested had a very high stack temperature with good potential for efficiency improvement.
7. Two boilers burning wood with gas or coal were amenable to application of air register adjustment, reduced excess air or burners out of service; reduction of 15 to 23% in NO<sub>x</sub> were observed. Fluctuations in wood flow present a problem in maintaining stable, repeatable emission levels.

8. The black liquor recovery boiler produced low NO<sub>x</sub> emissions. However, it was possible to reduce NO<sub>x</sub> by 30% with secondary air adjustment.
9. The boiler burning CO gas showed little response to combustion modifications, attributed to ammonia in the CO gas being converted to NO<sub>x</sub>.
10. The two reciprocating engines tested showed limited potential for NO<sub>x</sub> reduction by operational adjustments. Variation of load, speed, air, and fuel adjustments produced little change in NO<sub>x</sub> on a natural gas engine. Load reduction and inlet air temperature reduction produced slight reductions in NO<sub>x</sub> on a diesel engine.
11. Two boilers operating in gas turbine/boiler combined cycle units responded to burners out of service. Reductions in NO<sub>x</sub> of 14 and 38% were observed.
12. Only slight changes occurred in thermal efficiency on all units when combustion modifications were applied. Changes were both positive and negative with no specific trends observed.
13. Nearly all the known chemical elements were detected in the emissions from six units on which trace species and organics tests were conducted. Concentrations covered a very wide range from 0.11 µg/m<sup>3</sup> for mercury to 530,000 µg/m<sup>3</sup> for iron. All units emit one or more species that exceeds EPA MATE values.
14. Of the devices tested, a steel open hearth furnace produced highest emissions for most of the species.
15. The EPA Source Assessment Sampling System (SASS train), basically designed to sample exhaust from coal-fired utility boilers, proved to be adequate for other sources but redesign to increase flow rate, filter capacity should improve the collection.

## SECTION 2.0

### TEST UNIT SELECTION

#### 2.1 OBJECTIVE

The objective for selection of test units was to locate units that are representative of current industrial kilns, boilers, process heaters, furnaces, dryers, ovens, stationary internal combustion engines, and gas turbines. The determination was to be made with reference to existing data, and contact with manufacturers and associations. This emphasis on selection of representative units would enhance the widest possible applicability of the program results to many industrial combustion devices.

#### 2.2 APPROACH

The scope of the test program provided for tests of about 25 devices. Since there are several thousand industrial combustion devices, it would not be possible to select test units representative of all types of units in current use. The emphasis was therefore placed on selection of units within industries that are most significant in terms of national emissions of criteria pollutants ( $\text{NO}_x$ ,  $\text{SO}_x$ , CO, HC, and particulates) and of energy consumption.

The data used in unit selection were gathered from the U.S. EPA, including the computerized National Emissions Data System (NEDS), various contractor reports, equipment manufacturers, associations of manufacturers, and equipment operators.

With regard to the category of boilers, the survey was restricted to units that operate with unconventional fuels. Industrial boilers burning the conventional fuels, natural gas, fuel oil and coal, have been examined in detail in previous studies (Refs. 1 and 2.)

All criteria pollutant emissions were considered. However, the fact that NO<sub>x</sub> emissions are generally most amenable to reduction by combustion modifications leads to an emphasis on devices that are high in NO<sub>x</sub> emissions.

### 2.3 RESULTS

Results of a survey of industrial combustion equipment are presented in detail in Appendix A. Industries identified as having combustion equipment that are significant in terms of energy and emissions, ranked by NO<sub>x</sub> emissions are shown in the following table:

Industry	Combustion Device
Petroleum refining	Process heaters
Wood pulp and pulp board	Wood waste boilers Black liquor recovery boilers
Portland cement	Rotary kilns
Chemical	Charcoal retorts Ammonia reformers
Iron and steel	Open hearth furnaces Soaking pits Reheat furnaces Coke ovens Blast furnaces Heat treating furnaces
Glass containers	Melting furnaces
Various industries	Reciprocating engines Gas turbines

Information regarding each equipment type was gathered, as available, with regard to:

1. Major manufacturers
2. Associations
3. Basic equipment and combustor design
4. Current fuel use, trends and properties
5. Trends in equipment type, age, size and use
6. Total number and geographic distribution
7. Limitations in equipment uses and fuels
8. Quantity and geographic distribution of fuels used
9. Air pollutant emissions

This information is presented in Appendix A.

For many equipment types, specific data were not available in sufficient detail to allow completely representative test unit selection. In many cases, it was necessary to rely on industry contacts to suggest units they considered "typical".

The following sections summarize selection criteria established for each unit type based on the survey. Table 2-1 presents the lists of unit types and number selected for testing.

#### 2.3.1 Petroleum Refinery Process Heaters

Heaters are used in most of the various refining processes from crude distillation to petrochemical feed stock production. There is, therefore, a substantial variety of heater types, but most are basically either (1) vertical tube cylindrical shell type, or (2) horizontal tube box type. Heaters are either of forced or natural draft. The majority are of natural draft design and most are fired with refinery gas with limited use of fuel oil and waste fuels. There is a trend toward increased use of forced draft with air preheat for efficiency improvement. No information was available on heater sizes. However, the average refinery size is about 8000 m<sup>3</sup> of oil/day (50,000 barrels/day) with an average of about 26 heaters per refinery, or about 7,000 heaters total in the 260 refineries in the U.S.

Selection of test units was concentrated in refineries close to the average size. Both natural draft and forced draft units were included with operation on refinery gas and fuel oil.

#### 2.3.2 Wood Bark Boilers

These boilers are somewhat similar to coal fired boilers in the use of underfed grates, traveling grates or spreader stokers. Provision for supplemental firing of oil or gas is common. There is a high variability in wood moisture and salt content. Very limited information on number and typical size was available. Alabama, Georgia, and Texas are the states which appear to have the highest concentration of capacity.

TABLE 2-1. TEST UNITS INITIALLY SELECTED

Type	Industry	Number of Units
Petroleum Refinery Heater	Petroleum Refining	7
Carbon Monoxide Boiler	Petroleum Refining	1
Rotary Cement Kiln	Cement	2
Ceramic Tunnel Kiln	Ceramic	1
Glass Container Furnace	Glass	1 *
Wood Bark Boiler	Pulp, Paper, Paperboard	2
Black Liquor Recovery Boiler	Pulp, Paper, Paperboard	1
Aluminum Melter	Aluminum	1
Blast Furnace Gas Boiler	Iron and Steel	1 *
Open Hearth Furnace	Iron and Steel	1
Soak Pit Furnace	Iron and Steel	1
Reheat Furnace	Iron and Steel	1
Combined Cycle Gas Turbine	Electric Generation	2
Simple Cycle Gas Turbine	Electric Generation	1 *
Natural Gas Fueled ICE	Gas Pumping	1
Diesel Fueled ICE	Electric Generation	1
		25

\*These units were not tested.

6002-471

Based on limited data, the average size boiler appears to be rated at about 113,000 kg/hr (250,000 lb/hr) steam flow and selection of units in this size range was the objective.

### 2.3.3 Black Liquor Recovery Boilers

These boilers are significantly different in design compared with conventional boilers. Their function is to burn the wood organics out of the black liquor and to recover sodium sulfate for reuse in the wood digestion process. Black liquor is the organic residue from the wood digestion process. Combustion of black liquor requires separation of furnace areas into an upper oxidizing zone and a lower reducing zone. Air injection control is quite critical. An average unit has a heat input of 117 MW ( $400 \times 10^6$  Btu/hr) and there are about 274 units. Georgia, Louisiana and Alabama have the highest total capacity. At the average heat input rate, the average unit produces 136,000-159,000 kg/hr (300,000-350,000 lb/hr) of steam.

### 2.3.4 Portland Cement Kilns

Cement kilns are large rotating cylinders up to 183 m long and 8 m in diameter. Refractory lining results in very high temperature and long residence times that result in high  $\text{NO}_x$  formation. Units are about equally divided between wet and dry feed processes. With proper burner design, almost any fuel can be used. Heat recovery by air preheat is used on all kilns in cooling the cement clinker product. There are about 412 kilns in the U.S. with the average size rated at  $206 \times 10^6$  kg of cement/year (227,000 tons/year). Pennsylvania, Texas and California are the states with the most kilns and greatest total capacity.

### 2.3.5 Iron and Steel Furnaces

Open hearth furnaces are major sources of  $\text{NO}_x$  emissions in the steel industry. These furnaces are being replaced by basic oxygen furnaces (BOF) and no new open hearth units are being built. However, the flexibility of open hearths to scrap/hot metal ratio is greater than for the BOF so that

use of open hearths is expected to continue for some time. The open hearth process is cyclic and NO<sub>x</sub> emissions vary widely over the typical 8-hour heating cycle. One heating cycle is termed a "heat". Currently, there are up to 189 furnaces in operation at an average size of 227,000 kg of metal per heat (250 tons/heat). Pennsylvania, Ohio and Indiana have 70% of the open hearth capacity. These units all have one burner at each end of the hearth fired with natural gas, oil, pitch, tar or coke oven gas. Some units may also have burners in the roof that may be fed with either air or oxygen.

Soaking pits heat steel ingots in preparation for initial forming operations and are batch type furnaces. One or two high volume flow burners circulate hot gas in the furnace and designs differ in circulation patterns. Natural gas is the predominant fuel but oil and waste fuels are used. Data indicates about 1435 units exist but there is no information on typical sizes.

Reheating furnaces reheat partially formed steel for further processing. These units, numbering about 1260, have 10-30 burners in 2 to 5 zones for uniform and controlled heating. Most are fired with natural gas. No data on sizes were available.

Coke ovens and blast furnaces are important in the steel industry. However, they are relatively low in NO<sub>x</sub> emissions and have burners that are dissimilar to other combustion devices. These devices were therefore not considered in selection of test units. Therefore, a large number of heat treating furnaces (about 4,500) that are also believed to be low in total emissions, compared with other furnaces. This, together with very strict requirements on temperature and atmosphere control, indicates low probability of successful application of combustion modifications.

#### 2.3.6 Glass Container Melting Furnaces

Glass melting furnaces are large refractory lined tanks with high air preheat (1400 K, 2000 °F). There are two basic designs: end port and side port. This refers to burner locations. End port units have two burners and side port units have 6 to 10 burners. Only one-half the burners fire at one time with air reversal through exhaust-heated checker bricks for preheating.

About one-half the total glass industry is devoted to glass container manufacture and there are about 334 melting furnaces in 117 glass container plants. Details on all furnaces are not available. However, data from one large company indicates a representative side port furnace produces 141,000 kg of glass/day (155 tons/day) with a melter area of  $84 \text{ m}^2$  ( $900 \text{ ft}^2$ ). End port furnaces are slightly smaller with average production of 120,000 kg of glass/day (132 tons/day) and an area of  $60 \text{ m}^2$  ( $645 \text{ ft}^2$ ). Most furnaces use natural gas fuel with standby oil.

No glass furnaces were tested because they are constructed with very simple pipe burners that cannot be adjusted without affecting glass quality.

### 2.3.7 Stationary Reciprocating Engines

There are a large number of designs and sizes of industrial reciprocating engines. Basic types are compression ignition (diesel) and spark ignition (gas or oil) and each type can be either a 2 or 4 stroke cycle. Fuel consumption energy is about 75% natural gas with the remainder as diesel fuel, residual oil, and gasoline. There are about 290,000 engines in current use in the oil and gas production industries, with 90% of these being small natural gas fueled engines at an average power rating of 11 kW (15 hp). The remaining 25,000 are larger diesel and natural gas engines ranging from 150-1900 kW (250 to 2500 hp) in average power for various applications. A survey of oil refineries in Southern California indicated an average engine size of 330 kW (440 hp).

Numbers and sizes of engines in various other applications vary widely as indicated in Appendix A. The largest number of engines in a single application (160,000) occurs for diesel engines used for electric power generation.

Based on the survey, the test program concentrated on natural gas engines in the oil and gas industry and on industrial diesel engine generator sets.

### 2.3.8 Stationary Gas Turbines

Gas turbines are used in three basic system configurations: simple cycles, regenerative, and compound (or combined) cycles. The majority of installations are of simple cycle type, i.e., a conventional gas turbine

without heat recovery. Primary applications are for electrical generation and pipeline pumping. Fuels are predominantly natural gas and distillate oils but residual oils and refinery gas are used. No information was found available to determine the average unit size.

The design of gas turbine combustion systems is such that there is no provision for field adjustments or combustion modifications. Some engines are equipped with water injection systems for NO<sub>x</sub> control. These engines are mainly the large electric utility gas turbines. None of the industrial gas turbines are believed to have water injection. Test unit selection is therefore limited to the utility units.

While direct gas turbine combustion system modifications are not practical, units that operate in conjunction with fired waste heat boilers can be evaluated for the potential of NO<sub>x</sub> reduction through boiler modifications. Staged combustion in the boiler has promise for destruction of NO<sub>x</sub> from the gas turbine and resultant turbine/boiler emissions lower than for a turbine operating alone. Test unit selection therefore included combined cycle gas turbines for evaluation of this effect.

#### 2.3.9 Other Devices

The list at the beginning of Section 2.3 includes several combustion devices that were not selected for test: charcoal retorts, coke ovens, ammonia reformers, and blast furnaces. Also, some devices were selected for test that were not specifically considered in the equipment survey. This section discusses these devices.

Charcoal retorts and coke ovens are similar in processing carbonaceous materials in a deficiency of air. These processes do not use burners directly but use burners for external heat generation. Coke ovens have fixed design orifice burners and adjustments can only be made to stack dampers. No specific information was found on charcoal retort designs. Both of these devices were not believed to be particularly suited for the types of combustion modifications planned but may warrant further consideration in future studies.

An ammonia reformer was inspected as a candidate for test. These units have many burners and very critical gas temperature profile criteria and much effort is expended in balancing and optimizing the combustion process. Based on the inspection, it was decided that modifications planned for the current program would not be feasible on these devices.

Blast furnaces depend primarily on coke charged with the ore feed for combustion heat although external burners are being used. The exhaust gas does not enter the atmosphere but is recovered as fuel partly used to preheat blast furnace air with the balance used as fuel in the steel mill devices. Previous tests have shown blast furnace emissions to be relatively low and not particularly suited for application of combustion modifications (Ref. 5).

Four devices not specifically evaluated in the equipment survey were selected for test: a refinery carbon monoxide boiler, a ceramic tunnel kiln, an aluminum melter, and a blast furnace gas boiler. Carbon monoxide boilers are air pollution control devices consuming CO emitted by petroleum refinery catalytic cracking units. These emissions are a significant fraction of total industrial boiler emissions in areas where large refineries are located (Ref. 5).

A ceramic tunnel kiln was selected as representative of stationary (as opposed to rotary) kiln processes. These kilns are classified together with cement kilns in national fuel consumption (Appendix A) and have a large number of fuel burners to which combustion modifications could be applicable.

An aluminum melting furnace was selected on the basis of recommendations from a previous survey as discussed in Appendix A. The survey in the current program did not indicate high emissions from aluminum furnaces and the purpose of the test was to resolve the apparent differences between survey results.

A blast furnace gas boiler was selected on the basis of a previous study that indicated a significant contribution to industrial boiler NO<sub>x</sub> emissions (Ref. 5). However, a test site for this type of boiler could not be obtained.

### SECTION 3.0

#### INSTRUMENTATION AND TEST PROCEDURES

The emission measurements were made using analytical instruments and equipment contained in a government-furnished mobile instrumentation laboratory contained in an 2.4 x 9.1 meter (8 x 30 ft) trailer. A plan and side view of the trailer are shown in Appendix B. Gaseous emission measurements were made with the following analytical instruments:

<u>Emission Species</u>	<u>Manufacturer</u>	<u>Measurement Method</u>	<u>Model No.</u>
Hydrocarbon	Beckman Instruments	Flame Ionization	402
Carbon Monoxide	Beckman Instruments	IR Spectrometer	865
Oxygen	Teledyne	Polarographic	326A
Carbon Dioxide	Beckman Instruments	IR Spectrometer	864
Nitrogen Oxides	Thermo Electron	Chemiluminescent	10A
Sulfur Dioxide	Dupont Instruments	UV Photometric	400

Total oxides of sulfur were measured by wet chemistry methods using the sampling train and analytical procedure of the Shell-Emeryville method. Total particulate measurements were made using an EPA Method 5 sampling train manufactured by Western Precipitation Division of Joy Manufacturing Co. Particulate size distribution was made using either an Andersen 200 Cascade Impactor or a Brink Model B Cascade Impactor depending upon the grain loading. Smoke density was measured using an automated Bacharach smoke spot pump. Samples for trace species and organic analysis were taken with a high volume sampling train called the Source Assessment Sampling System (SASS train). Stack opacity readings were made during particulate tests according to EPA Method 9.

### 3.1 GAS SAMPLING AND CONDITIONING SYSTEM

A flow schematic and description of the flue gas sampling and analyzing system is presented in detail in Appendix B. Briefly, the sampling system uses pumps to continuously draw flue gas from the boiler into the laboratory. A high capacity positive displacement diaphragm pump is used to draw a high volume of flue gas into the unheated portion of the system to provide adequate system response. The pump pulls from a manifold connected to 24 unheated sample lines. Selector valves allow composites of up to 12 points to be sampled at one time. The probes are connected to the sample manifold with 0.0095 m (3/8 in.) nylon line. Stainless steel quick disconnect couplings are provided to facilitate the connection between the sample lines and the instrumentation laboratory. The sample from each line then passes into individual water traps. The water traps consist of glass bubblers used to collect water condensed from the sample and drain valves for emptying the traps are provided. A positive displacement diaphragm sample pump draws unheated sample gas through a refrigerated condenser to reduce the dew point to 275 K (35 °F), a rotameter with flow control valve, the sample pump, a 1 micron filter, and to the O<sub>2</sub>, NO, CO, and CO<sub>2</sub> instrumentation. Flow to the individual analyzers is measured and controlled with rotameters and flow control valves. Excess sample is vented overboard.

Special precautions are required to obtain a representative sample for the analysis of NO<sub>2</sub>, SO<sub>2</sub>, and hydrocarbons. These precautions consist simply of insuring that the sample is kept above its dew point, since these constituents are quite soluble in water. For this reason, a separate electrically heated sample line is used to bring the sample into the laboratory for analysis. The line is 9.5 mm (3/8 in.) stainless steel line, electrically traced and insulated. Metal bellows pumps provide sample to the hydrocarbon, SO<sub>2</sub>, and NO<sub>x</sub> analyzers.

### 3.2 GASEOUS EMISSIONS

The laboratory is equipped with analytical instruments to continuously measure concentrations of NO, NO<sub>2</sub>, CO, CO<sub>2</sub>, O<sub>2</sub>, SO<sub>2</sub>, and hydrocarbons. The sample gas is delivered to the analyzers at the proper condition and flow rate through the sampling and conditioning system described in the previous sections. Appendix B describes the analytical instrumentation.

### 3.3 PARTICULATE EMISSIONS

Particulate samples are taken at the same sample port as the gas sample using a Joy Manufacturing Company portable effluent sampler. This system, which meets the EPA design specifications for Test Method 5, Determination of Particulate Emissions from Stationary Sources (Federal Register, Volume 36, No. 27, page 24888, December 23, 1971) is used to perform both the initial velocity traverse and the particulate sample collection. Dry particulates are collected in a heated case that contains, first, a cyclone to separate particles larger than 5 microns and, second, a 100 mm glass-fiber filter for retention of particles down to 0.3 microns. Condensible particulates are collected in a train of 4 Greenburg-Smith impingers in a chilled water bath.

### 3.4 TRACE ELEMENT AND ORGANIC EMISSIONS

Particulate and gaseous samples for analysis of trace elements and organics are taken at the same ports as the gas and standard particulate samples. The sampling system is based on a modified Aerotherm high volume sampling system which is called the Source Assessment Sampling System (SASS train). Dry particulates are collected in a heated case that contains three cyclones to separate particles larger than 10  $\mu\text{m}$ , 3-10  $\mu\text{m}$ , and 1-3  $\mu\text{m}$ . Particles less than 1  $\mu\text{m}$  are collected on a 142 mm glass-fiber filter. Filtered sample gas is then cooled to 293 K to 333 K (68 to 130 °F) and passed through an organic adsorbent consisting of XAD-2 chromosorb type adsorbent. Condensate is collected in a trap and the dried gas passes through an impinger train in a chilled water bath. The first impinger contains a hydrogen peroxide solution for  $\text{SO}_2$  scrubbing and the second and third impingers contain reagents for volatile trace species collection. The fourth impinger contains Drierite for final drying prior to flow control and volume measurement equipment. Operating procedures and analytical methods are discussed in Appendix C.

### 3.5 UNIT OPERATIONAL DATA

Industrial combustion devices of the types tested under this contract have a variety of adjustments, controls, and instrumentation. A complete set of operational data is taken for each test. If available, process rates, temperatures, flows, and combustion parameters are recorded. Typically, fuel flow rate, pressure, air flow, pressure, stack gas temperature, and various draft readings are made. The positions of air registers, dampers, and other manual controls are recorded for each test. Appendix D discusses methods for obtaining thermal efficiency and Appendix E contains the data recording formats employed for the program. A data supplement report containing all raw data collected during the study is available.

### 3.6 TEST PROCEDURES

Prior to a test, the test site was inspected to determine equipment location, sample acquisition points, pertinent unit operational instruments and recording units, and specific combustion modifications to be performed. Tests were outlined with unit operating personnel.

Most tests, excluding trace species and organics sampling, were accomplished in 4 to 6 days. The initial day was devoted to test equipment set-up, coordination with the unit operating personnel, a thorough review of instruments, process and operational characteristics, and initiation of sampling for baseline operational and emissions data.

Following baseline data acquisition, the proposed combustion adjustments were implemented individually. All unit operational and emissions data were recorded for each adjustment implemented. Fuel samples were obtained at pertinent points during the test period.

## SECTION 4.0

### TEST RESULTS

This section summarizes the emission and efficiency data collected for the units tested. The combustion devices tested were selected from equipment types as discussed in Section 2. Within each class, the given test results summarize the equipment characteristics, special instrumentation requirements, gaseous and particulate emissions data, combustion modifications, efficiency, and conclusions.

#### 4.1 PETROLEUM PROCESS HEATERS

A total of seven process heaters were tested at Locations 4, 5, 7, and 12.\*

##### 4.1.1 Process Heater (Location 4)

###### Equipment Characteristics--

The process heater tested at Location 4 was a vertically fired natural draft refinery heater installed in 1970. The purpose of this unit is to heat the feed stock to approximately 672 K (750 °F) before spraying into a flash chamber to separate the various hydrocarbons. A secondary function is to generate steam in the economizer coils in the convection section. The heater was fired with 32 combination oil/gas burners in two cells of 16 burners each. The heater had a heat input rating of 25 MW ( $86.6 \times 10^6$  Btu/hr). It was equipped with an optimizer system to keep the unit operating at a minimum excess air level with limits on process temperature and furnace pressure. There was a manual override on the optimizer so that the operator could control the excess air. The unit normally operates on gas but has the capability of firing oil. When the unit switches to oil, it is base loaded with oil and control is effected with gas burners. A schematic of the tubular natural draft fired heater is shown in Figure 4-1.

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\*Location numbers were assigned to each plant in which units were tested.

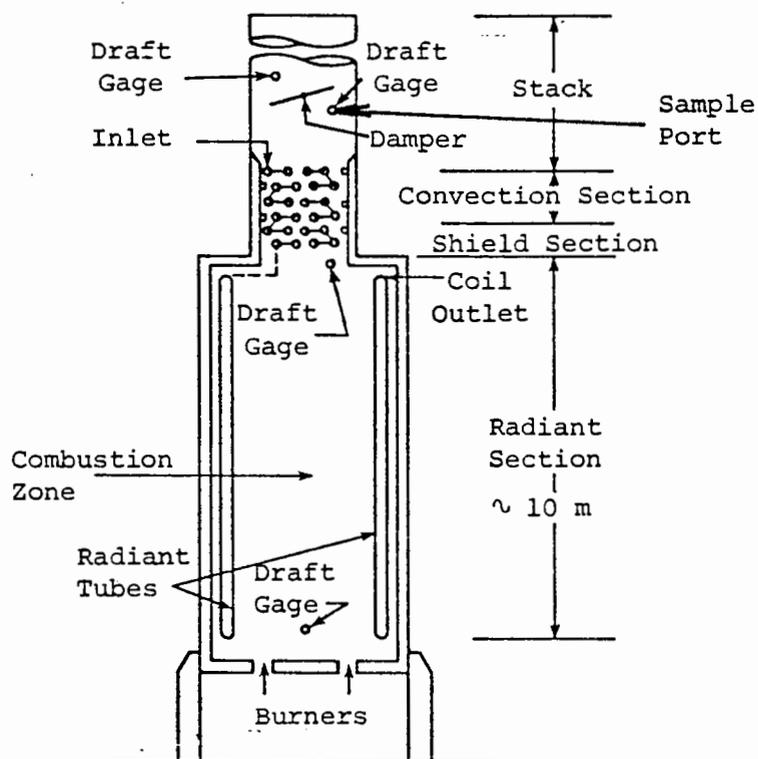


Figure 4-1. Vertical fired heater, Location 4.

Under normal conditions when the unit is firing refinery gas, the optimizer system is used to minimize operator attention to the combustion process. The optimizer system was designed to allow furnace operation at minimum excess air at the design conditions. An  $O_2$  analyzer was installed on the unit to give a continuous indication of excess  $O_2$  in the stack. The furnace damper was controlled by sensing furnace pressure. If product temperature changes, a fuel flow change is necessary. Any change in fuel flow causes the damper to open. The damper then begins to slowly ramp closed until the minimum air, consistent with the required furnace pressure, is reached. The damper remains in this position until perturbed by a change in fuel flow.

A heater with no optimizer will experience excess air fluctuations as fuel properties change. The purpose of testing the unit with an optimizer was to determine the effectiveness of the optimizer as a means of emissions minimization.

The test series at location 4 provided an evaluation of the effect of fuel variation on emissions and efficiency. The heater was tested with the "normal" fuel gas (a mixture of refinery gas and purchased natural gas), an enriched gas in which propane was added replacing the natural gas, and finally oil firing in combination with gas firing for control. Analyses of the fuel gas samples are presented in Table 4-1. The analysis of the oil sample is presented in Table 4-2. These analyses were performed by an independent testing laboratory. Samples were analyzed by gas chromatography and results were presented as volume percent.

TABLE 4-1. SUMMARY OF FUEL GAS ANALYSES  
FOR LOCATION 4 TESTS, % by Volume

Test No.	4-1	4-2	4-5	4-6	4-8
Oxygen	--	<0.01	0.13	0.21	0.10
Nitrogen	0.43	0.07	1.11	1.68	2.10
Carbon Dioxide	0.45	0.06	0.32	0.059	0.14
Carbon Monoxide	0.65	0.71	0.54	0.62	0.57
Hydrogen	11.64	12.9	12.8	12.7	11.8
Methane	64.88	49.11	61.01	49.4	52.42
Ethane	12.07	17.2	12.8	16.2	14.3
Ethylene	1.34	0.96	1.41	1.71	1.62
Total C3 (Propane)	6.57	16.2	7.44	14.7	15.1
Total C4	1.28	1.72	1.55	1.92	0.91
Total C5	0.63	0.96	0.79	0.73	0.86
Total C6	0.06	0.11	0.10	0.068	0.087
Heating Value (BTU dry/SCF)	1169	1372	1186	1325	1301
( $10^6$ J/m <sup>3</sup> )	43.6	51.16	44.23	49.41	48.52

TABLE 4-2. ULTIMATE ANALYSIS OF FUEL OIL  
SAMPLE FROM LOCATION 4 TESTS

Carbon, %	87.38
Hydrogen, %	11.87
Nitrogen, %	0.28
Sulfur, %	0.40
Ash, %	0.004
Oxygen (by difference), %	0.07
Gross Heat of Combustion	44,357 J/g (19,070 Btu/lb)
Net Heat of Combustion	41,821 J/g (17,980 Btu/lb)

#### Special Instrumentation Requirements at Location 4--

In addition to the emissions measurements described previously, a complete set of control room operating data were taken for each test. These data were specific for each heater depending upon the service requirements. In general, the process rate and condition (temperature and pressure), heater input/output data (fuel type, flow, pressure, stack temperature, etc.) and critical temperatures (where available) were recorded.

Gaseous emissions measurements were taken using a single heated sample line connected to a probe installed in the heater stack. The location of the sample probe is shown in Figure 4-1 at a position below the stack damper.

#### Baseline Emissions Results, Process Heater (Location 4)--

Location 4 baseline testing was conducted with the heater operating in the "as found" condition. Gaseous emissions data were measured at 30-min intervals for a period of 2-1/2 hours and fuel gas samples were taken at the start and end of the test period. The normal fuel being burned consisted of approximately 75% refinery gas and 25% natural gas. Baseline NOx emissions were 44.9 ng/J (88 ppm reported on a dry basis, corrected to 3% O<sub>2</sub>). No particulate tests were conducted on this unit since sample ports were of inadequate size.

#### Combustion Modifications, Process Heater, Location 4--

Location 4 combustion modification tests were conducted to evaluate the effect of fuel changes on emissions and burner patterns on emissions and efficiency. The results of baseline and the combustion modification tests are summarized in Table 4-3. The fuel gas was enriched by adding approximately 100 bbl/day propane, replacing the natural gas. Propane addition increased the specific gravity from 0.68 to 0.79. The  $\text{NO}_x$  emissions increased from 44.9 ng/J (88 ppm) at the baseline condition to 47.9 ng/J (94 ppm) with propane addition.

The effect of oil firing on the emissions from the heater was evaluated by adding 10 oil guns. Four burners, the end burner in each row, were out of service. The unit was base loaded with the oil guns and control of the unit was effected with the gas burners taking the swings in load. This is the normal operating mode when firing oil. The  $\text{NO}_x$  emissions increased to between 90.1 and 91.7 ng/J (169 and 172 ppm) when the unit was firing oil.

The optimizer system, which minimizes excess air, was switched to the manual mode to determine the effect on emissions. No effect on emissions was evident. The overall system response--return to normal conditions--was faster in the manual mode than with the optimizer operating.

Several burner patterns were evaluated to determine whether burner geometry had an influence on gaseous emissions in this heater. The normal operation has the end burner in each row out of service. The various patterns which were tested are shown in Figure 4-2. When burners were taken out of service, the fuel flow to the remaining burners was increased to keep the total input constant. The air registers to the BOOS were left open in an effort to have a staged combustion effect. Because of the nature of the design of this unit, very little mixing was accomplished in the firebox and the resulting  $\text{NO}_x$  emissions were higher than for the baseline condition. The  $\text{NO}_x$  varied from 47.9 ng/J (94 ppm) to 54.3 ng/J (106 ppm) (approximately 11%) for the burner pattern tests. The  $\text{O}_2$  level in the stack was higher than baseline for all BOOS tests and could not be lowered to the normal  $\text{O}_2$  operating level due to furnace pressure limitations. No discernable difference in CO or HC emissions was measured.

TABLE 4-3. SUMMARY OF GASEOUS EMISSIONS DATA  
LOCATION 4 - PETROLEUM REFINERY HEATER

Test No.	Date 1976	Process Load m <sup>3</sup> /d	Heat Input** MW	O <sub>2</sub> (%)	CO <sub>2</sub> (%)	NO <sub>x</sub> * (ppm)	NO <sub>x</sub> (ng/J)	NO* (ppm)	NO (ng/J)	HC* (ppm)	CO* (ppm)	SO <sub>2</sub> (ppm)	Comments <sup>†</sup>	
4-1	5/24	1004.9	28.6	4.0	10.0	88	44.9	97	44.4	1	10	38	As found - gas	
4-2	5/24	↓	32.2	3.8	9.8	94	47.9	93	47.4	1	11	45	C <sub>3</sub> H <sub>8</sub> addition to fuel gas, no natural gas	
4-3	5/24		28.6	3.8	10.0	86	43.9	85	43.4	1	10	54	As found - gas	
4-4	5/25		28.6	3.9	11.7	172	91.7	170	90.6	2	11	133	Oil and gas; 10 of 32 burners firing oil	
4-5	5/25		28.6	4.1	11.5	169	90.1	168	89.5	1	13	124	Oil and gas	
4-6	5/26		31.7	4.2	10.4	116	59.3	115	58.8	-	14	---	Gas, nat. gas, & propane	
4-7	5/26		31.7	5.4	9.8	109	55.8	108	55.3	-	9	---	Baseline - gas	
4-8	5/27		33.6	4.3	9.8	---	--	102	52.2	-	11	---	BOOS (1 & 16) - gas	
4-9	5/27		30.3	4.8	9.6	95	48.6	94	48.1	1	9	18	BOOS (4,7,10 & 13) - gas	
4-10	5/27		32.2	5.1	9.6	103	52.7	102	52.2	2	11	28	BOOS (4,8,9 & 13) - gas	
4-11	5/27		31.7	5.0	10.0	107	54.8	106	54.3	2	13	31	BOOS (6,8,9 & 11) - gas	
4-12	5/28		915.84	33.1	5.3	10.2	139	71.2	138	70.6	0	11	57	3 oil burners installed

\*Dry, corrected to 3% O<sub>2</sub>

\*\*10<sup>6</sup> Btu/hr = MW/1.05

†Stack was clear during all tests.

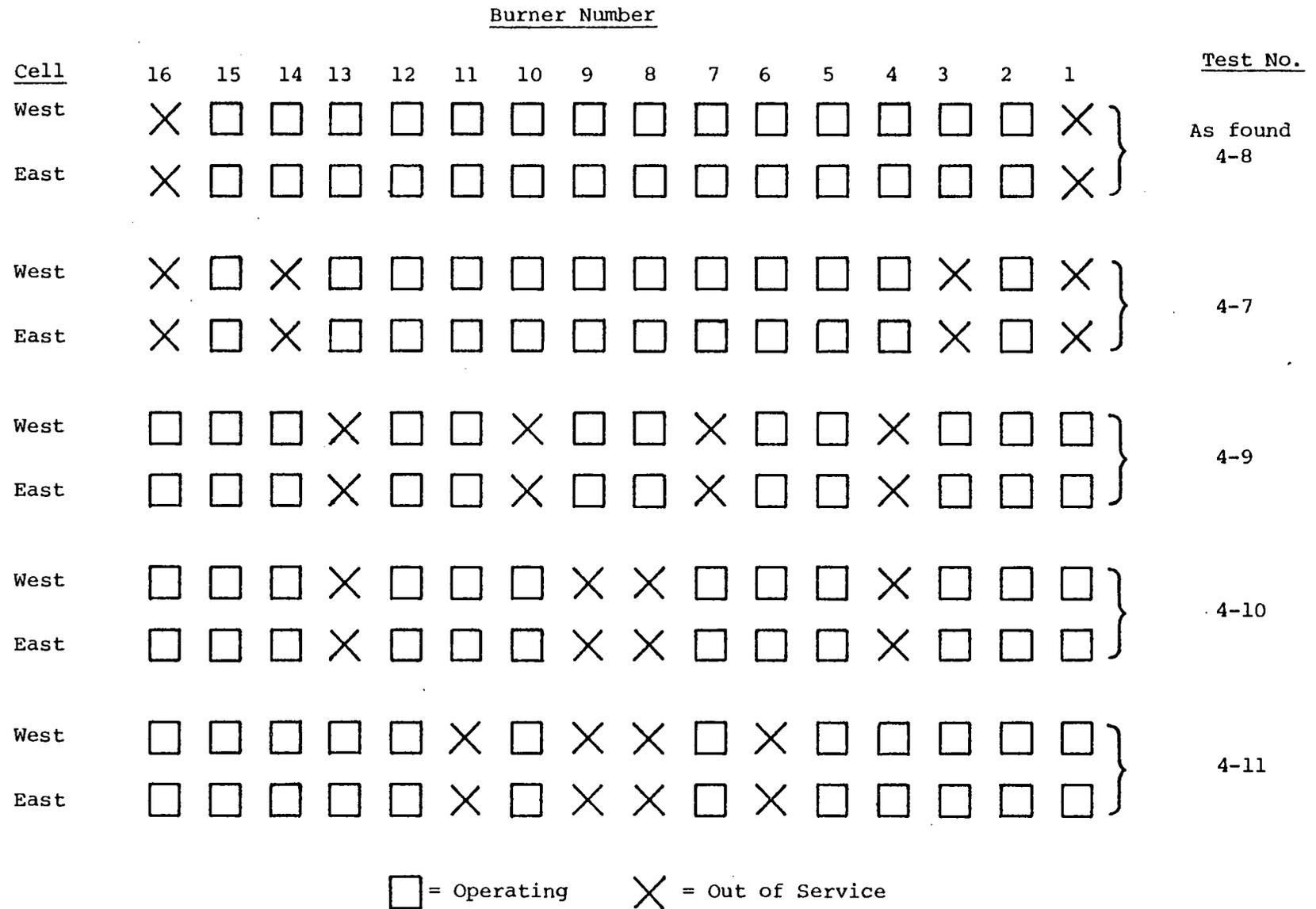


Figure 4-2. Burner patterns for refinery heater burner out of service (BOOS) tests (location 4 tests).

The limits on furnace pressure are critical for natural draft units. Negative pressure is a requirement to prevent hot gas or flame from coming out of furnace cracks and causing fires or structural overheating. Buoyant effects produce a pressure rise from the bottom to the top of the furnace. Controls are set so that pressure taps at the top just below the damper indicate a slightly negative pressure for normal operation. Any attempt to reduce excess air by closing the damper would result in a positive pressure at the top of the furnace.

The results of the fuel evaluation tests showd a slight [3.0 ng/J (6 ppm)] NO<sub>x</sub> increase when propane was added to the fuel gas in place of natural gas. Combination oil and gas firing (approximately 40% oil) resulted in NO<sub>x</sub> emissions being nearly double [91.7 ng/J (172 ppm)] compared with gas alone [44.9 ng/J (88 ppm)]. Use of the optimizer system had no effect on emissions but manual operation allowed faster response to upset conditions.

Changes in the burner pattern in which burners were taken out of service resulted in higher overall emissions. Several burner patterns were tried, all of which had higher emissions than the baseline configuration. The overall O<sub>2</sub> level could not be lowered to a value comparable to the baseline condition due to furnace pressure limitations leading to higher NO<sub>x</sub> emissions.

#### 4.1.2 Process Heaters (Location 5)

##### Equipment Characteristics--

Two process heaters were tested at Location 5 to evaluate the effect of process rate (load) on emissions and efficiency. Three process rate conditions were tested in each of the heaters. Burner adjustments were also made to determine the effect on emissions.

The test units at Location 5 were new (1974) vertically fired natural draft refinery heaters. Both heaters are part of a reformer unit consisting of five heaters that exhaust into common stacks. Sample connections were made at existing sample ports in the convection section before the flue gases enter the stack (Figure 4-3). The first unit has 16 floor-mounted burners in a single line; six were in operation during the test. The design rating was

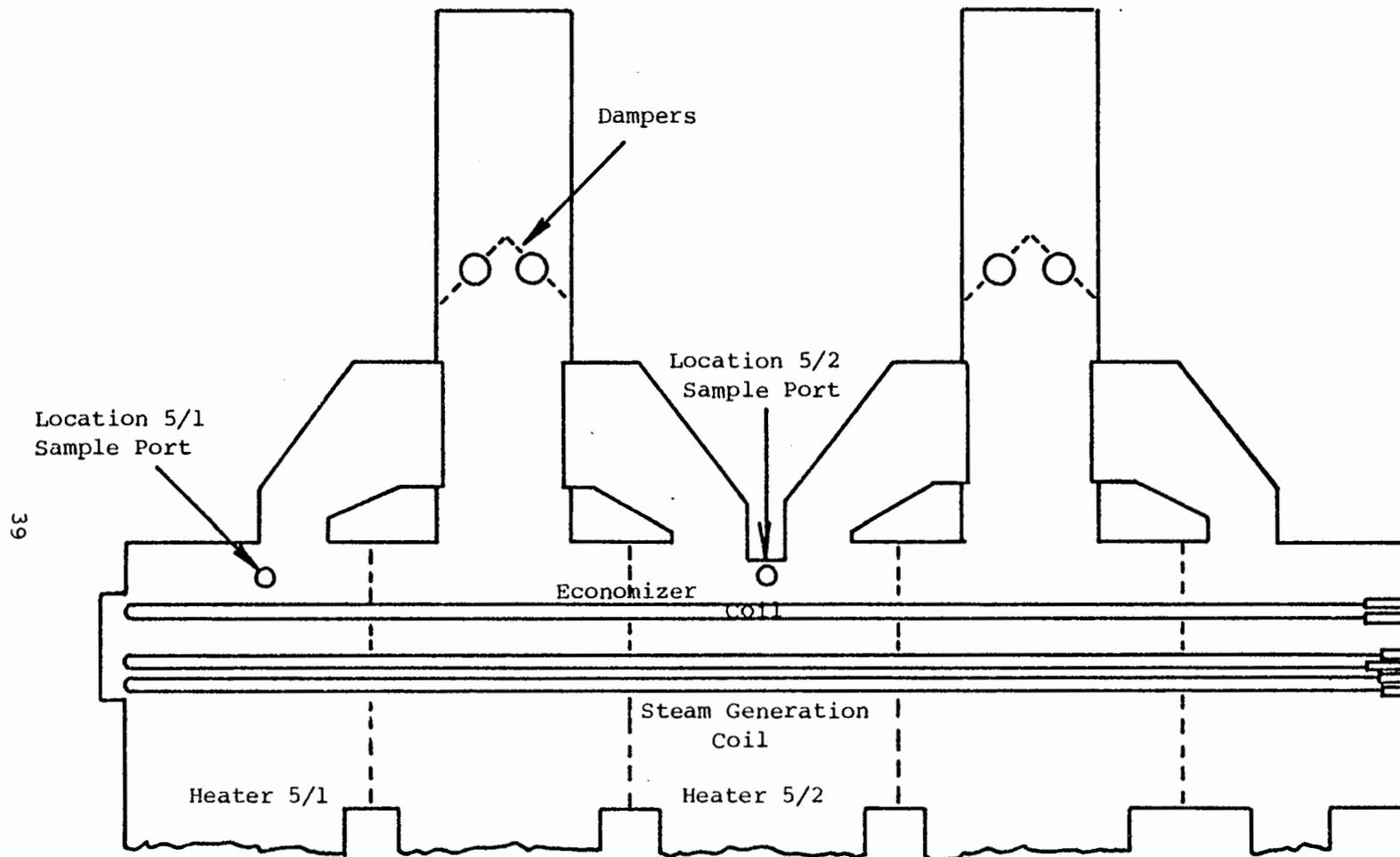


Figure 4-3. Schematic of Location 5 process heaters.

15.9 MW ( $54.4 \times 10^6$  Btu/hr). The second heater has ten floor-mounted burners in line; four were operating at the time of test. The design rating was 10.1 MW ( $34.6 \times 10^6$  Btu/hr). Normal operation is with refinery gas, but oil guns are available to convert to oil firing when required. However, oil guns were not operable during the tests.

The reformer unit was operating at approximately 50% of capacity so that load variation tests were possible. The process rate was varied  $\pm 318$  m<sup>3</sup>/day ( $\pm 2000$  bbl/day) from the nominal 1908 m<sup>3</sup>/day (12,000 bbl/day) for both heaters.

Fuel gas samples were taken during the testing and sent to an independent laboratory for analysis. Analyses of the fuel gas samples are given in Table 4-4 as volume percent.

TABLE 4-4. SUMMARY OF FUEL GAS ANALYSES  
FOR LOCATION 5 TESTS

Test No.	5/1-1	5/1-2	5/1-3	5/2-1
Oxygen	0.03	0.02	0.06	0.05
Nitrogen (by difference, O <sub>2</sub> +N <sub>2</sub> )	2.07	1.11	1.40	1.15
Carbon Dioxide	0.31	1.02	0.67	1.23
Carbon Monoxide	0.11	0.071	0.10	0.092
Hydrogen	8.70	7.62	10.03	7.40
Methane (by difference, HC)	47.18	56.76	46.78	53.46
Ethane	7.28	6.63	8.12	7.07
Ethylene	0.06	0.05	0.06	0.05
Total C3	17.6	14.9	18.0	16.2
Total C4	14.5	10.3	12.9	11.6
Total C5	1.93	1.34	1.53	1.42
Total C6	0.23	0.18	0.35	0.28
Heating Value (Btu dry/SCF) ( $10^6$ J/m <sup>3</sup> )	1645 55.75	1495 59.89	1606 57.88	1552 61.34

#### Baseline Emission Results, Process Heaters, Location 5--

Location 5 baseline tests were conducted on the first heater in the "as-found" condition. Gaseous emissions and control room data were taken at 30-minute intervals for a period of 2-1/2 hours. Baseline NO<sub>x</sub> emissions were 49.5 ng/J (97 ppm) at the nominal process rate of 1908 m<sup>3</sup>/day (12,000 bbl/day) and operating O<sub>2</sub> level of 4.4%. The baseline emissions for the second heater

were 39.0 ng/J (76 ppm) NO<sub>x</sub> at 3.9% O<sub>2</sub> and a process rate of 1908 m<sup>3</sup>/day (12,000 bbl/day). No particulate or SO<sub>x</sub> tests were possible at this location because of port size.

#### Combustion Modifications, Process Heaters, Location 5--

Location 5 combustion modification tests consisted of process rate variations and air register adjustments for both heaters. Following the baseline tests, the process rate was varied from 1590 m<sup>3</sup>/day (10,000 bbl/day) to 2,225 m<sup>3</sup>/day (14,000 bbl/day). Following the heater load variation tests, a series of tests was conducted in which burner adjustments were made to evaluate the influence on emissions. These tests were conducted at a process rate of 1908 m<sup>3</sup>/day (12,000 bbl/day), the normal rate. The results of all load changes and burner adjustment tests are presented in Table 4-5 for both heaters. Fuel gas samples were taken during the test series and analyzed for composition and heating value.

The effect of process rate on NO<sub>x</sub> emissions for heater No. 1 is shown in Figure 4-4. The NO<sub>x</sub> emissions from heater No. 1 dropped from 54.3 ng/J (106 ppm) at 1,590 m<sup>3</sup>/day (10,000 bbl/day) to 42.3 ng/J (83 ppm) at 2,226 m<sup>3</sup>/day (14,000 bbl/day). The O<sub>2</sub> level varied from 5.4% at 1,590 m<sup>3</sup>/day (10,000 bbl/day) to 3.4% at 2,226 m<sup>3</sup>/day (14,000 bbl/day) with the same burner pattern and air register setting. These tests were conducted with six of the 16 burners in service. A constant O<sub>2</sub> level over the load range was not possible. The unit has steam generating provisions in the convection section of the heater and the O<sub>2</sub> level is maintained at a high level at low fire conditions to maintain the steam flow rate. The same effect of process rate on NO<sub>x</sub> emissions is shown in Figure 4-5 for heater No. 2.

Tests on heater No. 1 were also conducted at a constant process rate with varying O<sub>2</sub> levels due to burner air register adjustment. The effect of excess O<sub>2</sub> on NO<sub>x</sub> for heater No. 1 is shown in Figure 4-6. The burner patterns are shown in Figure 4-7. The first burner adjustment (Test No. 5/1-4B) consisted of opening the air registers on the burners out of service (BOOS) and closing the air registers on the burners in service (Nos. 2, 4, 6, 9, 13 and 15). The NO<sub>x</sub> decreased to 41.0 ng/J (80 ppm) but the O<sub>2</sub> increased to 10.0%.

TABLE 4-5. SUMMARY OF GASEOUS EMISSIONS DATA  
LOCATION 5 - PETROLEUM REFINERY HEATERS

Test No.	Date 1976	Heat Input MW	Process Load		O <sub>2</sub> (%)	CO <sub>2</sub> (%)	NO <sub>x</sub> * (ppm)	NO <sub>x</sub> (ng/J)	NO* (ppm)	NO (ng/J)	HC* (ppm)	CO* (ppm)	SO <sub>2</sub> * (ppm)	Comments <sup>+</sup>
			m <sup>3</sup> /d	bbl/d										
<u>HEATER #1</u>														
5/1-1	6/2	18.5	1980	12,000	4.4	10.2	97	49.5	95	48.4	4	11	6	Baseline test
5/1-2	6/2	18.1	1590	10,000	5.4	9.7	106	54.4	104	53.4	4	16	10	Low load
5/1-3	6/3	19.6	2226	14,000	3.4	10.9	83	42.5	82	42.0	1	10	8	High load
5/1-4A	6/3	18.9	1908	12,000	5.0	10.0	95	48.6	93	47.6	0	9	6	Baseline
5/1-4B	6/3	23.8	1908	12,000	10.0	6.6	80	41.0	75	38.4	0	12	6	Air register adj. number 1
5/1-4C	6/3	22.4	1908	12,000	8.9	7.4	76	38.9	73	37.4	2	10	9	Air register adj. number 2
5/1-4D	6/3	20.6	1908	12,000	5.5	10.4	129	66.0	128	65.5	0	12	10	Air register adj. number 3
<u>HEATER #2</u>														
5/2-1	6/4	9.7	1908	12,000	3.9	10.5	76	39.0	76	39.0	1	10	3	Baseline test
5/2-2	6/4	10.6	2226	14,000	2.3	11.9	60	30.8	58	29.8	8	8	2	High load
5/2-3	6/4	10.1	1908	12,000	4.1	10.8	77	39.5	76	39.0	1	11	2	Baseline check
5/2-4	6/7	9.7	1908	12,000	3.5	10.8	77	39.5	75	38.5	2	12	5	Baseline
5/2-5	6/7	9.0	1590	10,000	5.2	9.8	101	51.8	100	51.3	1	13	6	Low load
5/2-6	6/7	10.8	2226	14,000	1.9	12.0	61	31.3	58	29.8	1	14	8	High load/normal O <sub>2</sub>
5/2-7	6/7	11.0	2226	14,000	4.0	10.2	63	32.3	61	31.3	1	13	8	High load/air register adj.

\*Dry, corrected to 3% O<sub>2</sub>.

<sup>+</sup>Stack was clear during all tests.

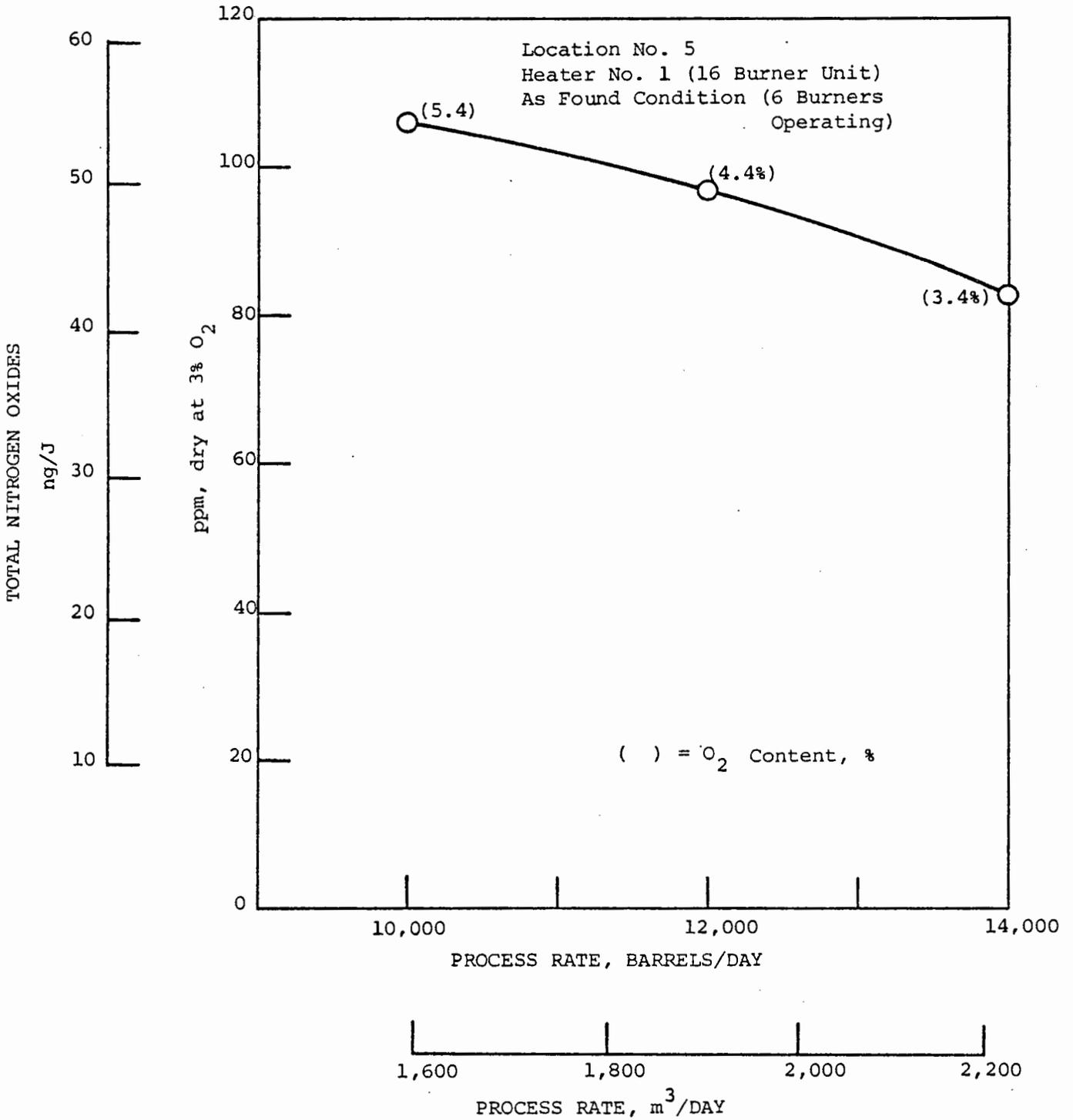


Figure 4-4. NO<sub>x</sub> emissions from refinery process heater 5/1 as a function of process rate.

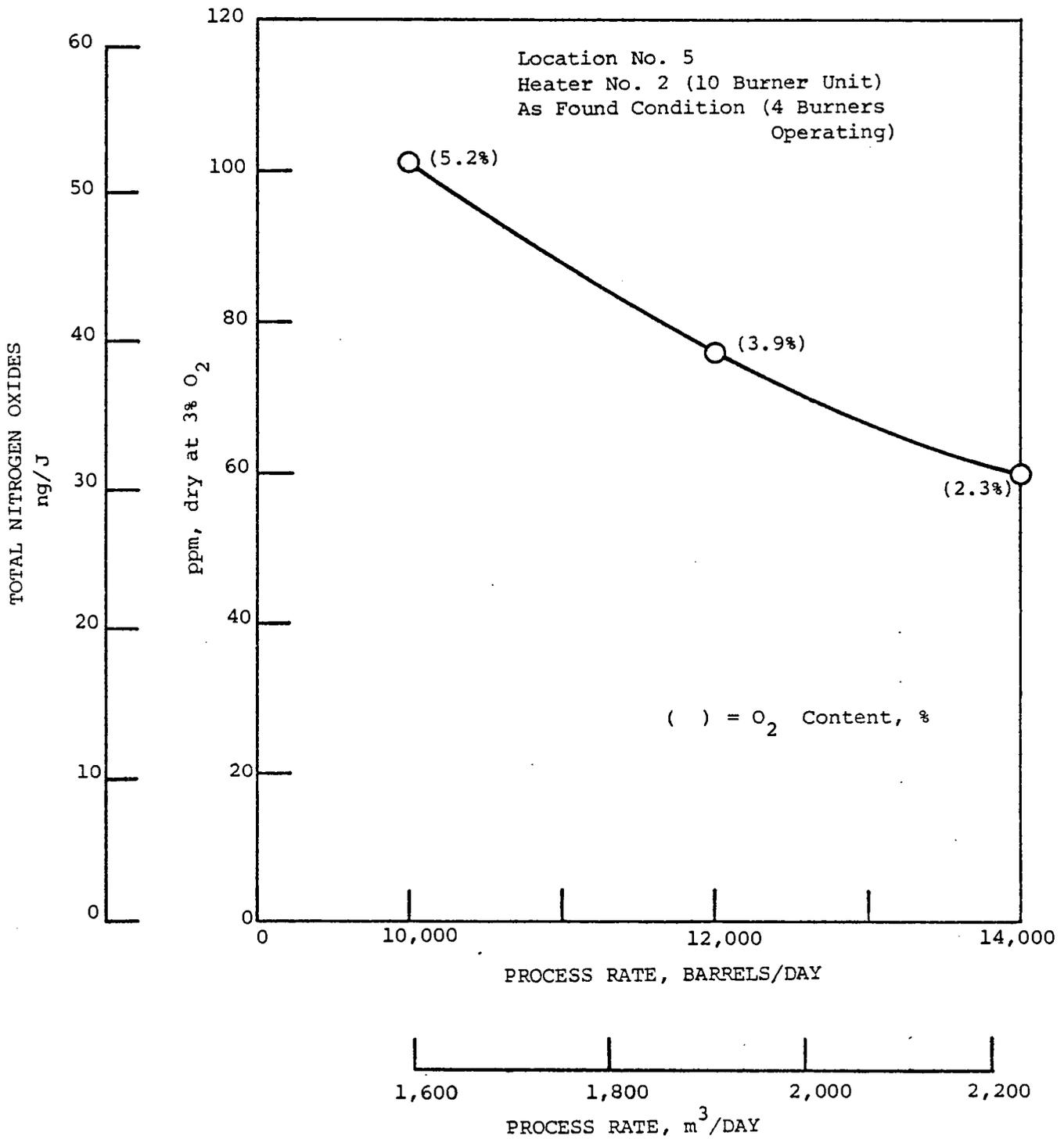


Figure 4-5. NO<sub>x</sub> emissions from refinery process heater 5/2 as a function of process rate.

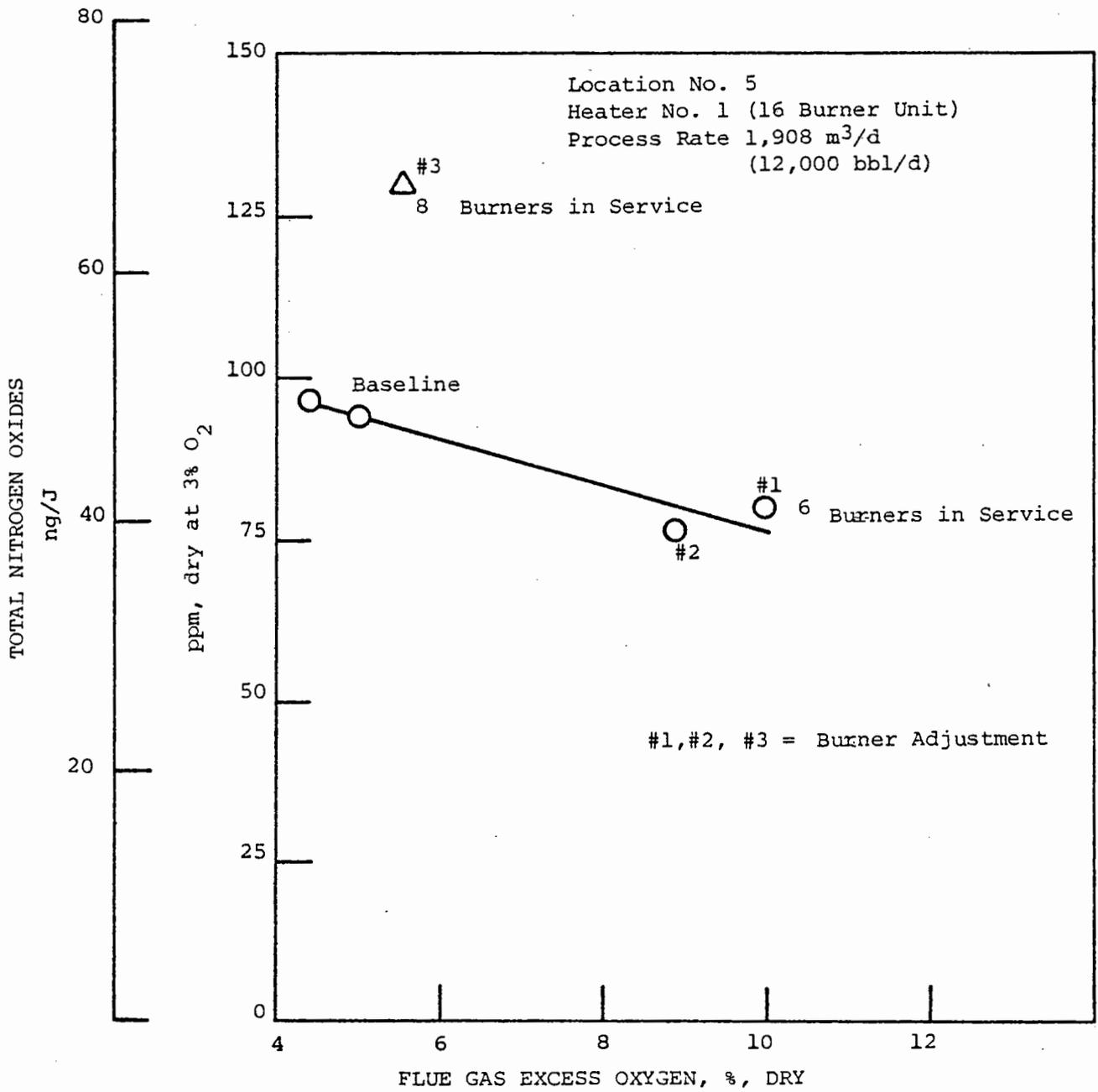
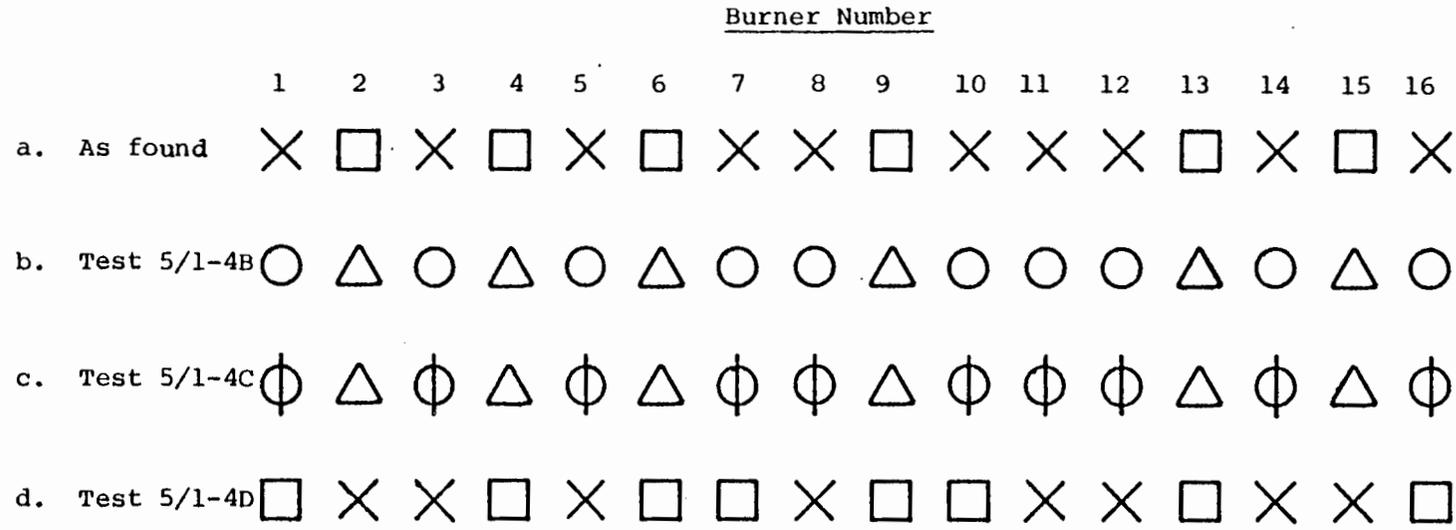


Figure 4-6. NO<sub>x</sub> emissions from refinery process heater 5/1 as a function of excess oxygen.



46

- Gas on and air registers open 100%
- △ Gas on and air registers partially closed
- Gas off and air registers full open
- ⊕ Gas off and air register partially open
- X Gas off and air register closed

Figure 4-7. Burner patterns tested on No. 1 petroleum refinery heater at location 5.

The second adjustment was the partial closing of the air registers of the BOOS. This adjustment lowered the O<sub>2</sub> to 8.9% with a slight reduction in the NO<sub>x</sub> to 38.9 ng/J (76 ppm). The final burner adjustment was closing the BOOS air registers and increasing the number of operating burners to eight (1, 4, 6, 7, 9, 10, 13, and 16). The O<sub>2</sub> was lowered to 5.5% but the NO<sub>x</sub> showed an increase of 33% to 66 ng/J (129 ppm) compared with baseline emissions.

A similar test series was conducted on heater No. 2, which has only 10 burners (four of which were operating in the "as-found" condition). The NO<sub>x</sub> emissions from heater No. 2 showed little or no dependence on excess O<sub>2</sub> as shown in Figure 4-8, although the range of O<sub>2</sub> was quite limited.

All tests at all conditions showed insignificant levels of HC, CO, and SO<sub>2</sub> emissions. These levels were unaffected by changes in operating parameters.

#### 4.1.3 Process Heaters, Location 7

##### Equipment Characteristics--

Location 7 tests were conducted on two petroleum process heaters. The first unit tested (No. 7/1) was a vertically fired natural draft recycle gas heater manufactured in 1967. It was designed to fire refinery gas and was installed as part of a hydrocarbon cracking unit. The furnace is rated at 15.5 MW (52.8x10<sup>6</sup> Btu/hr) absorbed with 16 burners equally spaced along the floor. Combustion air is normally controlled through individual air registers on each burner. Furnace draft is controlled with a manual damper in the stack. A sample probe was installed in the stack before the damper using an existing sample port. Location of the sample port was as previously shown schematically in Figure 4-1.

Heater No. 7/2 was a vertically fired natural draft process heater manufactured in 1970 as part of a reformer unit. The heater was rated at 11 MW (37.6x10<sup>6</sup> Btu/hr) and was fired by 12 burners located on the centerline of the heater floor. Furnace draft was controlled manually with a damper in the stack. Combustion air to the burners is adjusted with louvres located at one side of the air plenum.

Fuel gas analyses were obtained for each day of testing. Table 4-6 summarizes the fuel gas analyses at location 7.

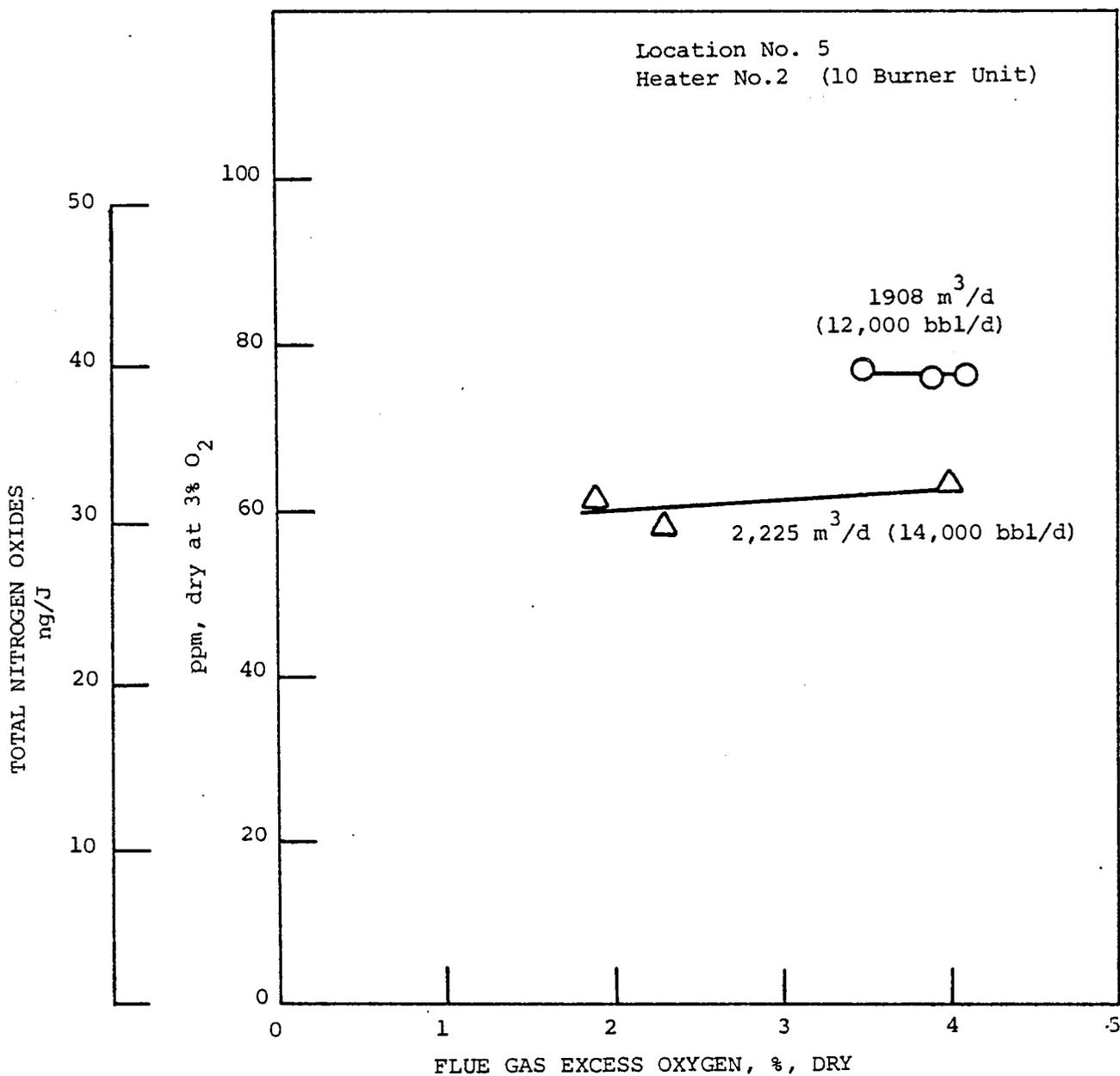


Figure 4-8. NO<sub>x</sub> emissions from a refinery process heater as a function of excess oxygen.

TABLE 4-6. SUMMARY OF FUEL GAS  
CHROMATOGRAPHIC ANALYSES

	Test No.					
	7/1-1	7/1-2	7/1-4	7/2-1	7/2-2	7/2-3
Date	7/13	7/14	7/15	7/19	7/20	7/21
H <sub>2</sub>	26.3	24.8	22.3	28.2	11.5	11.7
N <sub>2</sub>	2.6	1.6	1.6	2.4	3.0	1.6
CO <sub>2</sub>	0.7	0.7	0.8	0.8	1.0	0.7
C <sub>1</sub>	56.5	58.8	63.0	53.2	72.3	73.0
C <sub>2</sub>	5.4	5.1	4.9	4.9	4.9	4.7
C <sub>2</sub> <sup>=</sup>	0.9	0.8	0.9	0.8	1.0	1.0
C <sub>3</sub>	4.3	4.5	3.7	4.3	3.9	3.6
C <sub>3</sub> <sup>=</sup>	1.3	0.6	0.6	3.2	0.8	1.1
iC <sub>4</sub>	0.8	1.0	0.8	0.7	0.7	0.8
nC <sub>4</sub>	0.7	0.9	0.8	0.8	0.8	0.9
iC <sub>4</sub> <sup>=</sup>	0.1	0.1	0.1	0.1	--	0.1
iC <sub>5</sub>	0.4	1.0	0.5	--	--	0.8
nC <sub>5</sub>	--	--	--	--	--	--
C <sub>5</sub> <sup>=</sup>	--	--	--	0.6	0.1	--
C <sub>6</sub> <sup>+</sup>	--	--	--	--	--	--
Htg Value MJ/m <sup>3</sup>	35.8	37.1	36.5	35.4	38.1	39.7
(Btu/cf)	(961)	(998)	(980)	(953)	(1024)	(1060)

Note: All values reported on a volume percent basis.

#### Baseline Emissions, Process Heaters, Location 7--

The purpose of the process heater tests at Location 7 was to evaluate the effect of excess air on emissions and efficiency and to determine whether off-stoichiometric firing could be effected in a natural draft process heater. Baseline test measurements on heater No. 7/1 show the NO<sub>x</sub> emissions to be 51.6 ng/J (103 ppm) with the heater operating at 7.8% O<sub>2</sub>. The baseline NO<sub>x</sub> emission for heater No. 7/2 was 49.1 ng/J (98 ppm) with the unit operating at 8.5% O<sub>2</sub>. The O<sub>2</sub> analyzers installed in both units were far out of calibration and were indicating 4% to 5% higher O<sub>2</sub> than actual. Opacity readings were made on both units; no visible smoke was observed.

#### Combustion Modifications, Process Heaters, Location 7--

Location 7 combustion modification testing at heater No. 7/1 consisted of air register adjustments to lower excess air and various burners out of service to attempt staged combustion. All burner air registers were highly corroded and very little adjustment was possible. The O<sub>2</sub> was lowered to 6.6% with a slight decrease in NO<sub>x</sub> to 48.1 ng/J (96 ppm). Due to operational limitations, only three burners were able to be taken out of service. Various combinations of three burners were taken out of service with no appreciable effect on NO<sub>x</sub> emissions.

Combustion modifications to heater 7/2 consisted of trying to lower excess air and various burner patterns. Adjusting the air registers resulted in a decrease in NO<sub>x</sub> of up to 12 ng/J (24 ppm) or a 25% reduction. Only two burners were able to be removed from service and two combinations were tried. No significant change in emissions were measured by taking burners out of service.

A summary of gaseous emissions data from the Location 7 refinery heaters is presented in Table 4-7.

TABLE 4-7. SUMMARY OF GASEOUS EMISSIONS DATA  
LOCATION 7 - PETROLEUM REFINERY HEATER

Test No.	Date 1976	Process Load m <sup>3</sup> /d	Heat Input** MW	O <sub>2</sub> (%)	CO <sub>2</sub> (%)	NO <sub>x</sub> * (ppm)	NO <sub>x</sub> (ng/J)	NO* (ppm)	NO (ng/J)	HC* (ppm)	CO* (ppm)	SO <sub>2</sub> (ppm)	Comments <sup>†</sup>
Process Heater No. 1													
7/1-1	7/13	5410	16.5	7.8	7.7	103	51.6	103	51.6	12	12	0	Baseline-refinery gas
7/1-2A	7/14	5645	17.6	7.2	8.2	98	49.1	98	49.1	12	8	0	Baseline
7/1-2B	7/14	5625	16.6	6.6	8.4	96	48.1	96	48.1	10	13	0	Air register adjust
7/1-3	7/14	5550	15.9	7.2	8.2	99	49.6	99	49.6	8	6	51	BOOS 4 & 8
7/1-4	7/15	5540	16.3	6.8	8.0	97	48.6	95	47.6	13	8	10	Baseline
7/1-4A	7/15	5495	15.9	6.8	8.0	95	47.6	95	47.6	0	10	0	BOOS 4 & 13
7/1-4B	7/15	5440	14.8	7.0	8.2	98	49.1	98	49.1	7	9	4	BOOS 4, 9 & 13
7/1-4C	7/15	5440	15.1	7.0	8.2	98	49.1	96	48.1	6	10	2	BOOS 6, 9 & 12
Process Heater No. 2													
7/2-1	7/19	6575	14.9	8.5	7.0	98	49.1	93	46.6	5	14	6	Baseline-refinery gas
7/2-2A	7/20	6490	15.6	8.4	7.4	95	47.6	88	44.1	12	11	2	Baseline
7/2-2B	7/20	6590	15.6	9.0	7.0	78	39.1	76	38.1	9	8	1	Air register adjust
7/2-2C	7/20	6500	15.4	8.6	7.8	71	35.6	70	35.1	7	18	2	Air register adjust
7/2-3A	7/21	6755	16.7	7.8	7.8	86	43.1	82	41.1	10	8	0	Baseline
7/2-3B	7/21	6790	16.6	7.9	7.4	82	41.1	77	38.6	5	8	0	Air register adjust
7/2-3C	7/21	6760	16.6	8.6	7.2	77	38.6	76	38.1	4	14	0	BOOS 5 & 7
7/2-3D	7/21	6810	16.8	8.6	7.6	77	38.6	74	37.1	2	12	0	BOOS 2 & 11
7/2-3E	7/21	6885	16.7	8.0	8.0	81	40.6	76	38.1	7	12	0	Baseline repeat

\*Dry, corrected to 3% O<sub>2</sub>.

\*\*10<sup>6</sup> Btu/hr = MW/0.293

† Stack was clear during all tests.

#### 4.1.4 Thermal Efficiency of Natural Draft Process Heaters

Calculations of heater efficiency were made utilizing a KVB computer program. The efficiency is calculated by the heat loss method as outlined in ASME Power Test Code PTC-4.1. The fuel gas analyses obtained for each test were used for input data. The flue gas measurements and stack temperature measurements were used to calculate the stack losses. Radiation losses were estimated using the ABMA Standard Radiation Loss Chart which is included in PTC-4.1.

The efficiencies of the natural draft process heaters tested were significantly lower than boiler efficiencies since none of the heaters had air preheaters. This is typical of the petroleum industry although there is a trend to include air preheat in new units. However, this also requires conversion to forced draft. Process heater efficiencies are summarized in Table 4-8. Efficiency is basically a function of excess air. Combustion modifications resulted in efficiency variations of about 2% up or down dependent on the change in % O<sub>2</sub>. In one case, test 5/1-48, air register adjustment resulted in a 4% decrease in efficiency.

#### 4.1.5 Conclusions, Natural Draft Process Heaters

Five natural draft process heaters were tested to evaluate the effect of fuel composition, excess air, two-stage firing, and load on emissions and efficiency. Air preheat was not used on any of the units.

The effect of fuel gas higher heating value on NO<sub>x</sub> emissions was minor. There was approximately a 6% increase in NO<sub>x</sub> when the heating value was increased 10% by propane addition. Firing oil for supplying approximately 45% of the input increased the NO<sub>x</sub> emissions by 95%.

The effect of lowering excess air on NO<sub>x</sub> emissions was difficult to evaluate because the process heaters are limited, by the process, in the amount of air adjustment. In two cases the equipment was in such poor condition that it was impossible to make adjustments to the air registers. On some heaters air register adjustments resulted in NO<sub>x</sub> reductions of 7% to 28%, while in one case NO<sub>x</sub> increased (compared with baseline levels).

TABLE 4-8. SUMMARY OF NATURAL DRAFT PROCESS HEATER EFFICIENCIES

Test No.	Date 1976	O <sub>2</sub> (%)	Exit Temperature		Efficiency (%)	Comments
			(K)	(°F)		
4-1	5/24	4.0	548	527	78.8	Baseline
4-2	5/24	3.8	546	523	79.4	Propane addition
4-3	5/24	3.8	551	532	78.8	Baseline
4-4	5/25	3.9	549	528	78.9	Oil & gas
4-5	5/25	4.1	549	528	78.8	Oil & gas
4-6	5/26	4.2	558	544	78.3	Baseline
4-7	5/26	5.4	564	556	77.3	BOOS (1, 3, 14 & 16)
4-8	5/27	4.3	557	542	77.9	BOOS (1 & 16)
4-9	5/27	4.8	556	540	77.6	BOOS (4, 7, 10 & 13)
4-10	5/27	5.1	557	542	77.4	BOOS (4, 8, 9 & 13)
4-11	5/27	5.0	557	542	77.4	BOOS (6, 8, 9 & 11)
4-12	5/28	5.3	543	518	77.9	Oil & gas
5/1-1	6/2	4.4	478	401	79.9	Baseline - 1908 m <sup>3</sup> /day
5/1-2	6/2	5.4	478	400	78.7	Low load - 1590 m <sup>3</sup> /day
5/1-3	6/3	3.4	481	406	80.6	High load - 2226 m <sup>3</sup> /day
5/1-4A	6/3	5.0	480	405	79.5	Baseline - 1908 m <sup>3</sup> /day
5/1-4B	6/3	10.0	494	430	75.5	Air register adjustment
5/1-4C	6/3	8.9	493	427	76.6	Air register adjustment
5/1-4D	6/3	5.5	488	419	78.9	Air register adjustment
5/2-1	6/4	3.9	481	406	79.0	Baseline - 1908 m <sup>3</sup> /day
5/2-2	6/4	2.3	482	407	80.2	High load - 2226 m <sup>3</sup> /day
5/2-3	6/4	4.1	481	406	79.0	Baseline - 1908 m <sup>3</sup> /day
5/2-4	6/7	3.5	478	400	79.3	Baseline - 1908 m <sup>3</sup> /day
5/2-5	6/7	5.2	477	398	77.9	Low load - 1590 m <sup>3</sup> /day
5/2-6	6/7	1.9	480	405	80.3	High load/normal O <sub>2</sub>
5/2-7	6/7	4.0	482	407	79.6	High load/register adjustment
7/1-1	7/13	7.8	593	608	73.8	Baseline
7/1-2A	7/14	7.2	592	605	74.5	Baseline
7/1-2B	7/14	6.6	585	593	75.4	Air register adjustment
7/1-3	7/14	7.2	583	589	74.9	BOOS (4 & 8)
7/1-4	7/15	6.8	586	594	74.0	Baseline
7/1-4A	7/15	6.8	585	593	74.0	BOOS (4 & 13)
7/1-4B	7/15	7.0	583	590	73.9	BOOS (4, 9 & 13)
7/1-4C	7/15	7.0	582	580	74.0	BOOS (4, 9 & 12)
7/2-1	7/19	8.5	780	945	60.3	Baseline
7/2-2A	7/20	8.4	780	945	60.4	Baseline
7/2-2B	7/20	9.0	765	917	60.2	Air register adjustment
7/2-2C	7/20	8.6	763	913	61.1	Air register adjustment
7/2-3A	7/21	7.8	782	948	61.9	Baseline
7/2-3B	7/21	7.9	776	937	62.1	Air register adjustment
7/2-3C	7/21	8.6	763	913	61.6	BOOS (5 & 7)
7/2-3D	7/21	8.6	786	954	60.2	BOOS (2 & 11)
7/2-3E	7/21	8.0	775	935	62.0	Baseline

Process rate or load showed a fairly pronounced effect on NO<sub>x</sub> emissions but the O<sub>2</sub> varied as load changed and it is believed that the O<sub>2</sub> change was the predominant effect. However, the NO<sub>x</sub> shows a decrease of 22% as load was increased 28% with one heater while another heater exhibited a 40% decrease in NO<sub>x</sub> over the same load change.

An attempt was made on each heater to achieve two-stage combustion by varying the burner pattern--taking burners out of service. All the heaters tested had the burners in line on the furnace floor firing vertically upward. Very little mixing between burners is accomplished with this type of arrangement and the laminar type flame. Another consideration in taking burners out of service is to not disrupt the temperature distribution in the firebox with cold spots or flame impingement. In most cases, little measurable change in NO<sub>x</sub> emissions was accomplished by taking burners out of service on any heater tested. In only one test, 7/2, was there any significant reduction--20% of original baseline NO<sub>x</sub>. However, recheck of baseline conditions also gave lower emissions indicating negligible influence of the modification.

#### 4.1.6 Process Heaters, Location 12, Unit 1

##### Equipment Characteristics--

The process heater tested at Location 12, Unit 1 was a forced draft heater with air preheat. The unit, shown schematically in Figure 4-9, was built in 1973 to heat charge stock for desulfurization prior to catalytic cracking. The rated capacity of the unit was 3291 m<sup>3</sup>/day (20.7x10<sup>3</sup> bbl/day) of charge stock and the unit was operating at 100% capacity during the test period. Heater specification data are presented in the following table.

##### REACTOR CHARGE HEATER SPECIFICATIONS, LOCATION 12/1

Design Heat Input:	27.5 MW (94x10 <sup>6</sup> Btu/hr)
Heater Furnace Pressure:	-124 Pa (-0.5 in. H <sub>2</sub> O)
Max. Ambient Temperature:	317 K (110 °F)
Combustion Air Temperature:	658 K (725 °F)

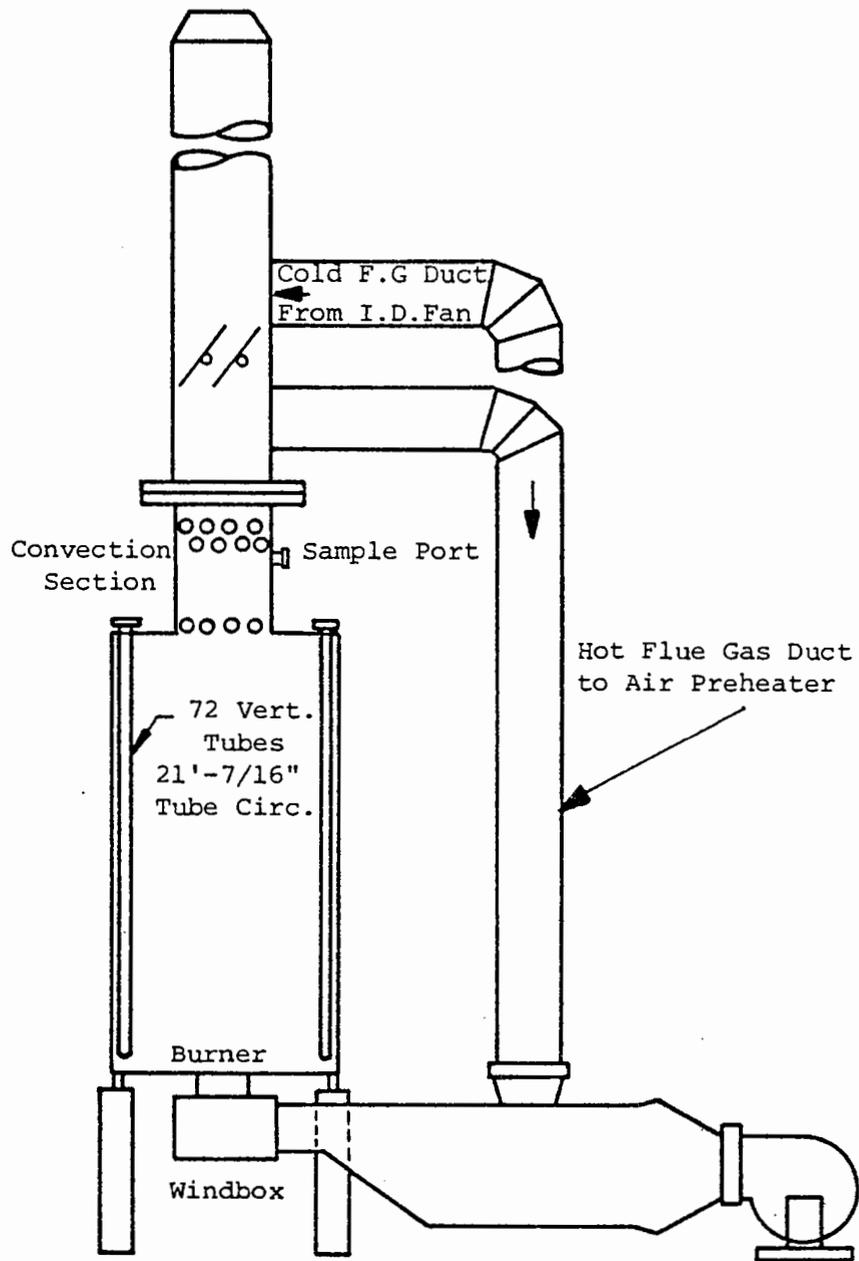


Figure 4-9. Schematic of Location 12/1 process heater.

A single burner supplied the fuel to the heater and was designed to fire either gas or No. 6 oil. Combustion air was preheated with a Ljungstrom air heater. Probes were installed in three ports in the convection section of the heater.

#### Baseline Emissions, Process Heater, Location 12/1--

Baseline emissions were measured firing both refinery gas and No. 6 oil. The  $\text{NO}_x$  emissions were 163 ng/J (320 ppm) with the unit firing refinery gas with 1.85% excess  $\text{O}_2$  in the flue gas. Baseline  $\text{NO}_x$  emissions for the unit when firing No. 6 oil were 113 ng/J (222 ppm) with the unit at 3.3% excess  $\text{O}_2$  in the flue gas. Particulate emissions were not measured in this unit due to the excessively high temperature in the convection section where sampling was being performed. Gas temperature at the sample point was approximately 1033 K (1400 °F) which precluded particulate sampling due to probable probe failure. Stack opacity and smoke were both zero for all tests. An attempt was made to measure  $\text{SO}_x$  emissions at this point but the pyrex probe melted and collapsed preventing the drawing of a sample. Table 4-9 presents a summary of the emissions data measured for this unit.

The analysis of the fuel burned during the tests at Location 12 is presented in Table 4-10.

#### Combustion Modifications, Process Heater, Location 12/1--

Combustion modification testing consisted of varying the excess air level. The excess air was changed by changing the inlet dampers on the combustion air fan. The effect of excess  $\text{O}_2$  on  $\text{NO}_x$  emissions is shown in Figure 4-10. Excess  $\text{O}_2$  in the flue gas varied from 1.3% to 3.1% for refinery gas firing. The data show an increase in  $\text{NO}_x$  of about 20.4 ng/J (40 ppm) per %  $\text{O}_2$  increase for refinery gas. For No. 6 oil firing, the  $\text{O}_2$  varied from 1.5% to 3.3% and little if any variation in  $\text{NO}_x$  was measured. Little  $\text{NO}_x$  reduction was possible since this unit was normally operated at low  $\text{O}_2$ .

TABLE 4-9. SUMMARY OF FIELD MEASUREMENTS  
LOCATION 12/1 PROCESS HEATER WITH AIR PREHEAT

Test Run No.	Date 1976	Load m <sup>3</sup> /d	Heat Input MW	Fuel	O <sub>2</sub> %	CO <sub>2</sub> %	NO <sub>x</sub> * ng/J (ppm)	NO* ng/J (ppm)	HC* ng/J (ppm)	CO* ng/J (ppm)	SO <sub>2</sub> * ng/J (ppm)	Stack Temp. K (*F)	Eff. %	Comments <sup>†</sup>
12/1-1	10/12	3291	27.7	RG*	1.85	9.9	163 (320)	168 (311)	1 (5)	5 (17)	173 (244)	397 (254)	86.3	Baseline test
12/1-2	10/12	3291	27.2	RG	2.0	12.4	167 (327)	162 (317)	1 (4)	5 (17)	238 (335)	398 (256)	86.3	O <sub>2</sub> variation
12/1-3	10/12	3291	27.7	RG	2.8	12.0	181 (356)	177 (347)	1 (5)	6 (18)	215 (303)	398 (257)	86.2	O <sub>2</sub> variation
12/1-4	10/12	3291	28.1	RG	3.1	11.0	189 (371)	188 (369)	2 (10)	5 (16)	118 (166)	396 (253)	86.4	O <sub>2</sub> variation
12/1-5	10/13	3291	28.5	RG	2.2	10.2	151 (296)	150 (295)	-	2 (8)	50 (70)	394 (250)	86.4	O <sub>2</sub> variation
12/1-6	10/13	3291	33.2	RG	1.3	11.3	--	163 (320)	-	14 (44)	82 (115)	400 (261)	86.2	O <sub>2</sub> variation
12/1-7	10/13	3291	33.2 <sup>§</sup>	RG	2.2	10.6	--	189 (371)	-	8 (27)	9 (13)	390 (243)	86.7	O <sub>2</sub> variation
12/1-8	10/14	3291	33.2 <sup>§</sup>	#6 Oil	3.3	12.8	--	113 (222)	-	12 (35)	330 (422)	398 (257)	89.2	Baseline test
12/1-9	10/14	3291	33.2 <sup>§</sup>	#6 Oil	2.2	13.2	132 (235)	132 (235)	-	9 (27)	340 (436)	403 (266)	89.6	O <sub>2</sub> variation
12/1-10	10/14	3291	33.2 <sup>§</sup>	#6 Oil	1.5	14.0	126 (224)	125 (222)	-	10 (31)	406 (516)	404 (267)	89.8	O <sub>2</sub> variation
12/1-11	10/14	3291	33.2 <sup>§</sup>	#6 Oil	1.9	13.6	155 (276)	146 (259)	-	12 (34)	369 (472)	400 (261)	89.8	O <sub>2</sub> variation

\*ppm reported on 3% O<sub>2</sub> dry basis.

<sup>†</sup>Stack was clear during all tests.

<sup>§</sup>Oil flow not measured, heat input estimated based on gas fuel tests.

RG - Refinery gas

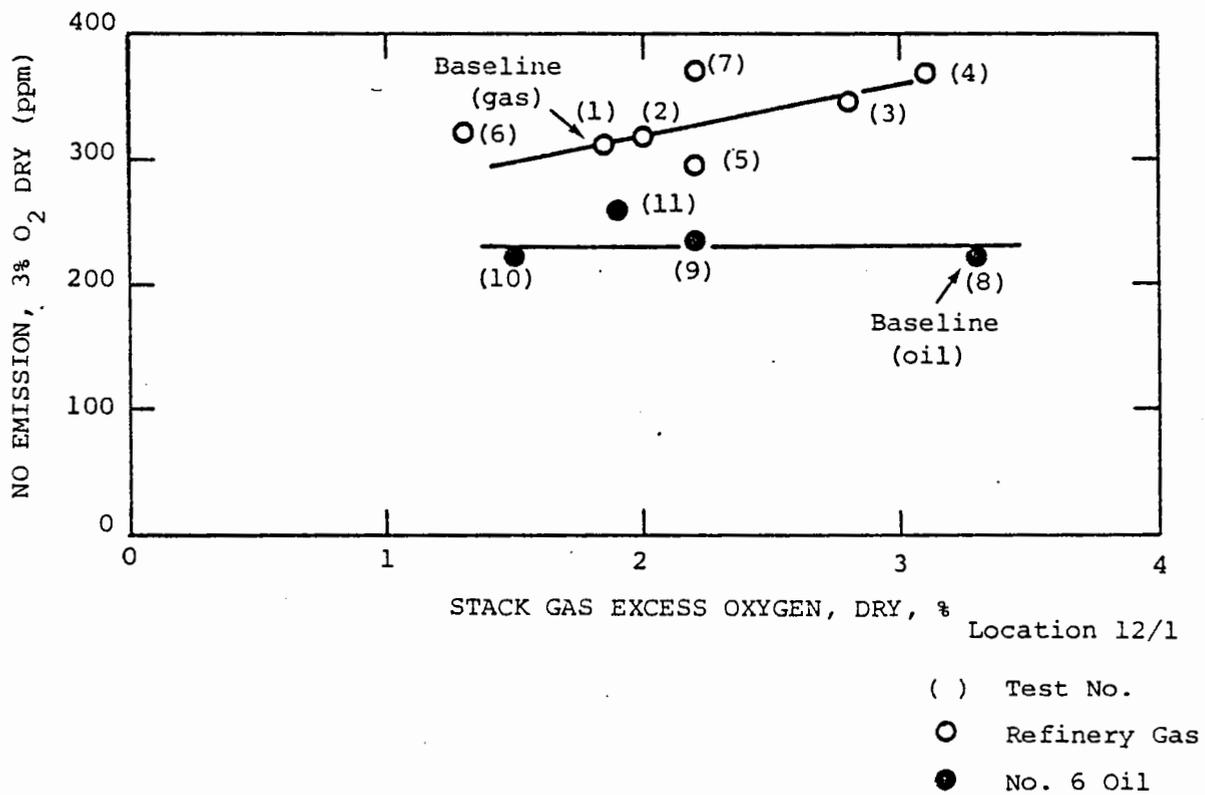


Figure 4-10. NO emission as a function of excess oxygen location 12/1 refinery heater with air preheat.

TABLE 4-10. FUEL ANALYSES, LOCATION 12

No. 6 Oil Fuel		
Test No.	12/1-8	12/2-2
Date	10/14/76	10/15/76
Carbon, %	87.37	87.22
Hydrogen, %	10.30	10.33
Nitrogen, %	0.27	0.27
Sulfur, %	1.16	1.14
Ash, %	0.044	0.035
Oxygen, % (by difference)	0.86	1.00
API Gravity at 60 °F	12.7	12.6
Heat of Combustion:		
Gross		
kJ/kg	42,900	42,800
(Btu/lb)	(18,450)	(18,380)
Net		
kJ/kg	40,700	40,600
(Btu/lb)	(17,510)	(17,440)
Refinery Gas		
Test No.	12/1-1	12/2-1
Date	10/12/76	10/16/76
CH <sub>4</sub>	64.3	18.5
C <sub>2</sub> H <sub>6</sub>	24.0	9.87
C <sub>3</sub> H <sub>8</sub>	7.4	11.4
C <sub>4</sub> H <sub>10</sub>	1.5	2.11
C <sub>5</sub> H <sub>12</sub>	--	0.42
C <sub>2</sub> H <sub>4</sub>	--	5.21
C <sub>3</sub> H <sub>6</sub>	1.3	--
C <sub>4</sub> H <sub>8</sub>	1.5	--
C <sub>6</sub> H <sub>6</sub>	--	0.22
O <sub>2</sub>	--	0.023
N <sub>2</sub>	--	1.00
CO <sub>2</sub>	--	0.013
CO	--	0.07
H <sub>2</sub>	--	51.2
Heat of Combustion:		
MJ/m <sup>3</sup>	51.1	37.1
Btu/CF	(1373)	(996)

#### Efficiency, Process Heater, Location 12/1--

The efficiency of the unit with air preheat averaged 86.4% firing refinery gas and 89.6% firing No. 6 oil. Variation in excess oxygen caused a change in efficiency of 0.6% -- from 89.2% at 3.3% O<sub>2</sub> to 89.8% at 1.5% O<sub>2</sub>. When firing refinery gas, the efficiency varied from a low of 86.2% at 2.8% O<sub>2</sub> to a high of 86.7% at 2.2% O<sub>2</sub>.

#### 4.1.7 Process Heater, Location 12, Unit 2

##### Equipment Characteristics--

The petroleum process heater tested at Location 12, Unit 2 was a forced draft dehexanizer reboiler without combustion air preheat. The heater was rated at 7362 m<sup>3</sup>/day (46,313 bbl/day). The unit was operating at approximately 45% of capacity during the test period. The single burner, capable of firing both gas and No. 6 oil fuel, was rated at 13.6 MW (46.5x10<sup>6</sup> Btu/hr) firing No. 6 oil with a LHV of 40,500 kJ/kg (17,400 Btu/hr). Sample probes were installed in the stack above the convection section. A schematic of heater showing the relative location of the sample port is shown in Figure 4-11.

##### Baseline Emissions--

Baseline NO<sub>x</sub> emissions for the non-preheated process heater (Unit 12/2) were measured in the stack above the convection section. Emissions were measured with the unit firing both refinery gas and No. 6 oil. Baseline NO<sub>x</sub> emissions were 109 ng/J (214 ppm) with the unit firing refinery gas and the excess oxygen at 4.3%. When firing No. 6 oil (62% heat input) and gas, the baseline NO<sub>x</sub> emissions were 97 ng/J (172 ppm) at 4.3% O<sub>2</sub>. Both baseline measurements were made with the unit in the "as-found" condition with the burner set by the operator. Baseline particulate measurements were made with the unit firing No. 6 oil and gas. Total particulate was 38.06 ng/J (0.088 lb/10<sup>6</sup> Btu). Solid particulate was 34.38 ng/J (0.080 lb/10<sup>6</sup> Btu) with 10% opacity.

The emissions measured from the process heater are summarized in Table 4-11. When operating with No. 6 oil alone, smoking occurred. Operators required partial gas firing to maintain a clear stack (zero opacity). Operators would not allow sufficient time when smoking to record opacity.

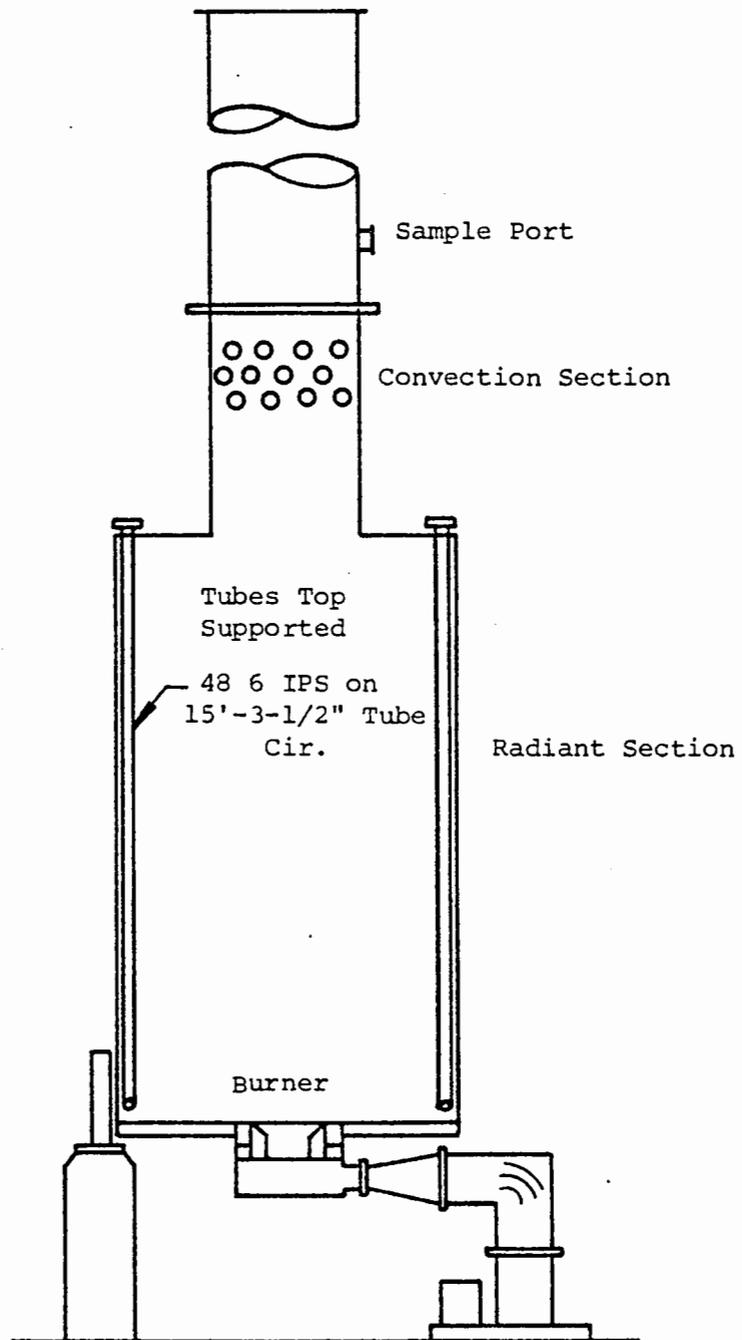


Figure 4-11. Schematic of dehexanizer reboiler (unit 12/2).

TABLE 4-11. SUMMARY OF EMISSIONS DATA  
LOCATION 12/2 - PROCESS HEATER WITHOUT AIR PREHEAT

Test Run No.	Date 1976	Heat Input MW	Load m <sup>3</sup> /d	Fuel	O <sub>2</sub> %	CO <sub>2</sub> %	NO <sub>x</sub> * ng/J (ppm)	NO <sup>a</sup> ng/J (ppm)	HC <sup>a</sup> ng/J (ppm)	CO <sup>a</sup> ng/J (ppm)	SO <sub>2</sub> * ng/J (ppm)	SO <sub>2</sub> ng/J (ppm)	SO <sub>3</sub> ng/J (ppm)	Total Particulates ng/J (lb/10 <sup>6</sup> Btu)	Solid Particulates ng/J (lb/10 <sup>6</sup> Btu)	Stack Temp. K (°F)	Eff. %	Comments
12/2-1	10-15	10.2	5405	RG	4.3	9.2	109 (214)	93 (183)	--	0 (0)	91 (128)	--	--	--	--	563 (554)	79.6	Baseline
12/2-2	10-15	10.2 <sup>§</sup>	5405	No. 6 Oil+RG	4.3	11.3	97 (172)	94 (167)	--	(22)	306 (391)	--	--	--	--	556 (541)	81.2	Baseline 38% Gas
12/2-3	10-18	8.3	5405	RG	3.85	9.45	43 (85)	43 (85)	--	3.1 (10)	43 (60)	--	--	--	0	559 (547)	79.6	SASS Test
12/2-4	10-19	8.4	5405	RG	3.4	9.2	66 (129)	64 (126)	--	4 (13)	86 (121)	122 (145)	20 (29)	--	--	557 (542)	80.0	SO <sub>x</sub> Test
12/2-5	10-19	8.4 <sup>§</sup>	5405	No. 6 Oil+RG	5.0	8.9	88 (157)	82 (146)	--	(45)	117 (150)	--	--	38.055 (0.0085)	34.384 (0.07995)	568 (562)	79.4	Par.Test: SS#4 43% Gas, 10% Opac
12/2-6	10-20	8.3	5405	RG	3.7	9.7	90 (138)	60 (133)	--	1.2 (4)	51 (72)	--	--	--	0	554 (537)	80.0	SASS Test
12/2-7	10-26	9.5	5405	RG	4.8	9.6 <sup>†</sup>	64 (126)	64 (126)	--	0 (0)	159 (224)	--	--	--	--	580 (585)	79.0	O <sub>2</sub> Variation
12/2-8	10-26	9.6	5405	RG	3.2	10.5 <sup>†</sup>	50 (98)	49 (97)	--	0 (0)	88 (124)	--	--	--	--	574 (574)	79.0	O <sub>2</sub> Variation
12/2-9	10-26	9.3	5405	RG	2.2	11.1 <sup>†</sup>	36 (71)	36 (70)	11.7 (66)	0 (0)	112 (158)	--	--	--	--	568 (562)	79.4	O <sub>2</sub> Variation
12/2-10	10-26	9.5	5405	RG	4.9	9.5 <sup>†</sup>	65 (128)	64 (126)	3.7 (21)	0 (0)	203 (285)	--	--	--	--	581 (586)	79.0	O <sub>2</sub> Variation
12/2-11	10-26	9.5 <sup>§</sup>	5405	No. 6 Oil+RG	5.0	12.0 <sup>†</sup>	92 (164)	88 (156)	2.3 (13)	7.8 (23)	482 (617)	--	--	--	--	570 (567)	80.4	O <sub>2</sub> Variation 43% Gas
12/2-12	10-26	9.5 <sup>§</sup>	5405	No. 6 Oil+RG	4.3	12.7 <sup>†</sup>	89 (158)	86 (152)	1.1 (6)	7.5 (22)	427 (546)	--	--	--	--	567 (561)	81.0	O <sub>2</sub> Variation 43% Gas
12/2-13	10-26	9.5 <sup>§</sup>	5405	No. 6 Oil+RG	3.8	13.1 <sup>†</sup>	82 (145)	81 (144)	0 (0)	10.6 (31)	429 (549)	--	--	--	--	563 (553)	81.6	O <sub>2</sub> Variation 43% Gas

\*ppm reported on 3% O<sub>2</sub> dry basis.

<sup>†</sup>CO<sub>2</sub> selector valve leaking - value corrected based on O<sub>2</sub> value and theoretical CO<sub>2</sub>.

<sup>§</sup>Oil flow not measured, heat input estimated based on previous all gas data point.

#### Combustion Modifications, Process Heater, Location 12/2--

Combustion modifications to this unit were limited to varying the excess air. The furnace excess air level was changed by adjusting the inlet dampers on the combustion air fan. The effect of excess O<sub>2</sub> variation on NO<sub>x</sub> emissions is shown in Figure 4-12 for both refinery gas and No. 6 oil fuels. Excess oxygen varied from 2.2% to 4.9% for refinery gas and from 3.8% to 5.0% for No. 6 oil. NO<sub>x</sub> emissions increased 20 ppm/% O<sub>2</sub> increase for refinery gas and 12 ppm/% O<sub>2</sub> increase for No. 6 oil. A 67% reduction in NO<sub>x</sub> from the baseline level was obtained while firing refinery gas. Little change was observed while firing No. 6 oil.

#### Efficiency, Process Heater, Location 12/2--

The unit averaged 79.5% efficiency on refinery gas and 81.0% on No. 6 oil. The efficiency varied from a low value of 80.4% at 5% O<sub>2</sub> to a high of 81.6% at 3.8% O<sub>2</sub> when firing No. 6 oil. Refinery gas firing showed an increase in efficiency of 1% over the range of excess oxygen. The lowest efficiency measured was 79.0% at 4.8% O<sub>2</sub> and the highest measured efficiency was 80.0% at 3.1% O<sub>2</sub>.

#### Trace Species and Organics Test, Location 12/2--

Two trace species and organic tests were conducted on the petroleum process heater at Location 12/2. Sampling and analytical procedures are described in Appendix C. The unit was firing refinery gas; Table 4-12 shows the sampling conditions. This unit also fires No. 6 oil which would be expected to have higher trace species and organic emissions. However, the tests were run with refinery gas because most of the fuel burned in process heaters in the U.S. is refinery gas. Samples of the refinery gas were taken for trace species and organic analysis for use in establishing mass balances. However, analysis by either atomic absorption (AA) or spark source mass spectrometry (SSMS) requires that samples be in either liquid or solid form. Procedures could not be developed for reducing the gas fuel or any trace components therein to a form suitable for analysis. As shown in the previous table, no solid particulates were collected in the SASS train cyclones; all material was in the gaseous phase.

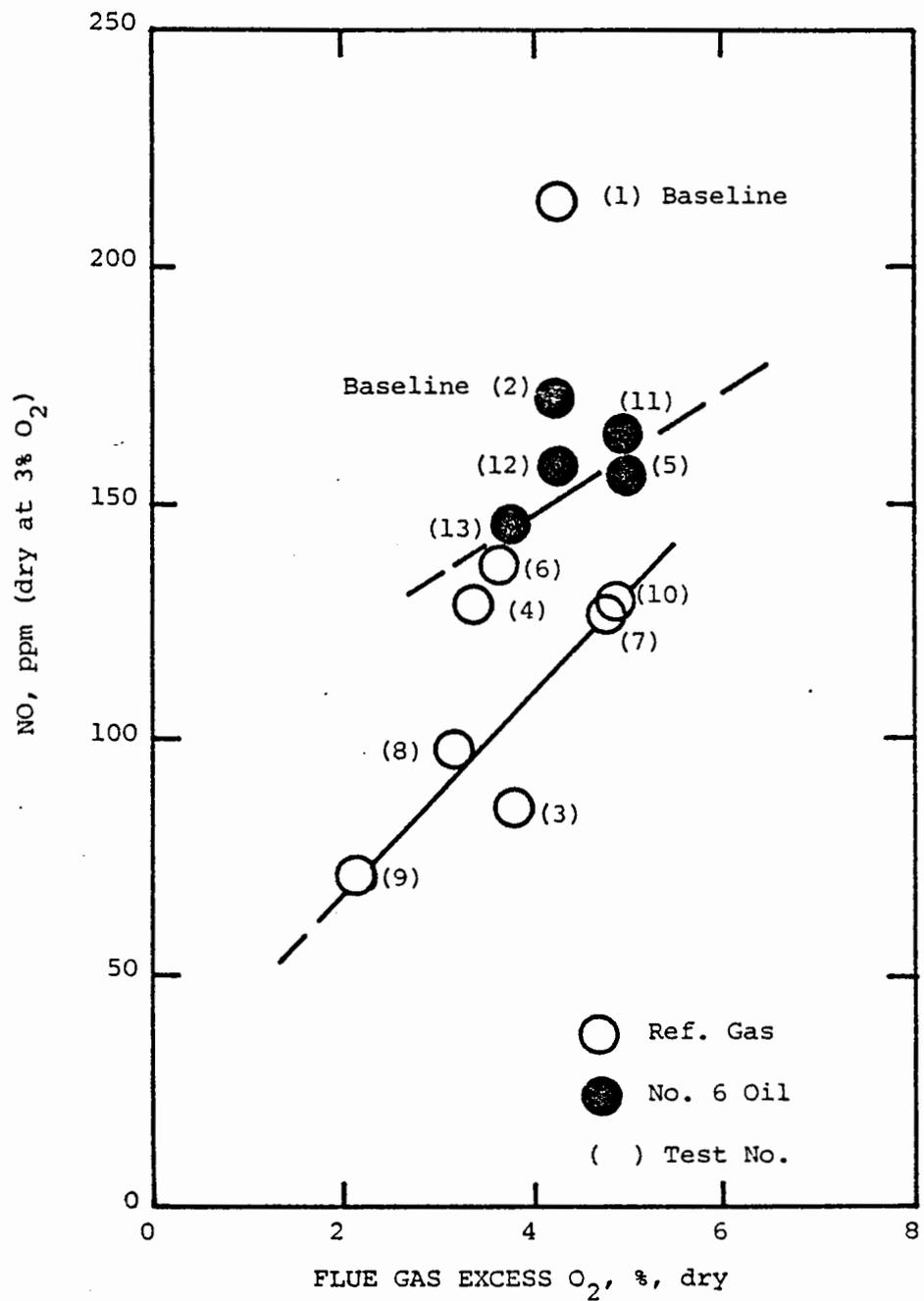


Figure 4-12. NO<sub>x</sub> emission as a function of excess oxygen Location 12/2 refinery heater without air preheat.

TABLE 4-12. TRACE SPECIES AND ORGANICS SAMPLING CONDITIONS  
 PETROLEUM PROCESS HEATER - LOCATION 12/2

TS&O Run No.	1	2
Test No.	12/2-3	12/2-6
Date	10/17/76	10/20/76
Port Location	G <sub>L</sub>	G <sub>L</sub>
Velocity, m/s (f/s)	3.39 (11.1)	3.42 (11.3)
Stack Temp., K (°F)	594 (609)	591 (604)
Oxygen Content, % dry	3.85	3.7
Moisture, %	16.8	13.0
Sample time, min.	300	300
Cyclone Flow, awcmm (awcfm)	0.0895 (3.16)	0.070 (2.46)
Isokinetic Rate, %	229	179
Oven Temp., K (°F)	477 (398)	480 (403)
XAD-2 Temp., K (°F)	293 (67)	293 (68)
Meter Temp., K (°F)	286 (56)	287 (57)
Nozzle Size, mm (in.)	12 (0.688)	12 (0.688)
No. Filters Used	1	1
Sample Flow, Dry, scmm (scfm)	0.046 (1.61)	0.037 (1.32)
Volume Collected, Dry, scm (scf)	13.67 (483)	11.24 (397)
Particulate weight, g	0	0
Solid Particulates, ng/J (lb/10 <sup>6</sup> Btu)	0	0
Stack Flow Rate, Nm <sup>3</sup> /s (scfm)	2.9 (6145)	3.03 (6420)

Table 4-13 shows the total emission concentrations determined by AA analysis for the species of primary interest for two duplicate test runs in the heater stack. Additional data tabulations are contained in Appendix F. Species that were present above the detection limits include cadmium, calcium, chromium, cobalt, copper, iron, lead, manganese, nickel, titanium, vanadium, zinc, chloride, fluoride, nitrates, sulfates, and POM. All other species including PCB were not detected. The source of these emissions is believed to be erosion of material deposited during operation of the unit on oil fuel.

In general, the same elements detected in the first test (12/2-3) were also detected in the second test (12/2-6). Exceptions were cobalt (detected in the first test, undetected in the second) barium, lead, and vanadium (all three undetected in the first test, detected in the second).

Comparing the AA results for the two tests as duplicate runs, the emission concentrations ( $\mu\text{g}/\text{m}^3$ ) are within a factor of about three with two notable exceptions. Cadmium emission for the first test was  $74,000 \mu\text{g}/\text{m}^3$  compared with  $7.7 \text{ to } 11 \mu\text{g}/\text{m}^3$  for the second test. Conversely, calcium emission was much lower on the first test,  $5 \mu\text{g}/\text{m}^3$ , compared with  $280,000 \mu\text{g}/\text{m}^3$  for the second test. Duplicate analyses performed indicated that these differences were not due to the precision of analytical methods. Differences between the tests may be due to possible intermittent flaking of materials deposited during oil firing.

Total POM concentration was above the detection limit only for test 12/2-6. Appendix F presents results of a detailed analysis by gas chromatography-mass spectrometry (GC/MS) to identify specific POM compounds. The compounds detected were anthracene, methyl anthracenes, fluoranthene, pyrene, and chrysene. The majority of the POM was collected in the SASS train organic module.

TABLE 4-13. TRACE SPECIES AND ORGANIC EMISSIONS  
 PETROLEUM PROCESS HEATER, LOCATION 12/2

Species Concentration,  $\mu\text{g}/\text{Nm}^3$

Sampling Location	Stack Exit	Stack Exit
Test No.	12/2-3	12/2-6
Antimony	< 700	< 850
Arsenic	< 40	< 47
Barium	< 40	140 < 150
Beryllium	< 10	< 10
Cadmium	74000	7.7 < 11
Calcium	5	280000
Chromium	110	170
Cobalt	4 < 300	< 390
Copper	120	29 < 33
Iron	1210	2500
Lead	< 3	28 < 32
Manganese	190	330
Mercury	< 30	< 10
Nickel	83 < 210	180
Selenium	< 60	< 73
Tellurium	< 2800	< 3100
Tin	< 3400	< 4200
Titanium	600 < 1100	2700 < 3300
Vanadium	< 110	112
Zinc	75	150
Chloride	6900	44 < 81
Fluoride	660	860 < 880
Nitrates	5.5	10.1
Sulfates	560000	19000
Total POM	< 13	0.6 < 15
Total PCB	< 12	< 15
For Additional Data, See Tables Noted in Appendix F	F-40 to F-42	F-43 to F-49

See Table F-1 for explanation of table values.

## 4.2 MINERAL KILNS

Three mineral kilns were tested at Locations 1, 3, and 9 during this program. The following sections describe the equipment characteristics, emissions measurement results, and conclusions.

### 4.2.1 Ceramic Kiln, Location 1

#### Equipment Characteristics--

The kiln tested at Location 1 was a linear ceramic tunnel kiln erected in 1954. The kiln has a capacity for 46 product cars, each 3.0 m (10 ft) long. The kiln is used for firing clay tile pipe and other clay tile products. The unfired product is placed on a car which is slowly moved on a metal track through the kiln. The kiln consists of three zones--a preheat zone, main firing zone, and cooling zone as shown schematically in Figure 4-13. Temperature-time profile is the primary constraint in the process. The temperature must steadily increase at a predetermined rate in the preheat zone and the temperature in the main firing zone must be controlled within 3 K (5 °F). Heat to the preheat zone is supplied from the cooling zone by means of fans and exterior ducts. Some of the hot gas from the cooling zone is also directed to drying rooms where wet product is dried prior to entry into the kiln.

The kiln is heated with combination natural gas-oil burners located along the side of the kiln. The kiln had 34 burners per side. Normal operation is with natural gas; oil is used only when natural gas supplies are curtailed. Combustion air is supplied to the burners by forced draft fans. The rated heat input was 9.4 MW ( $32 \times 10^6$  Btu/hr) and tests were conducted at 79% load.

The process control data collected for the tunnel kiln tests at Location 1 consisted of temperature profile data, fuel flow rate, and process rate. In addition to the normal instrumentation, a water cooled probe was used to measure the O<sub>2</sub> concentration at each burner along the main firing zone.

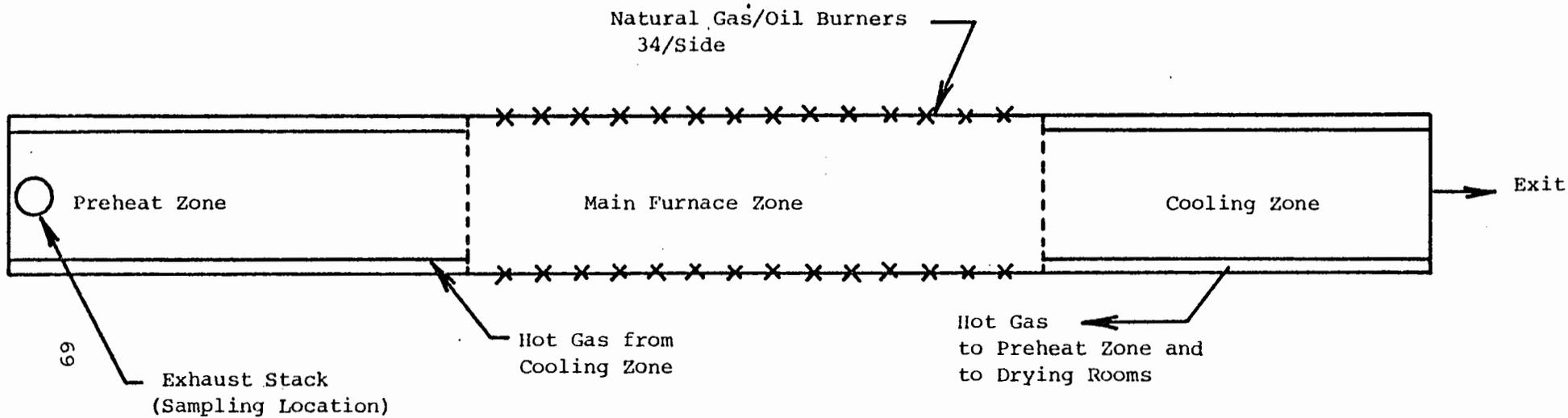


Figure 4-13. Schematic plan view of ceramic linear tunnel kiln.

#### Baseline Emissions--

Baseline emissions data were taken at the tunnel kiln at a process rate of 16 cars per day. The sampling location was in the stack upstream from the louvres which control furnace pressure. The baseline  $\text{NO}_x$  emission level was 46.2 ng/J (90 ppm) with the measured stack  $\text{O}_2$  at 17%. Particulate emissions were 12.5 ng/J (0.029 lb/10<sup>6</sup> Btu) when firing natural gas. All data from the tunnel kiln tests are tabulated in Table 4-14. The composition of natural gas fuel burned is given in Table 4-15. Only baseline testing was conducted at this test location; planned combustion modifications were not performed due to the likelihood of upsetting process temperatures.

The burners were sampled individually, at the tunnel kiln, using a water-cooled probe, to determine the excess  $\text{O}_2$  profile. Table 4-16 presents the data taken while sampling the gas burner ports. Burners 1 through 4, closest to the preheat zone, were out of service. The next five burners, 5 through 9, were burning at very reduced input. The excess oxygen at these burners was considerably higher than the burners which were operating at full capacity. Eight burners were not sampled because they are near the top of the kiln wall and were not accessible. The average  $\text{O}_2$  with all burners was 7.0% and 7.8% for the two tests. If the burners which were not at rated capacity are not included, the average  $\text{O}_2$  was 4.5% and 6.0%. A request was made to reduce the air to burners which had high  $\text{O}_2$  readings. The request could not be accepted because the excess air is necessary to prevent the burner tips from burning and to maintain process temperature.

The high degree of sensitivity of product quality to the combustion process represents a major limitation on the feasibility of modifications in mineral processing equipment.

An overall efficiency for the tunnel kiln was attempted but not completed due to the complexity of the process. Several flow paths were used for the extensive heat recovery system. Stack gas losses were calculated based on the flue gas composition and temperature. The stack gas loss (total of dry flue gas plus moisture in air plus moisture in flue gas due to combustion of hydrogen in the fuel) was calculated to be 14.6% of the fuel input. Stack gas temperature was measured at 330 K (134 °F).

TABLE 4-14. SUMMARY OF EMISSIONS DATA  
 LOCATION 1 - LINEAR CERAMIC TUNNEL KILN

Rated Load = 9.39 MW ( $32 \times 10^6$  Btu/hr); Test Load = 7.42 MW ( $25.3 \times 10^6$  Btu/hr)

Test No.	Date 1976	O <sub>2</sub> (%)	CO <sub>2</sub> (%)	NO* (ppm)	NO (ng/J)	NO <sub>x</sub> * (ppm)	NO <sub>x</sub> (ng/J)	CO* (ppm)	Particulate		Comments
									lb/10 <sup>6</sup> Btu	(ng/J)	
1-1	4/6	17.0	2.3	90	46.2	90	46.2	248	--	--	Baseline test
1-2	4/7	16.7	2.7	50	25.7	52	26.7	314	0.0029	12.5	Particulate test
71 1-3	4/8	17.0	2.2	77	39.6	86	44.2	135	--	--	Baseline
1-4	4/8	17.0	2.2	72	37.0	69	35.4	270	--	--	Baseline

\*Dry, corrected to 3% O<sub>2</sub>.

Rated process rate, 16 cars/day = 116.4 Mg/d (128 tons/d).

Stack was clear during all tests.

TABLE 4-15. NATURAL GAS FUEL ANALYSIS,  
LOCATION 1 CERAMIC KILN

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<u>Non-Combustible Gases</u>	
Carbon Dioxide	0.35 (% by volume)
Oxygen	0.12
Nitrogen	0.37
Water Vapor	0.050
<u>Combustible Gases</u>	
Methane	94.52
Ethane	4.26
Propane	0.20
i-Butane	0.025
n-Butane	0.037
Pentanes	0.032
Hexanes	0.032
Heating Value	38.82 MJ/m <sup>3</sup> (1042 Btu dry/SCF)
Specific Gravity (air = 1.00)	0.575

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TABLE 4-16. GAS BURNER OXYGEN MEASUREMENTS  
IN A LINEAR CERAMIC TUNNEL KILN

Burner No.	O <sub>2</sub> (%)	O <sub>2</sub> (%)
	4/7/76	4/8/76
* 5 <sup>†</sup>	16.5	15.0
6	14.6	14.3
7	14.0	14.2
8	15.8	14.2
9	14.5	13.7
10	8.0	6.5
11(top)	--	--
12	4.0	5.0
13	5.0	6.5
14(top)	--	--
15	3.9	1.5
16	0.8	0
17(top)	--	--
18	2.8	9.3
19	5.6	10.6
20(top)	--	--
21	5.4	7.5
22	9.2	8.0
23(top)	--	--
24	7.7	0.5
25	8.7	9.0
26(top)	--	--
27	4.8	3.9
28	3.0	10.5
29(top)	--	--
30	0.2	7.8
31	1.3	5.0
32(top)	--	--
33	6.0	5.2
34	2.2	4.5

\*Burners 1 through 4 were out of service.

† Burners 5 through 9 throttled back to approximately 1/4 input.

Little in the way of combustion modification is possible with the tunnel kiln due to process constraints. The kiln tested achieved very high efficiency by making extensive use of heat recovery techniques for cooling the fired product and drying and preheating the incoming product. The only heat loss which appeared to be amenable to reduction was radiation loss from the sidewalls and roof.

#### 4.2.2 Rotary Cement Kiln, Location 3

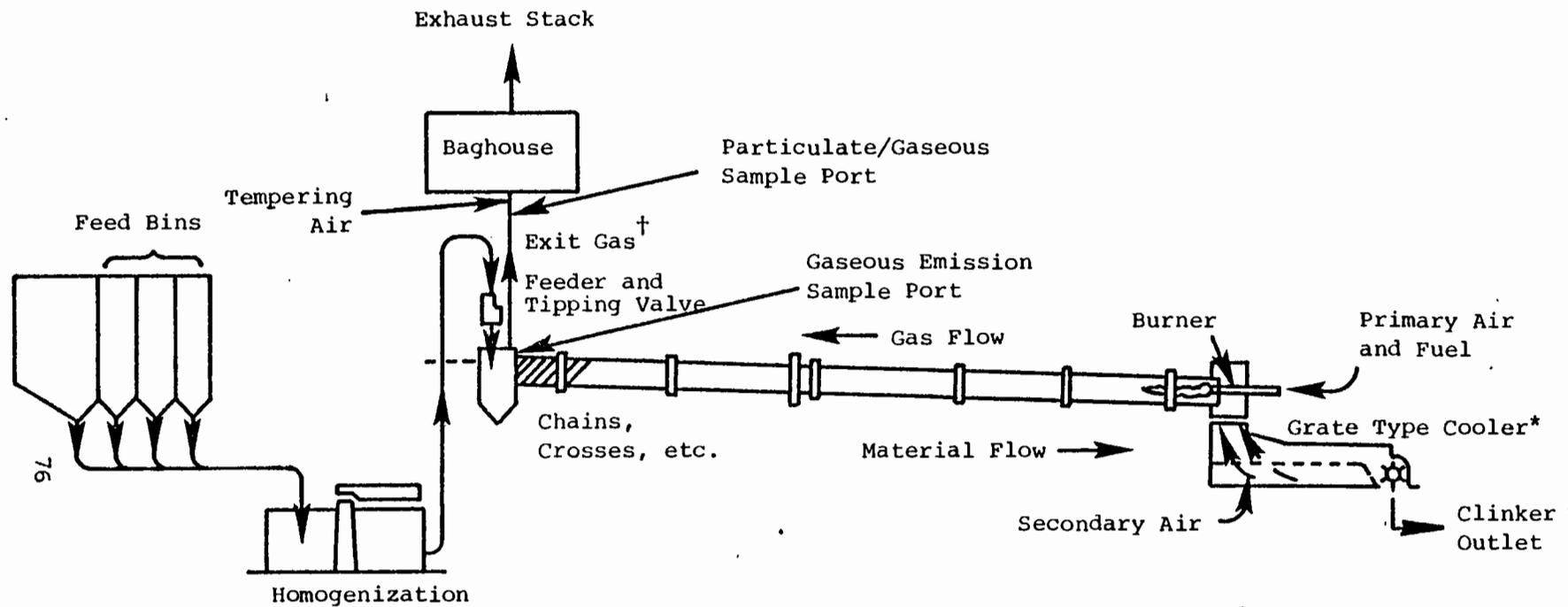
##### Equipment Characteristics--

The test unit at location 3 was a rotary cement kiln fueled with a combination of coke and natural gas with a rated heat input of 70.3 MW ( $240 \times 10^6$  Btu/hr). The dry-process kiln is shown schematically in Figure 4-14. The feed enters in the form of a finely divided powder, flowing from a feed silo. Homogenization equipment is used to assure uniformity of raw feed composition. A dust return system is used in conjunction with the feed system. The feed encounters a chain system in the feed end of the kiln to aid in heat exchange. After the chain section, the feed undergoes preheating, calcining, additional heating, and clinker formation stages.

Particulate from the process stream was removed with a multiclone separator at the kiln exit and a baghouse downstream of the multiclone. An induced draft fan at the stack provided motive power for the combustion air and baghouse tempering air. Combustion air was preheated by passing through the clinker grate which cooled the clinker.

Existing sample ports were located at the kiln exit and in the duct between the kiln and the baghouse. Particulate mass, particulate size distribution, and gaseous emissions data were measured in the duct between the multiclone and the baghouse. Gaseous emissions data only were taken at the kiln exit.

A complete set of control room data included process rate, fuel flow, temperatures of the material, exit gases, incoming air, etc. The particulate loading was so high at the kiln that the standard pitot probe plugged within 15 to 20 seconds of insertion, making a velocity traverse impossible. A pitot with larger nozzles was borrowed to make the velocity traverse. The probe for measuring gaseous emissions had a sintered stainless steel filter on the end with a metal shield around it as shown in Figure 4-15.



\* Cooling air not used for secondary air is exhausted through pollution device to atmosphere.

† Exhaust gases pass through pollution control device to atmosphere

Figure 4-14. Schematic of a dry process cement kiln system, Location 3.

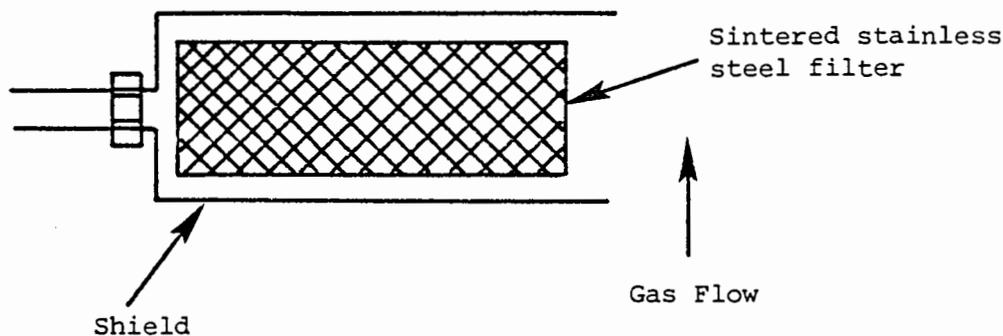


Figure 4-15. Sintered sampling probe filter, Location 3.

The cement kiln burned about 2/3 coke and 1/3 natural gas, on a heat input basis. The coke analysis is shown in Table 4-17.

TABLE 4-17. CEMENT KILN SOLID COKE FUEL ANALYSIS, LOCATION 3

	<u>% weight</u>
Carbon	82.68
Hydrogen	3.67
Nitrogen	2.38
Sulfur	1.94
Ash	6.19
Moisture	2.01
Oxygen (by difference)	1.13
Heating Value	32,360 kJ/kg (13,980 Btu/lb)

This kiln had been previously tested by KVB when operative entirely on natural gas and also on oil fuel. Those tests had indicated lower  $\text{NO}_x$  emissions on oil compared with gas. The purpose of the current test was to evaluate the effect of solid fuel on  $\text{NO}_x$  as compared with the prior data.

Baseline Emissions--

Baseline testing at the rotary cement kiln was conducted at a process rate of 43,000 kg/hr (47 tons/hr) of clinker. The measured  $\text{NO}_x$  emissions were 709 ng/J (1041 ppm) at a measured  $\text{O}_2$  concentration of 2%. Both total particulate and particulate size distribution were taken with the kiln at baseline conditions. Table 4-18 summarizes the emissions data taken. The table also shows data previously acquired on this same kiln (Ref. 5) for

TABLE 4-18. ROTARY CEMENT KILN EMISSION DATA SUMMARY\*

Data from Current Test Program, Coke and Natural Gas Fuel Combined

Test No.	Date	Fuel	Process Load kg/s	Heat Input MW	O <sub>2</sub> (%)	CO <sub>2</sub> (%)	NO <sup>†</sup>		NO <sub>x</sub> <sup>†</sup>		CO <sup>†</sup> (ppm)	SO <sub>2</sub> <sup>†</sup> (ppm)	HC <sup>†</sup> (ppm)	Particulate		Comments
							(ppm)	(ng/J)	(ppm)	(ng/J)				(lb/10 <sup>6</sup> Btu)	(ng/J)	
3-1	5/5 1976	Coke + Nat. gas	11.9	69.3	2.0	17.4	1014	691	1041	709	52	4	19	--	--	Baseline
3-2	5/6 1976	Coke + Nat. gas	11.1	68.9	2.05	17.1	950	647	961	655	38	11	26	--	--	Part. port kiln exit
			14.1	69.4	13.6	9.7	930	633	--	--	44	36	34	46.0	19800	Particulate port baghouse inlet
3-3	5/7 1976	Coke + Nat. gas			1.65	17.4	994	677	1038	707	28	20	9	--	--	Particulate size
Ref. 5	1973	Nat. gas	--	--	14	--	1460	903	--	--	--	--	--	--	--	Baseline, natural gas
Ref. 5	1973	Oil	--	--	14.5	--	640	430	--	--	--	--	--	--	--	Baseline, oil

\* Gaseous measurements are taken at kiln exit except as noted.

† ppm data are corrected to 3% O<sub>2</sub>, dry basis. Conversion from ppm to ng/J includes CO<sub>2</sub> flow from CaCO<sub>3</sub> in the feed of 48.9x10<sup>-9</sup> Nm<sup>3</sup>/J (1820 SCF/10<sup>6</sup> Btu), in addition to flue gas from fuel combustion of 257.6x10<sup>-9</sup> Nm<sup>3</sup>/J (9600 SCF/10<sup>6</sup> Btu) at stoichiometric air-fuel ratio.

Stack was clear during all tests.

natural gas operation and oil operation. Operation with fuel oil produced  $\text{NO}_x$  emissions about one-half that produced with gas. The current test indicates that combined coke and natural gas operation produces  $\text{NO}_x$  emissions that are 20-30% lower than with gas alone. The current trend for conversion of cement kilns to solid fuel operation should result in significant reductions of  $\text{NO}_x$ .

One test was conducted using the Brink cascade impactor with the kiln operating at baseline conditions. The impactor was inserted into the duct between the multiclone separator and baghouse as with the total particulate sampling train. The results of this test are presented in Figure 4-16 where particle diameter as a function of cumulative proportion of impactor catch is plotted. Approximately 15% of the particulate is below 3  $\mu\text{m}$ . A visual opacity reading taken during the particulate testing showed that the stack was completely clear. The baghouse for the kiln is very large and apparently very efficient.

#### Efficiency, Cement Kiln, Location 3--

Efficiency of the rotary cement kiln is conventionally expressed in terms of heat input per unit mass of clinker. The rotary kiln at Location 3 under baseline conditions was operating at a heat input of 60 MW ( $206 \times 10^6$  Btu/hr); the process efficiency was 5093 kJ/kg ( $4.38 \times 10^6$  Btu/ton) of clinker. This is below the national average of about 5230 kJ/kg ( $4.7 \times 10^6$  Btu/ton) of clinker (Ref. 6).

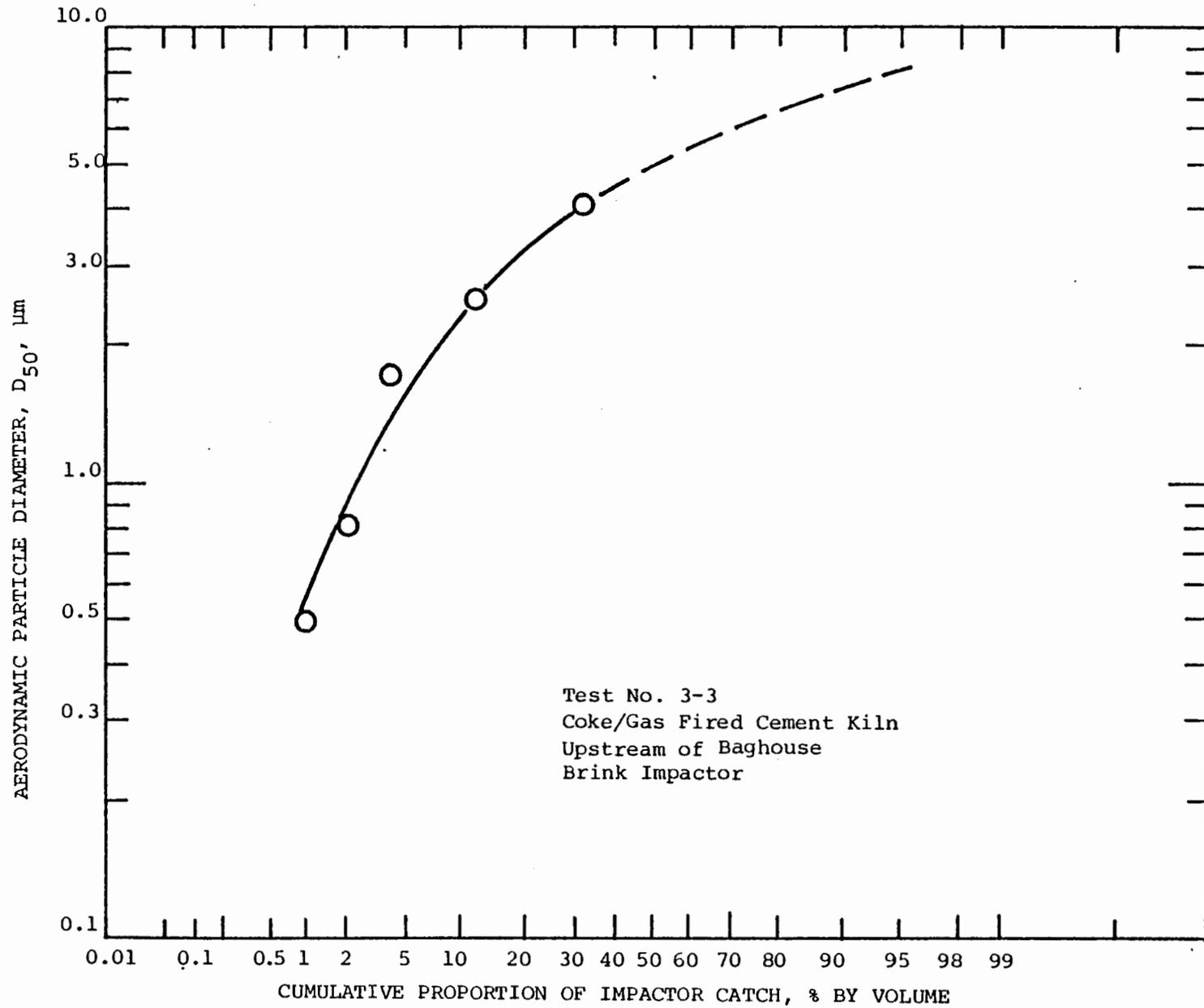


Figure 4-16. Particle size distribution for a cement kiln, location 3.

### 4.2.3 Rotary Cement Kiln, Location 9

Testing was conducted at Location 9 to determine the gaseous and particulate emissions from a wet process rotary cement kiln. Testing for trace elements was conducted with the SASS train.

#### Equipment Characteristics--

The test unit was a 137 m (450 ft) long by 3.67 m (12 ft) diameter wet process rotary kiln rated at 9.44 kg/s (900 tons/day). In a wet process kiln, the feed enters the kiln in the form of a slurry, having a moisture content of approximately 30%. The wet process is preferred over the dry type when the feed naturally exceeds about 18% moisture, but it is less efficient because of heat required to vaporize the water. A heat exchanger in the form of a chain section is used to remove this moisture from the slurry. Figure 4-17 shows a schematic of the rotary kiln.

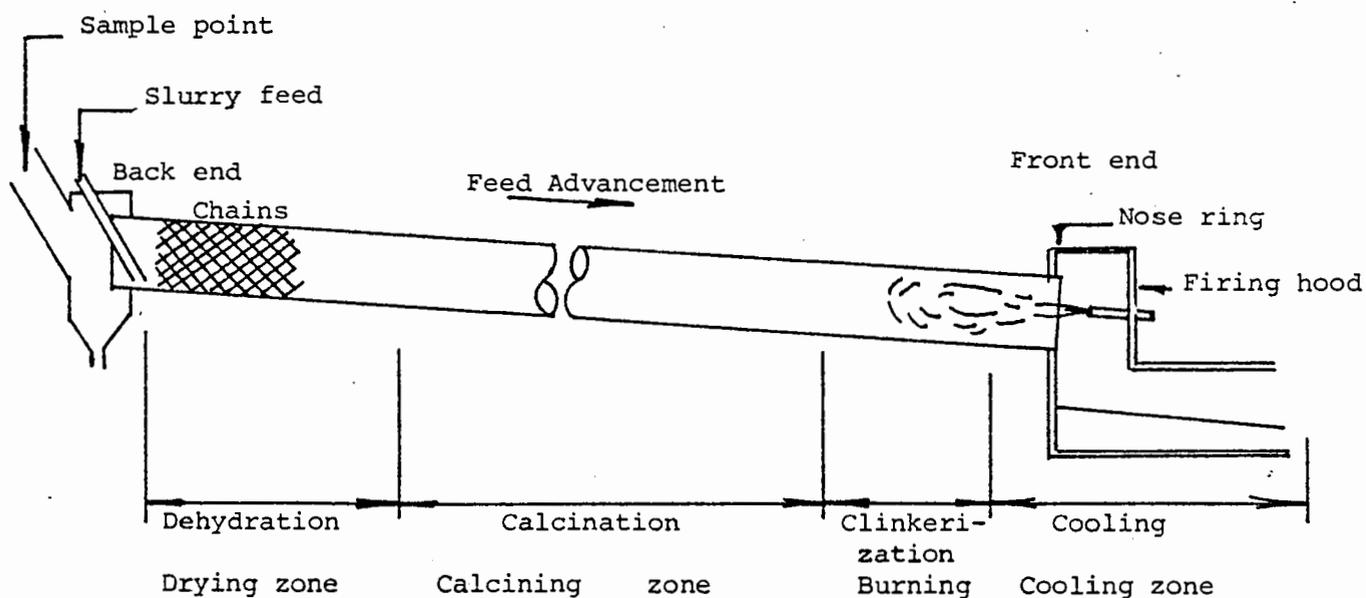


Figure 4-17. Schematic of wet process rotary kiln.

#### Emissions Sampling, Location 9--

The kiln is equipped with an electrostatic precipitator. However, all sampling was conducted at the kiln exit upstream of the precipitator.

The kiln was firing natural gas at a rate of 59 MW ( $200 \times 10^6$  Btu/hr) during the test period. An analysis of the natural gas is presented in Table 4-19. Analysis was by the gas chromatographic method.

TABLE 4-19. ANALYSIS OF FUEL GAS AT LOCATION 9

Component	Concentration - Mol %
Methane	95.64
Ethane	2.04
Propane	0.70
Iso-butane	0.15
N-butane	0.21
Iso-pentane	0.06
N-pentane	0.06
Hexanes +	0.16
Carbon dioxide	0.10
Nitrogen	0.88
Higher heating value	32.1 MJ/m <sup>3</sup> (999 Btu/CF)

#### Baseline Tests, Location 9--

The test series consisted of baseline measurement of particulate, particulate size and gaseous emissions followed by a series where the combustion air temperature was varied. An additional total particulate test and cascade impactor test were then conducted. Baseline gaseous emissions were conducted with the rotary kiln in the "as-found" condition. NO<sub>x</sub> emissions were 1408 ng/J (2400 ppm) corrected to 3% O<sub>2</sub>, dry basis, with the unit operating at 6.1% O<sub>2</sub>. Carbon monoxide which measured 30 ppm at baseline condition varied from 28 to 43 ppm for all conditions and HC emissions varied

from 11 to 24 ppm with the baseline measurement being 24 ppm. The initial particulate measurement was 9805 ng/J (22.8 lb/10<sup>6</sup> Btu) but calculations showed sampling conditions to be 148% of isokinetic. This was the result of a very high and variable moisture content of about 45%. A subsequent test was conducted at low NO<sub>x</sub> conditions for which the sampling conditions were 122% of isokinetic. The particulate emissions for this test were 9000 ng/J (21 lb/10<sup>6</sup> Btu). The results of emission measurements for all Location 9 tests are summarized in Table 4-20. Particulate size distributions were determined using a Brink cascade impactor which aerodynamically separates particle sizes. Two tests with the cascade impactor were made and the results presented in Figures 4-18 and 4-19 where particle size as a function of cumulative percentage smaller than a given diameter is plotted. These data show that 17 to 25% of the particulates entering the cement kiln precipitator are smaller than 3 μm diameter. Because of the extremely high particulate loadings, test durations were only eight minutes and four minutes before the cascade impactor plugged and flow stopped.

#### Combustion Modifications--

Process constraints in the wet process rotary kiln limited the combustion modifications testing. Combustion air temperature was varied in an effort to evaluate the influence on NO<sub>x</sub> emissions. Unfortunately, combustion air temperature, kiln temperature, and exit gas O<sub>2</sub> concentration cannot be varied independently and maintain product integrity. The effect of combustion air temperature on NO emissions is shown in Figure 4-20. As combustion air temperature increases, NO emissions increase for nearly constant O<sub>2</sub> concentration. The points which do not follow this trend are tests in which the O<sub>2</sub> was lower than normal or kiln temperature was much lower than normal. The effect of kiln temperature is shown in Figure 4-21 which shows increasing NO emissions with increasing kiln temperature.

These data indicate that at a given kiln operating temperature--approximately 1755 K (2700 °F)--a reduction in NO emissions of 160 ng/J (314 ppm) or 14%, was realized by reducing excess O<sub>2</sub> and increasing combustion air temperature to maintain kiln temperature.

TABLE 4-20. SUMMARY OF EMISSIONS FROM WET PROCESS ROTARY KILN, LOCATION 9

Rated Load 9.4 kg/s (900 tons/day)

Test No.	Date 1976	Process Load kg/s	Input Mw	O <sub>2</sub> (%)	CO <sub>2</sub> (%)	NO <sub>x</sub>		NO		HC (ppm)	CO (ppm)	SO <sub>2</sub> (ppm)	Particulate		Comb. Air Temp.		Kiln Temp		Comments
						(ppm)	(ng/J)	(ppm)	(ng/J)				10 <sup>6</sup> Btu	(ng/J)	(°F)	(K)	(°F)	(K)	
9-1A	8/11	9.4	59	6.0	16.0	2400	1408	2250	1319	24	30	0	22.8	9805	750	672	2700	1756	Baseline - part. test, 5-25% opacity
9-1B	8/11	↓	↓	6.1	16.0	2548	1494	2416	1417	12	34	0	--	--	810	706	2900	1867	Baseline test
9-1C	8/11	↓	↓	5.2	18.0	1729	1014	1709	1003	11	34	0	--	--	720	656	2450	1617	Upset kiln condition - cascade impactor test
9-2A	8/12	↓	↓	6.0	15.2	1409	826	1290	757	24	29	0	--	--	740	667	2200	1478	Low kiln temperature
9-2B	8/12	↓	↓	5.1	15.6	1386	813	1443	846	23	29	0	--	--	750	672	2450	1617	Low O <sub>2</sub> condition
9-2C	8/12	↓	↓	4.5	18.0	1858	1090	1936	1136	20	32	0	--	--	900	755	2750	1783	High combustion air temp, low O <sub>2</sub>
9-2D	8/12	↓	↓	5.7	16.8	2819	1654	2588	1518	21	36	0	--	--	900/ 830	755/ 772	2900	1867	High combustion air temperature
9-2E	8/12	↓	↓	5.7	17.9	2650	1554	2265	1329	20	28	0	--	--	930	772	2840	1833	High combustion air temperature
9-2F	8/13	↓	↓	4.2	19.3	1824	1070	1741	1021	17	43	0	20.9	9000	900/ 1000	755/ 811	2450	1617	Particulate test, low NO <sub>x</sub> , <5% opacity
9-2G	8/13	↓	↓	5.6	17.6	2044	1199	1929	1132	14	28	0	--	--	800/ 890	700/ 722	2650	1738	Cascade impactor test, low NO <sub>x</sub>
9-3	9/29	10.2	60.1	4.5	17.6	1230	720	1172	687	--	26	--	17	7307	1095	864	2960	1900	SASS, ESP inlet
9-4	9/30	9.4	62.6	2.3	19.6	693	406	674	395	48	587	--	12.9	5548	1150	894	2980	1911	SASS, ESP inlet
9-5	10/4	9.2	57.2	6.8	14.3	--	--	1740	1020	0	3	0	0.053	22.7	1005	814	2763	1790	SASS, ESP outlet
9-6	10/5	10.6	58.5	6.6	16.8	--	--	1062	623	44	50	0	0.069	29.5	928	771	2612	1707	SASS, ESP outlet

- NOTES: 1. ppm values for NO<sub>x</sub>, NO, HC, CO, and SO<sub>2</sub> are corrected to 3% O<sub>2</sub> dry basis.  
 2. All emissions were measured upstream of an electrostatic precipitator.  
 3. Conversion from ppm to ng/J includes added CO<sub>2</sub> of 32.2 x 10<sup>-9</sup> Nm<sup>3</sup>/J (1207 SCF/10<sup>6</sup> Btu) for CO<sub>2</sub> released from CaCO<sub>3</sub> in kiln feed, in addition to gas from the fuel combustion of 231 x 10<sup>-9</sup> Nm<sup>3</sup>/J (8622 SCF/10<sup>6</sup> Btu).

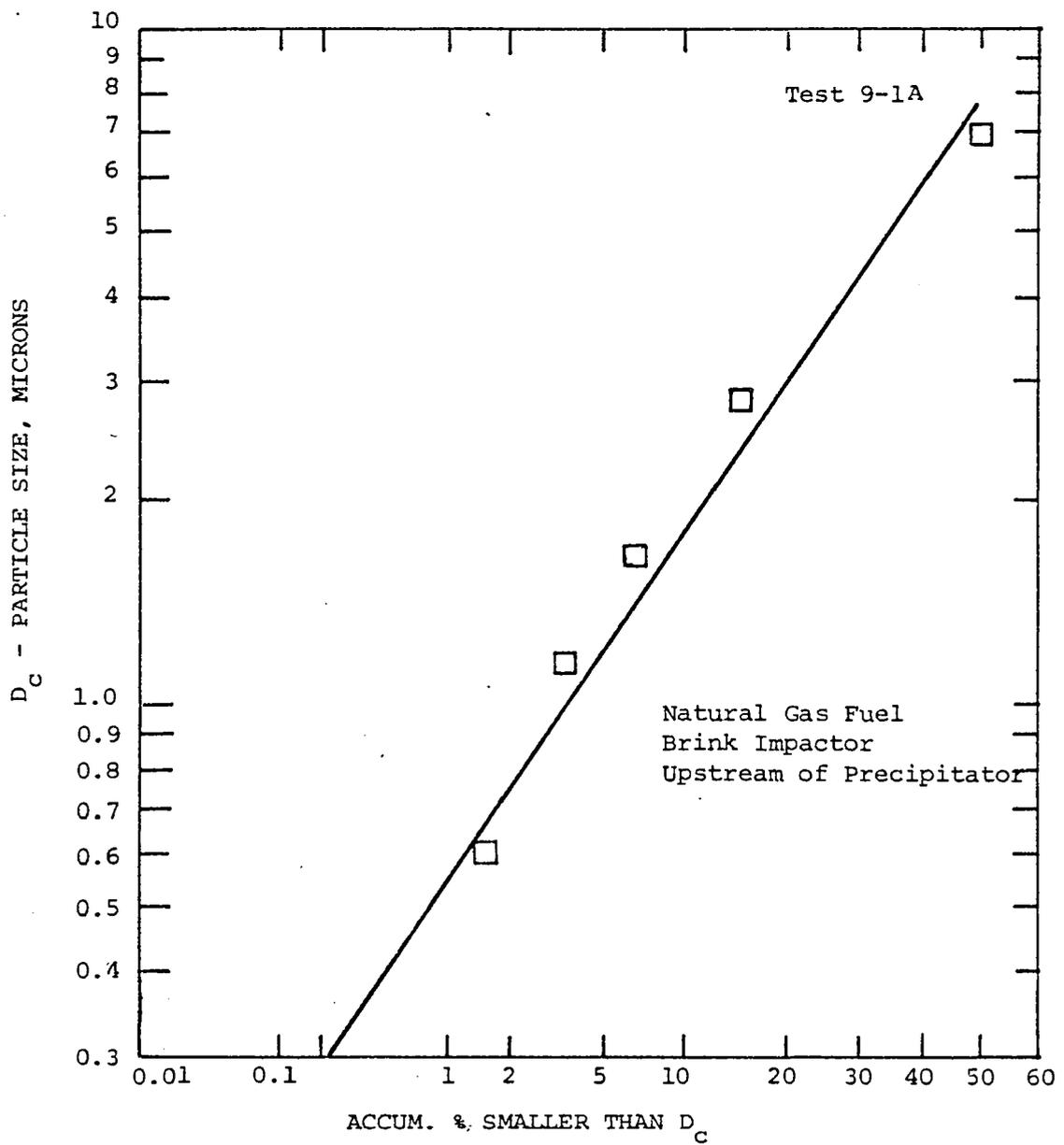


Figure 4-18. Cement kiln particulate size distribution, Location 9.

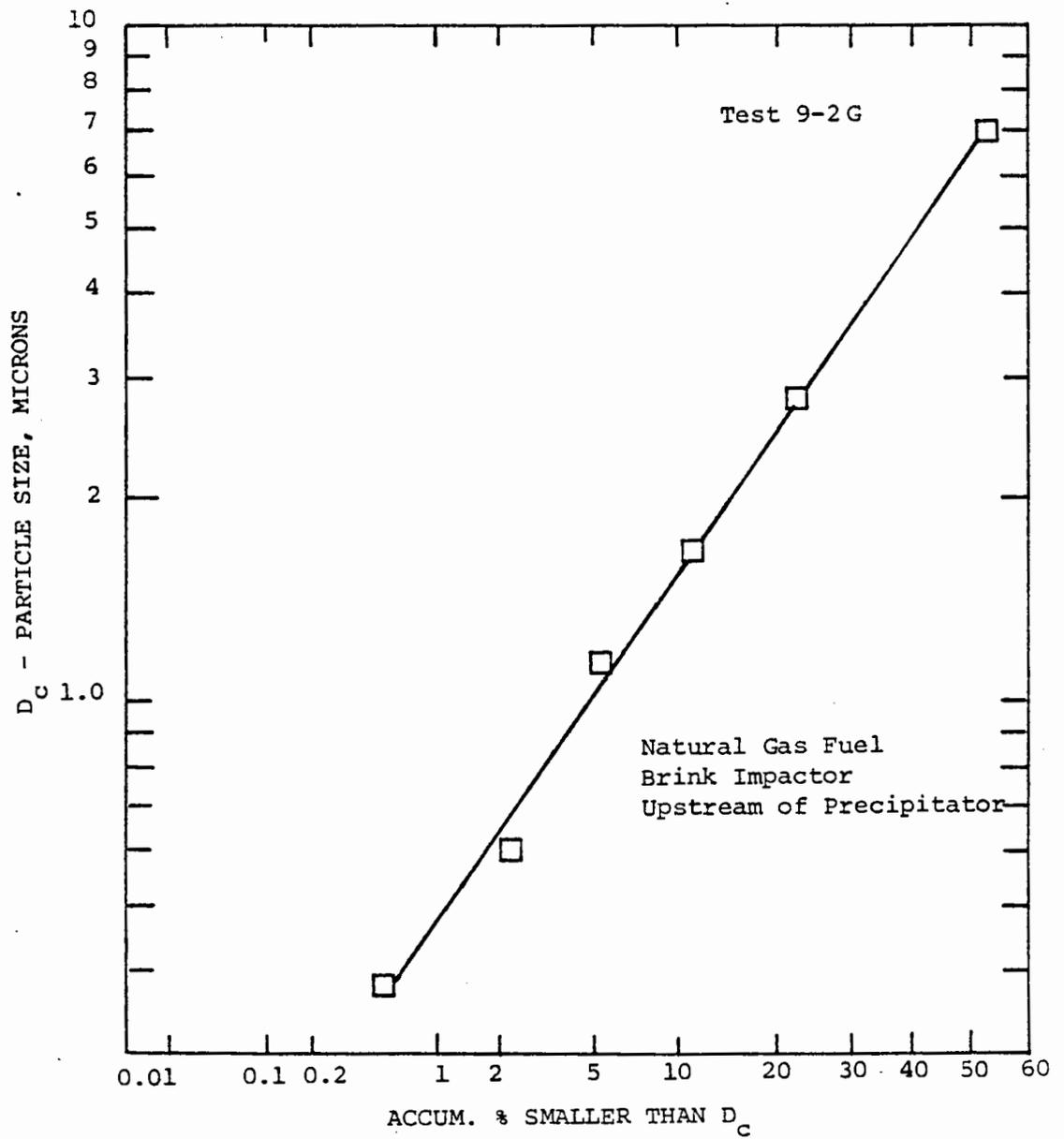


Figure 4-19. Cement kiln particulate size distribution, Location 9.

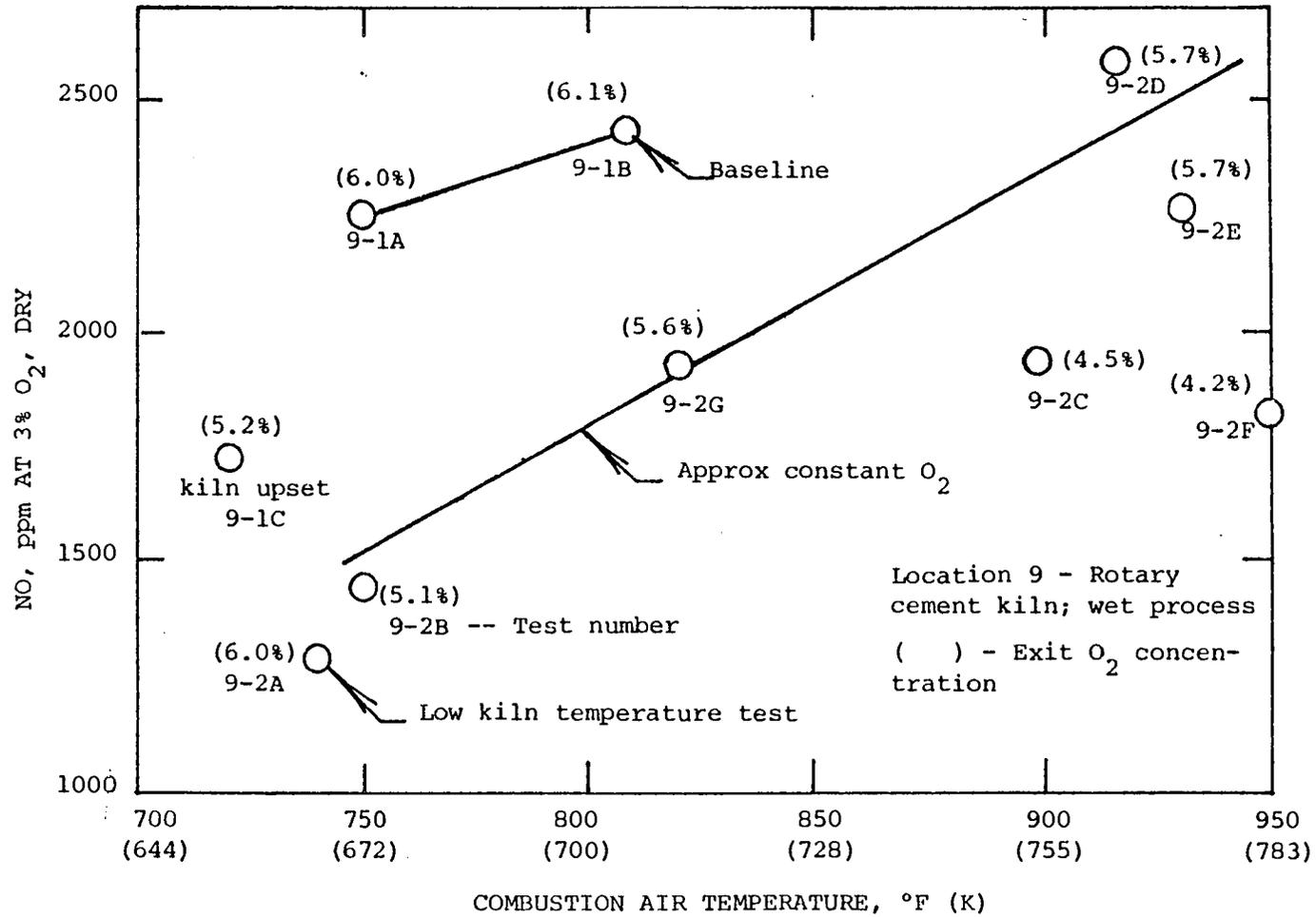


Figure 4-20. The effect of combustion air temperature on cement kiln NO emissions.

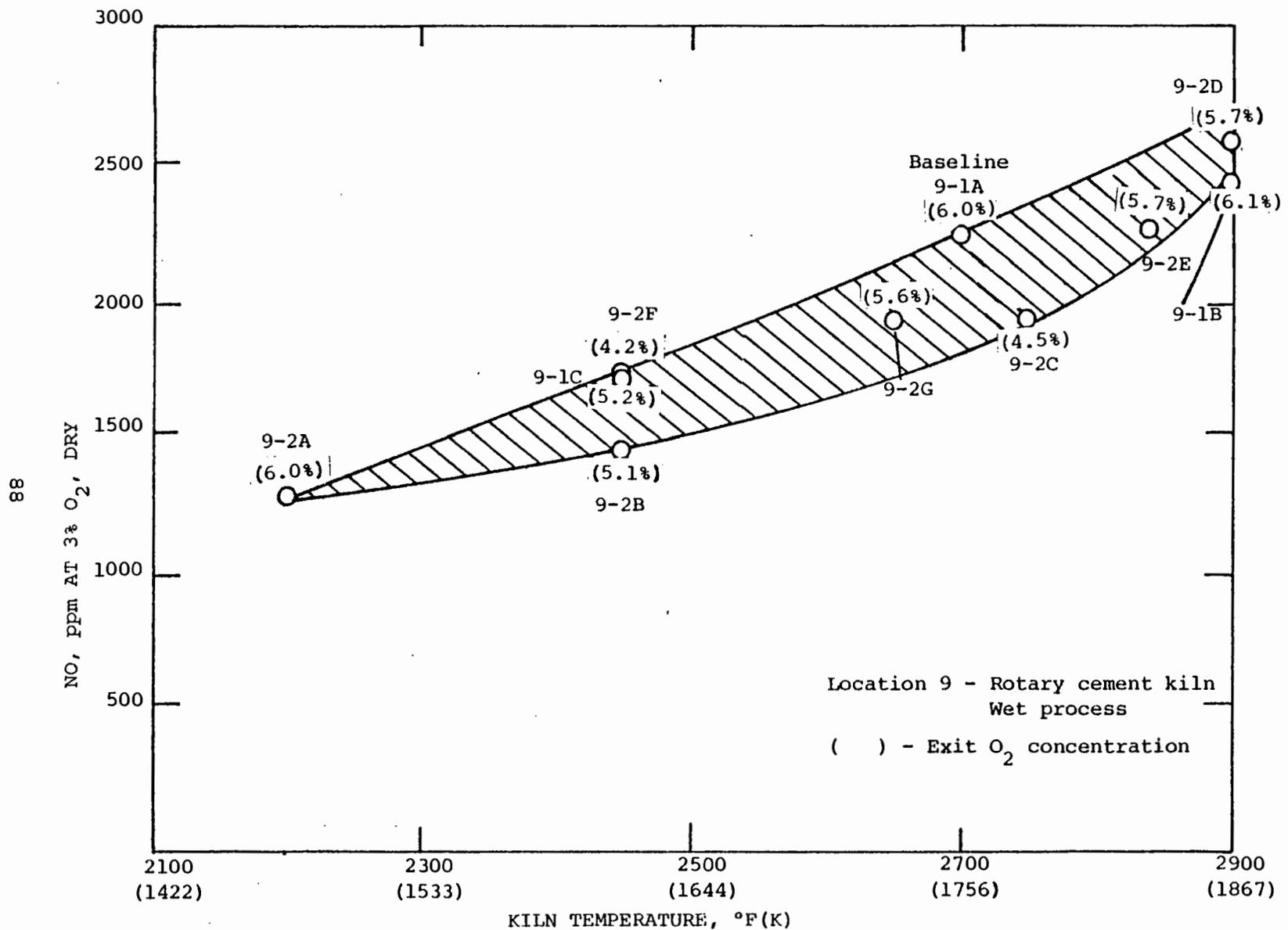


Figure 4-21. The effect of cement kiln temperature on NO emissions.

## Cement Kiln Trace Species Test, Location 9--

Trace species and organics tests were conducted on the natural gas fueled rotary cement kiln at Location 9. The slurry feed to the kiln undergoes moisture evaporation, heating, calcining, burning, and cooling as it flows countercurrent to the combustion products, finally emerging as a clinker. During the calcining process, a portion of the dry feed (approximately 36% by weight) is converted to CO<sub>2</sub> gas which exits the kiln along with the combustion products and evaporated moisture.

The kiln tested was fitted with an electrostatic precipitator. Sample ports were located upstream of the ESP and between the ID fan and stack, as shown in Figure 4-22. Samples of the feed slurry, clinker and precipitator catch were collected during each test.

Manual operation of this particular device is characterized by moderate fluctuations in most process variables of interest, e.g., kiln discharge temperature, combustion air temperature (a function of kiln discharge temperature and production rate), and natural gas usage. Thus, long time periods of relatively constant kiln operation are not possible. SASS train tests were not performed during periods of obvious kiln upset, however, tests were conducted during periods of normal fluctuations.

In the following discussion, mention will be made of several process variables - kiln discharge temperature, combustion air temperature, natural gas rate, and control room excess oxygen. An explanation of these variables as to their meaning and point of measurements is in order.

Kiln Discharge Temperature - This measurement is taken from the product side of the kiln refractories by a single color pyrometer in the burning zone, approximately 9.2-18.4 m (30-60 ft) prior to the kiln discharge and reflects, to some extent, the temperature of the clinker just prior to dumping on the cooler grate. Clinker discharge is normally between 1533 and 1644 K (2300-2500 °F).

Combustion Air Temperature - The main combustion air is preheated by passing it through the hot clinker. The air preheat level, therefore, increases with increasing clinker temperature and vice versa.

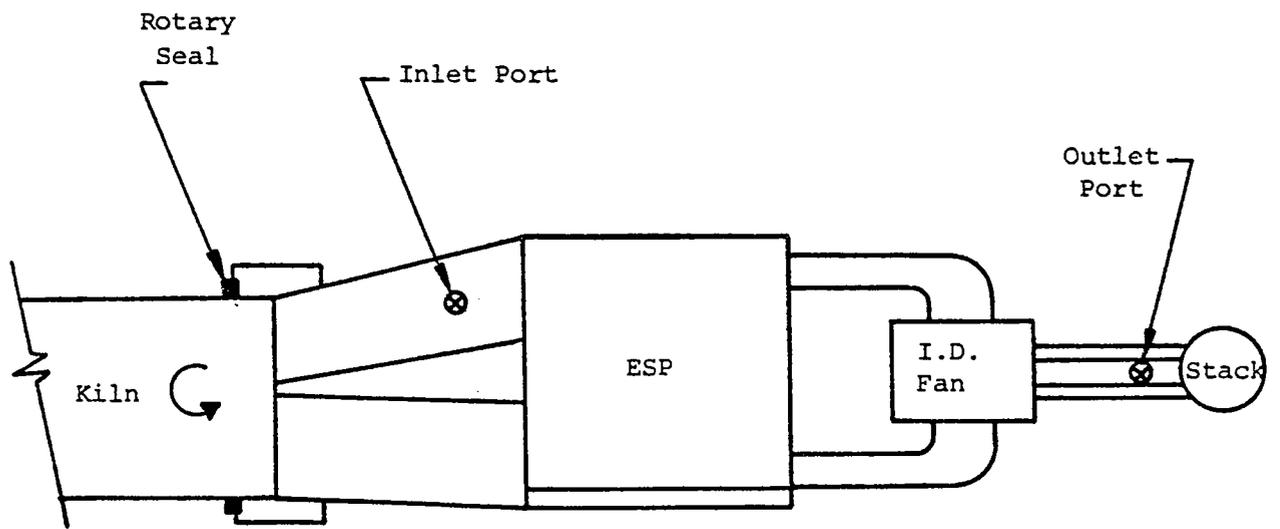


Figure 4-22. Rotary cement kiln - sample port locations, location 9.

Natural Gas Rate - Strip charts on the main gas line to the facility measure the total natural gas demand. Aside from several space heaters, this demand represents the natural gas flow to the kiln. (These space heaters were not in service during the test period.) The natural gas flow is manually set by the operator based primarily on his visual observation of clinker brightness and quality (e.g., size, adherence to the kiln wall, etc.) in the burning zone. As such, the operator is manually compensating for changes in feed rate, feed moisture content, etc.

Table 4-21 presents the trace specie sample train data and process weights. The following sections discuss each test. The total particulate weight for Tests 9-3 and 9-4 (upstream) of 7307 and 5548 ng/J, respectively, are somewhat lower than the Method 5 result of 9000-9800 ng/J.

#### Precipitator Inlet Test Conditions--

Test 9-3 was to be terminated when two filters had been plugged. After 75 minutes elapsed time, the vacuum pump inlet pressure limit, 76 kPa (22.5 in. HgVac) had been reached. An examination of the 1  $\mu$ m cyclone cup revealed that it, and not the filter, had plugged the system. The test was terminated based on this condition. The largest nozzle size available (19.1 mm, 3/4 inch) was not large enough to produce the nominal cyclone flow rate due to the relatively low gas velocity.

Control room data for this test are shown in Figure 4-23 and indicate a 2.9% increase in kiln discharge temperature over the test period (75 min.). Combustion air preheat is accomplished by passing the air through the hot clinker discharged from the kiln. Thus, combustion air temperature entering the kiln will increase as the clinker temperature increases, and vice versa. This is borne out by the observed 2.1% increase in combustion air temperature.

Test 9-4, a repeat of Test 9-3, was also terminated at 75 minutes elapsed time by a plugged 1  $\mu$ m cyclone. The gas moisture content for this test was significantly higher than the previous day's test (44.7% versus 34.3%). This effect caused a more marked departure from isokinetic sampling (118.3% versus 96.8%).

TABLE 4-21. TRACE SPECIES AND ORGANICS SAMPLING CONDITIONS  
LOCATION 9 - ROTARY CEMENT KILN

TS & O Run No.	5	6	7	8
Test Number	9-3	9-4	9-5	9-6
Date (1976)	9/29	9/30	10/4	10/5
Port Location	ESP inlet	ESP inlet	ESP outlet	ESP outlet
Velocity, m/s(f/s)	5.17 (16.95)	5.06 (16.60)	17.48 (57.35)	17.41 (57.10)
Stack Flow, $\text{dNm}^3/\text{s}$ ( $10^3$ SCFM)	20.1 (42.6)	19.0 (40.3)	21.1 (44.7)	21.7 (46.0)
Stack Temp. K (°F)	415 (287)	425 (305)	411 (280)	408 (274)
Oxygen Content, %	4.5	2.3	6.8	6.6
Moisture, %	34.31	44.74	37.55	38.21
Sample Time, min.	75	75	300	300
Cyclone Flow, awcmm (awcfm)	0.102 (3.591)	0.097 (3.435)	0.087 (3.067)	0.087 (3.078)
Isokinetic Rate, %	96.8	118.3	105.5	104.5
Oven Temp., K (°F)	478 (400)	478 (400)	478 (400)	478 (400)
XAD2 Temp., K (°F)	303 (85)	297 (75)	299 (77)	294 (69)
Meter Temp., K (°F)	311 (90)	319 (115)	309 (97)	310 (99)
Nozzle Size, mm (in.)	19.05 (0.75)	19.05 (0.75)	9.53 (0.375)	9.53 (0.375)
No. of Filters Used	1	1	1	1
Sample Flow, dry, scmm (scfm)	0.0342(1.382)	0.0386 (1.3631)	0.0351 (1.2384)	0.0345(1.2185)
Volume Collected, dry, scm (scf)	2.937 (103.64)	2.897 (102.23)	10.529 (371.53)	10.359 (365.55)
Particulate Catch, g	63.7780	54.17	0.6122	0.7939
Concentration, $\text{g/dNm}^3$	21.7	18.88	0.0581	0.0766
Total Particulates, ng/J(lb/MMB)	7307 (17.0)	5548 (12.9)	22.7 (0.053)	29.47 (0.069)
<u>Unit Conditions:</u>				
Test Time, min.	75	75	316.8	313.2
Nat. Gas Burned, $10^3$ scm( $10^3$ scf)	7.241 (255.5)	7.754 (273.6)	27.60 (973.7)	(28.46 (1004.1)
Dry Feed, $10^6$ g ( $10^3$ lb)	76.64 (168.6)	70.61 (155.4)	293.7 (646.0)	334.2 (735.2)
Slurry Feed, $10^6$ g ( $10^3$ lb)	119.0 (261.8)	108.6 (239.0)	462.5 (1017.4)	517.3 (1138.0)
Slurry Moisture, % weight	35.6	35.0	36.5	35.4
Clinker, $10^6$ g ( $10^3$ lb)	45.75 (100.7)	42.18 (92.69)	175.0 (385.1)	199.4 (438.6)
Precipitator Catch $10^6$ g ( $10^3$ lb)	2.131 (4.688)	2.131 (4.688)	9.375 (20.63)	9.375 (20.63)

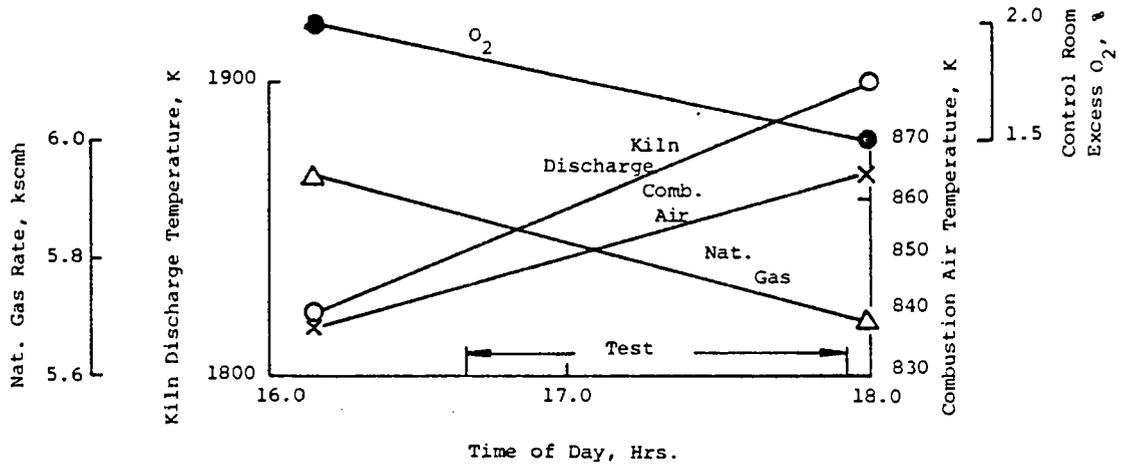


Figure 4-23. Trace species Test 9-3 at cement kiln precipitator inlet.

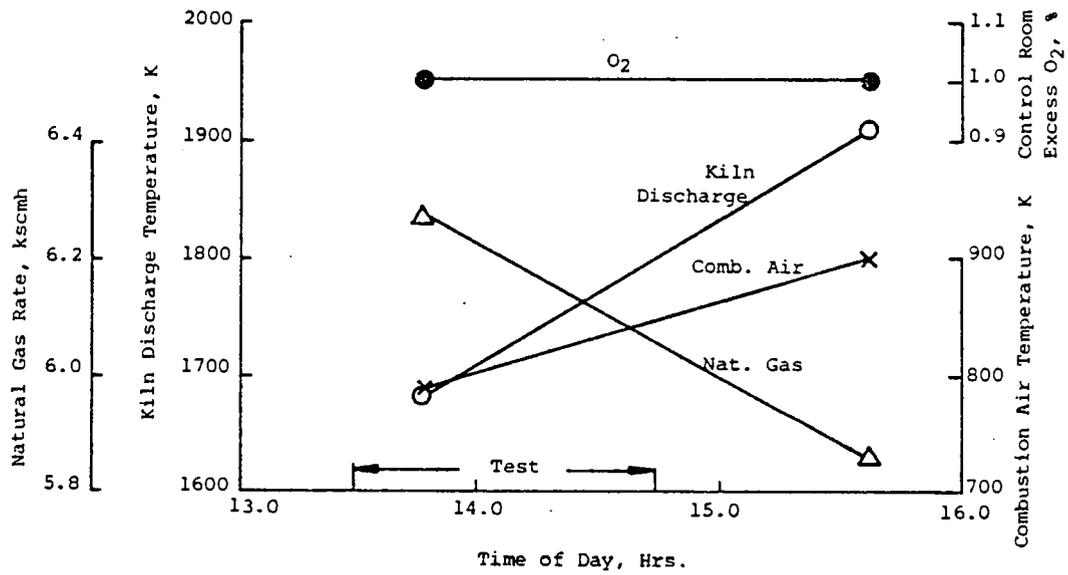


Figure 4-24. Trace species Test 9-4 at cement kiln precipitator inlet.

Relatively stable kiln operating conditions were observed during this test as shown in Figure 4-24. Kiln discharge temperature and combustion air temperature increased by 9.7% and 9.3%, respectively, while natural gas usage rate decreased by 4.7% as the operator attempted to maintain clinker quality.

#### Precipitator Outlet Test Conditions--

Outlet SASS Test 9-5 ran for a full five hours and used only one filter. The 9.53 mm (3/8 in.) nozzle used was somewhat undersize, as the cyclone flow rate was only 77% of the desired value.

Control room data for this test are shown in Figure 4-25. Kiln discharge temperature first decreased by 8.2%, then increased by 13.8% before reaching a steady value during the last 3.3 hours of the test. Combustion air temperature followed the variations in kiln discharge temperature. Variations in natural gas rate were, for the most part, opposite in sense to the kiln discharge temperature as the operator attempted to maintain appropriate clinker conditions. That is, as the clinker brightness increases (increase in burning temperature) above some subjective value, then the operator will decrease the natural gas rate to reduce the brightness.

Test 9-6 was to be a repeat of Test 9-5, i.e., five-hour sampling time. Kiln conditions, as shown in Figure 4-26, were more variable than the previous test. It appears that the manual setting of natural gas rate overcompensated for clinker "brightness" changes, for the kiln discharge temperature went through a relatively large amplitude (330 K, 549 °F) cycle. (Several consecutive cycles of this type had been observed on other occasions.)

In summary, device operating conditions encountered during the SASS train tests were normal for this particular kiln.

#### Cement Kiln Process Mass Balance--

The kiln feed consists of a dry solid-water slurry of variable (but measured) moisture content. Within the calcining zone approximately 36% (by weight) of the dry solids are converted to carbon dioxide gas, which exits the kiln along with the normal combustion products and evaporated water. The

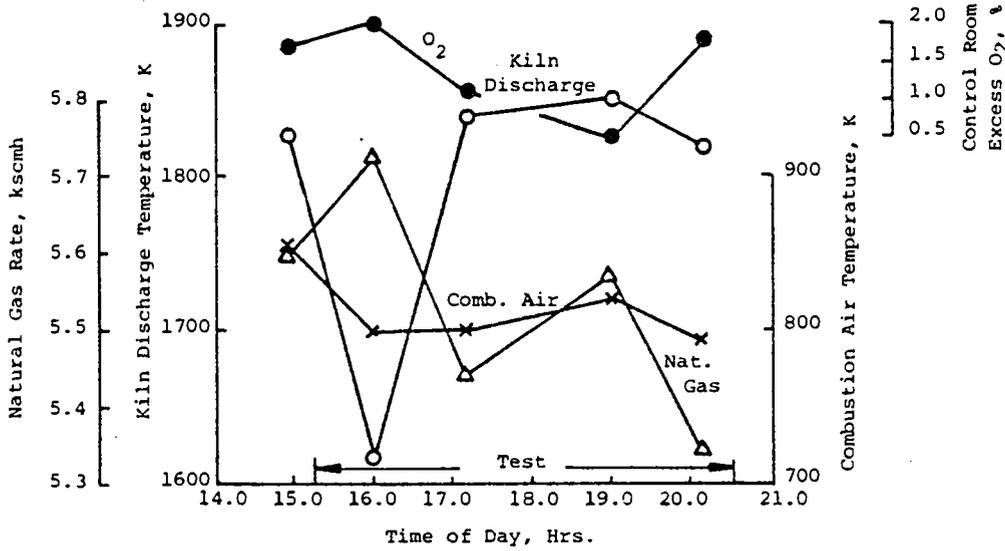


Figure 4-25. Trace species Test 9-5 at cement kiln precipitator outlet.

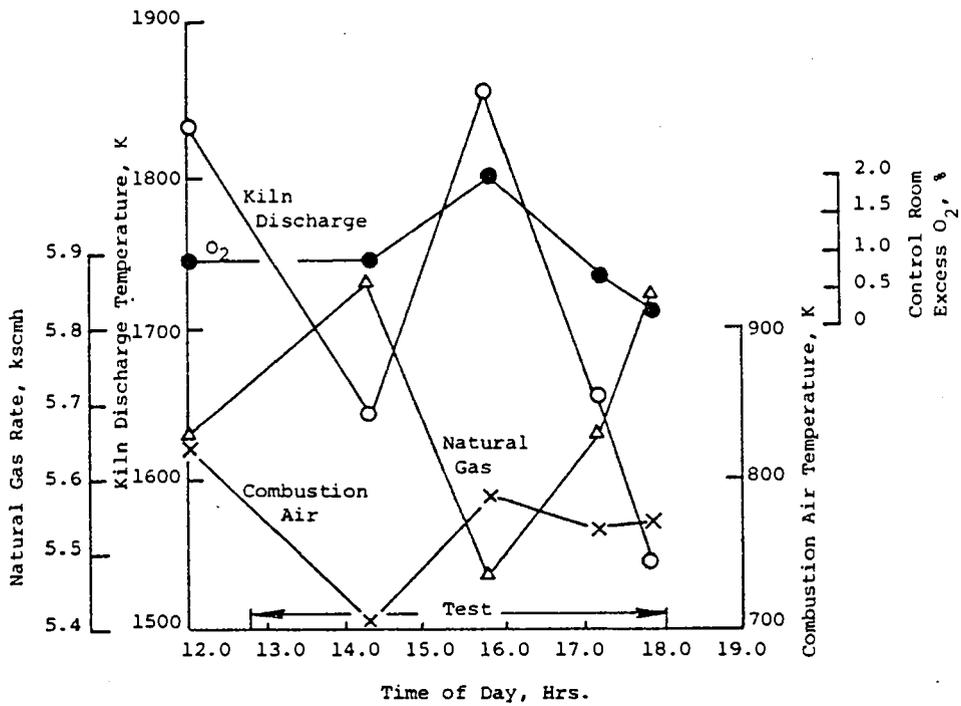


Figure 4-26. Trace species Test 9-6 at cement kiln precipitator outlet.

clinker (remaining solid material) exits the kiln at the discharge end. The electrostatic precipitator catch represents the remaining element in the system mass balance.

The following measurements are made:

1. The volume of slurry used is measured daily.
2. A slurry sample is taken daily to determine the moisture content. The dry sample is then burned to verify the 36% solid conversion to CO<sub>2</sub>.
3. Three times daily the ESP catch volume is measured as well as the catch density.

A precalculated chart is used to determine daily clinker production as a function of slurry moisture content and slurry volume used. This chart includes the solid conversion to CO<sub>2</sub> but does not include the ESP catch.

Table 4-22 shows the emission concentrations measured with the SASS for the four tests. Every specie was detected, in at least one of the tests, except for tellurium and PCB. Barium was not detected at the kiln exit but was detected at the ESP outlet. Mercury and tin were detected at the kiln exit but not the ESP outlet. Comparing duplicate tests, 9-3 versus 9-4, and 9-5 versus 9-6, most detectable specie concentrations are within a factor of two to three. As expected, concentrations for the precipitator outlet are less than at the kiln exit.

Average flow and emission rates, mass balances, and ESP efficiency are given in Table 4-23. Separate mass balances for the kiln, ESP, and overall are given. Mass balances were within  $\pm 20$  for beryllium, calcium, cobalt, copper, iron, nickel, vanadium, zinc, chloride, and fluoride. Mass balances were low for arsenic and titanium but were high for cadmium, chromium, manganese, and nitrates. Mass balances could not be obtained for antimony, barium, lead, mercury, selenium, tellurium, and tin.

The precipitator collection efficiency varied from 82% (chromium) to over 99% for several species.

TABLE 4-22. TRACE SPECIES AND ORGANIC EMISSIONS  
CEMENT KILN, LOCATION 9  
Species Concentration,  $\mu\text{g}/\text{Nm}^3$

Sampling Location	Kiln Exit		Precipitator Outlet	
	9-3	9-4	9-5	9-6
Test No.				
Antimony	< 3700	100 < 3800	110 < 990	340 < 1200
Arsenic	48 < 92	23 < 69	0.5 < 23	0.3 < 23
Barium	< 1600	< 1600	530 < 620	55 < 470
Beryllium	61 < 72	34 < 45	0.16 < 6	0.4 < 5
Cadmium	146 < 153	83 < 110	18 < 25	11 < 27
Calcium	$8.8 \times 10^6$	$6.6 \times 10^6$	420000	530000
Chromium	890	450	150	86
Cobalt	1500	660	300	47 < 100
Copper	1100	480	76	80
Iron	220000	240000	4700	1000
Lead	83 < 14000	48 < 13000	24 < 3300	16 < 48
Manganese	2400	1400	120	35
Mercury	5.1 < 26	29 < 38	< 9.1	< 39
Nickel	920	520	160	64
Selenium	11 < 370	< 350	< 110	< 110
Tellurium	< 7800	< 7200	< 29000	< 2800
Tin	1600 < 5800	< 5600	< 1900	< 1800
Titanium	51000	41000	23000	310 < 1700
Vanadium	890 < 1600	1100 < 1700	11 < 290	7.3 < 280
Zinc	950	760	98	48
Chloride	170000	66000	12000	18000
Fluoride	11000	5200	480	520
Nitrates	1200	330 < 480	2100	1300
Sulfates	82000	55000	5800	< 3100
Total POM	85 < 180	NR	NR	0.0072
Total PCB	85	NR	NR	NR
For Additional Data, See Tables Noted in Appendix F	F-2 to F-7	F-8 to F-10	F-11 to F-13	F-14 to F-19

See Table F-1 for explanation of table entries.

TABLE 4-23. TRACE SPECIES AND ORGANICS OVERALL MASS BALANCE, AVERAGES OF FOUR TESTS  
TESTS 9-3, 9-4, 9-5, and 9-6, CEMENT KILN

	Average Kiln Feed Slurry, 25600 g/s	Average Kiln Discharge Clinker, 9840 g/s	SASS Train at BSP Inlet, 20.3 m <sup>3</sup> /s	Electric Precipitator (ESP) Catch, 485 g/s	SASS Train at ESP Outlet, 20.5 m <sup>3</sup> /s	1 Kiln Mass Balance by SASS Train	2 Kiln Mass Balance by ESP Catch	3 ESP Mass Balance	4 ESP Collection Efficiency	5 Overall Mass Balance
Units	µg/s	µg/s	µg/s	µg/s	µg/s	--	--	--	--	--
<u>Species</u>										
Antimony	< 510000	< 490000	1000 < 78000	< 24000	4700 < 23000	> 0.002	< DL	4.7	0	> 0.009
Arsenic	46000	19000	740 < 1700	970	8.0 < 470	0.43 < 0.46	0.43	1.3	0.99	0.43
Barium	< 360000	< 200000	< 35000	< 9700	5700 < 23000	< DL	< DL	< DL	--	> 0.16
Beryllium	16000	13000	980 < 12000	730	5.3 < 110	0.88	0.88	0.75	0.99	0.88
Cadmium	25000	44000	2300 < 2700	2000	310 < 530	1.8 < 1.9	1.8	1.0	0.86	1.8 < 1.9
Calcium	3.3x10 <sup>9</sup>	3.6x10 <sup>9</sup>	160x10 <sup>6</sup>	92x10 <sup>6</sup>	9800000	1.2	1.1	0.64	0.93	1.1
Chromium	200000	280000	14000<15000	9200	2500	1.5	1.5	0.84	0.82	1.5
Cobalt	380000	300000	23000<25000	15000	3500 < 4100	0.84 < 0.87	0.84	0.80	0.85	0.84
Copper	190000	150000	16000	4900	1600	0.89	0.79	0.41	0.90	0.79
Iron	240x10 <sup>6</sup>	230x10 <sup>6</sup>	4700000	5300000	59000	0.96	1.0	1.14	0.99	1.0
Lead	<3100000	<2000000	100000<290000	< 97000	410 < 35000	< DL	< DL	< DL	--	--
Manganese	1300000	13x10 <sup>6</sup>	39000	32000	1600	10	10	0.86	0.96	10
Mercury	< 3300	< 2000	310 < 660	< 97	< 490	> 0.094	< DL	< 1.9	--	--
Nickel	330000	250000	15000 < 16000	11000	2300 < 2700	0.82	0.79	0.89	0.85	0.79
Selenium	< 100000	< 39000	120 < 7400	< 2000	0.031 < 2300	> 0.0012	< DL	< DL	--	--
Tellurium	< 770000	< 490000	5300 < 150000	< 24000	< 660000	> 0.0069	< DL	< 129	--	--
Tin	< 770000	< 490000	18000 < 120000	< 24000	< 39000	> 0.023	< DL	< 3.5	--	--
Titanium	120x10 <sup>6</sup>	23x10 <sup>6</sup>	940000<980000	1.0x10 <sup>6</sup>	26000<45000	0.20	0.20	1.1	0.97	0.2
Vanadium	590000	600000	21000	20000	190 < 5900	1.1	1.1	1.2	0.99	1.1
Zinc	310000	320000	18000	20000	1500	1.1	1.1	1.2	0.92	1.1
Chloride	2000000	180000	2500000	1400000	310000 < 330000	1.4	0.8	0.69	0.88	0.95
Fluoride	1300000	660000	170000	730000	10000 < 15000	0.49	1.1	4.4	0.94	1.1
Nitrates	26000<51000	< 13000	19000 < 21000	4000	35000	0.73 < 1.3	0.15 < 0.65	2.1	0	1.5
Sulfates	1200000	< 400000	1400000<1500000	8800 < 23000	59000 < 110000	1.2 < 1.6	0.007 < 0.35	0.05 < 0.1	0.93	0.06 < 0.5

1. Kiln Mass Balance by SASS = (Clinker Output + Kiln Outlet by SASS)/(Feed Slurry Input)
2. Kiln Mass Balance by ESP = (Clinker Output + ESP Catch)/(Feed Slurry Input)
3. ESP Mass Balance = (ESP Catch + ESP Outlet by SASS)/(ESP Inlet by SASS)
4. ESP Collection Efficiency = (ESP Inlet by SASS - ESP Outlet by SASS)/(ESP Inlet by SASS)
5. Overall Mass Balance = (Clinker Output + ESP Catch + ESP Outlet by SASS)/(Feed Slurry Input)

See notes on Table F-1 for explanation of table values.

86

Data on the distribution of species by particle size is given in Appendix F, Tables F-2, F-8, F-11, and F-14.

Twelve POM compounds were detected at the ESP outlet, Test 9-6. Table F-20, Appendix F, shows that anthracene and fluoranthene were largest in concentration and the amounts of these two were unchanged in passing through the ESP (Tests 9-3 vs. 9-6). Methyl anthracenes, pyrene, and chrysene were also detected at both locations and were relatively unchanged by the ESP. The remaining several compounds (Table F-2) were detected at the ESP outlet (5 hour sample) but undetected at the kiln exit (75 minute sample).

4.3 METAL PROCESSING FURNACES

4.3.1 Open Hearth Furnace, Location 14

Equipment Characteristics--

The open hearth furnace at Location 14 is a balanced draft unit with the furnace being slightly positive. The furnace incorporates eight burners - six in the roof and one on each end. The furnace is rated at approximately 57 MW ( $195 \times 10^6$  Btu/hr) and the average process rate is approximately  $3.04 \times 10^5$  kg per heat (335 ton per heat) and the average cycle time per heat is 7 hours. The charge for normal operation is 30% hot metal and 70% scrap metal. Roof burners fire only natural gas and end burners normally fire 60% natural gas and 40% No. 6 oil. A schematic of the open hearth furnace is shown in Figure 4-27. Table 4-24 gives the analysis of the No. 6 fuel oil.

TABLE 4-24. LOCATION 14 FUEL ANALYSES,  
OPEN HEARTH FURNACE

Natural Gas Test 14-1 (11/18/76) % by Volume		No. 6 Fuel Oil Test 14-1 (11/18/76) % by Weight	
Nitrogen	35.2	Carbon	86.3
Oxygen	8.54	Hydrogen	11.28
CO <sub>2</sub>	0.42	Nitrogen	0.30
CO	<0.05	Sulfur	1.34
H <sub>2</sub>	<0.1	Ash	0.022
CH <sub>4</sub>	54.4	Oxygen (diff)	0.74
C <sub>2</sub> H <sub>6</sub>	1.22	API gravity	16.1
C <sub>3</sub> H <sub>8</sub>	0.15	(60 °F)	
C <sub>4</sub>	0.056	Heating value	
C <sub>5</sub>	0.034	gross, kJ/kg	43310
C <sub>6</sub>	0.015	(Btu/lb)	(18620)
Heating value		Net, kJ/kg	40910
kJ/m <sup>3</sup>	21600	(Btu/lb)	(17590)
(Btu/dry SCF)	580		

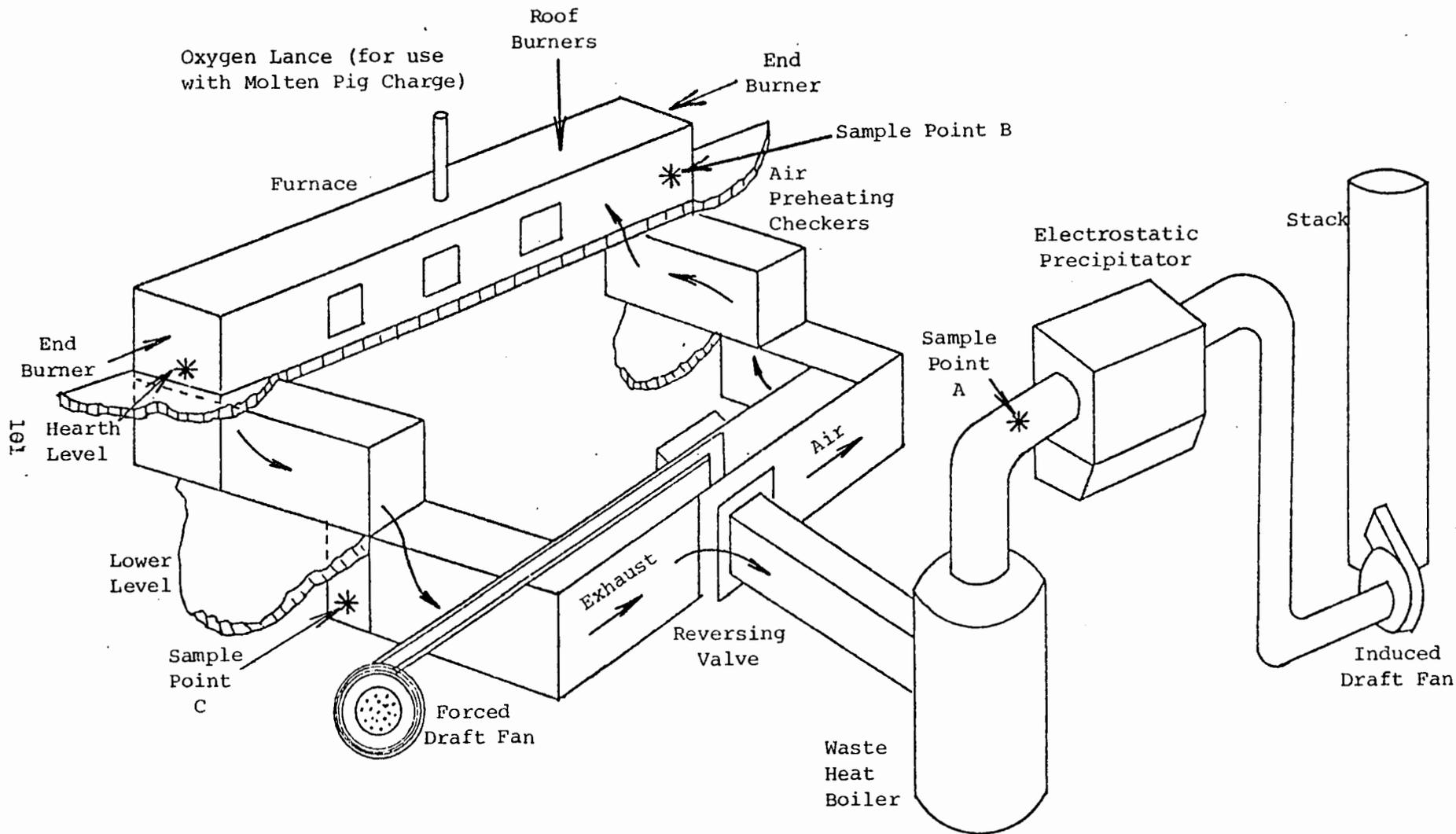


Figure 4-27. Schematic of an open hearth furnace.

### Emissions Sampling--

Gaseous emissions measurements were made in the flue gas duct between the waste heat recovery boiler and the electrostatic precipitator, sample point A in the schematic. This sample point was also used to conduct total particulate measurement, cascade impactor tests and trace species and organics tests. Measurements of furnace oxygen were made at sample points B and C shown in the schematic.

During testing the average process rate was 340 Mg per heat (376 tons per heat) and the average heat input was 30.3 MW ( $103 \times 10^6$  Btu/hr).

### Baseline Tests--

Gaseous emission measurements were taken at 30-minute intervals throughout three entire 6 1/2 hour cycles. The first cycle tested was a baseline test. The second cycle was also a baseline test conducted four months after the first test. The third cycle test was conducted immediately after the second and involved reduction of excess air.

The emissions data for this test unit are presented in graphical form as a function of time, rather than in the tabular form used for the test data reported on other equipment. Because of the rapidly fluctuating nature of the process, tabular data are not meaningful and could be misinterpreted.

Emissions of  $\text{SO}_2$  fluctuated from 53 to 129 ppm (corrected to 3%  $\text{O}_2$ , dry). Hydrocarbons ranged from 9 to 63 ppm (3%  $\text{O}_2$ ). Smoke spot and opacity were both zero. Particulates emissions were 2157 ng/J ( $5.0 \text{ lb}/10^6$  Btu).

The NO emission as a function of time is shown in Figure 4-28 for the first heat cycle. Major events during the cycle are indicated on this figure. The CO and  $\text{O}_2$  concentrations as a function of time are shown in Figure 4-29. NO emissions vary widely throughout the cycle. Peak values of over 3000 ppm were measured during the charging process while the minimum values measured were less than 1000 ppm after completion of the hot metal charge. The NO emission as a function of excess  $\text{O}_2$  is shown in Figure 4-30 for Test No. 14-1. A least-squares linear regression was calculated for the data and the line plotted on the figure. The data show a very strong influence on NO emissions by excess  $\text{O}_2$ . The slope of the least-squares line is 548 ppm NO per percent  $\text{O}_2$ . The calculated correlation coefficient for the data (without the point where

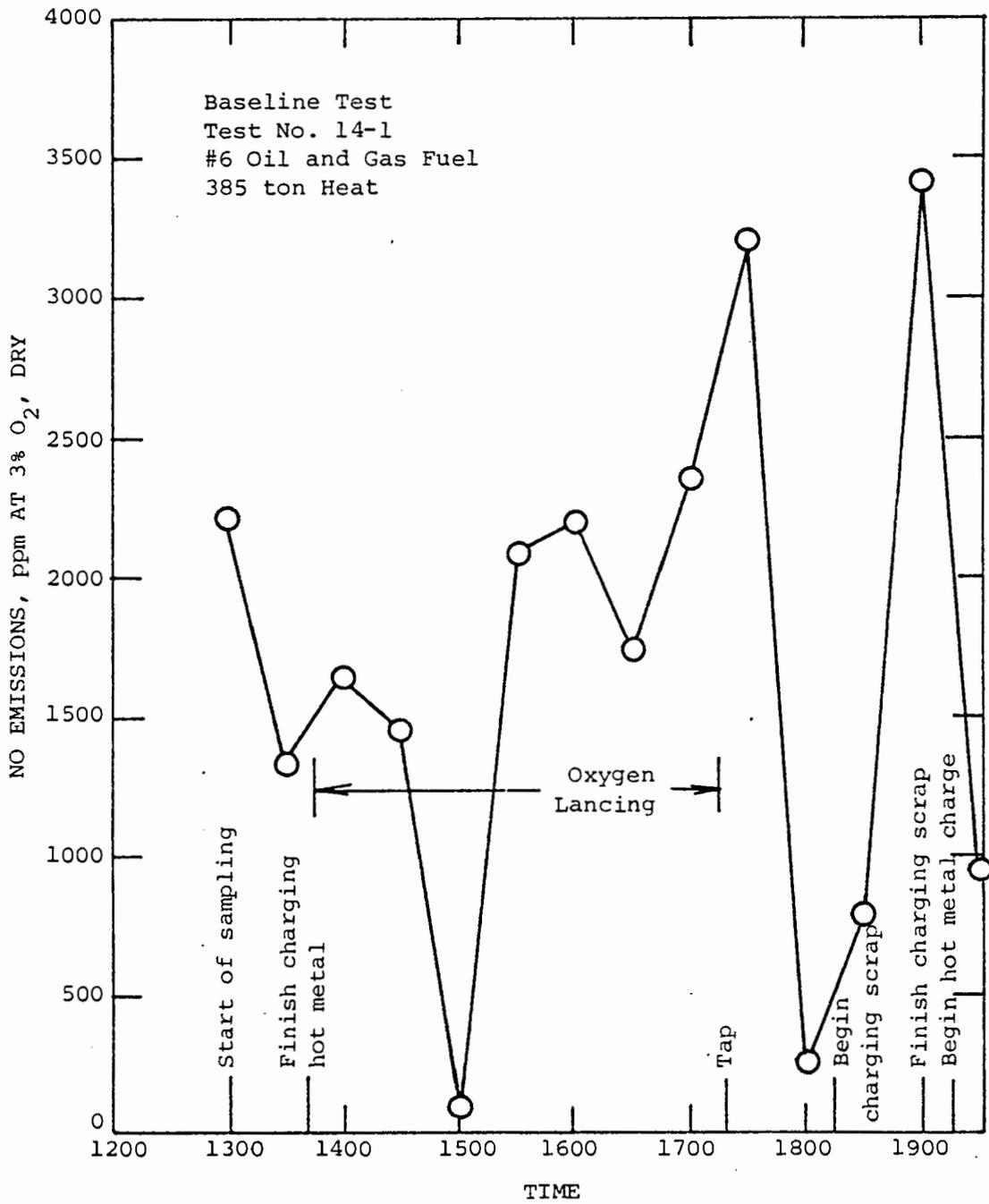


Figure 4-28. NO emissions as a function of time for an open hearth furnace, Test No. 14-1.

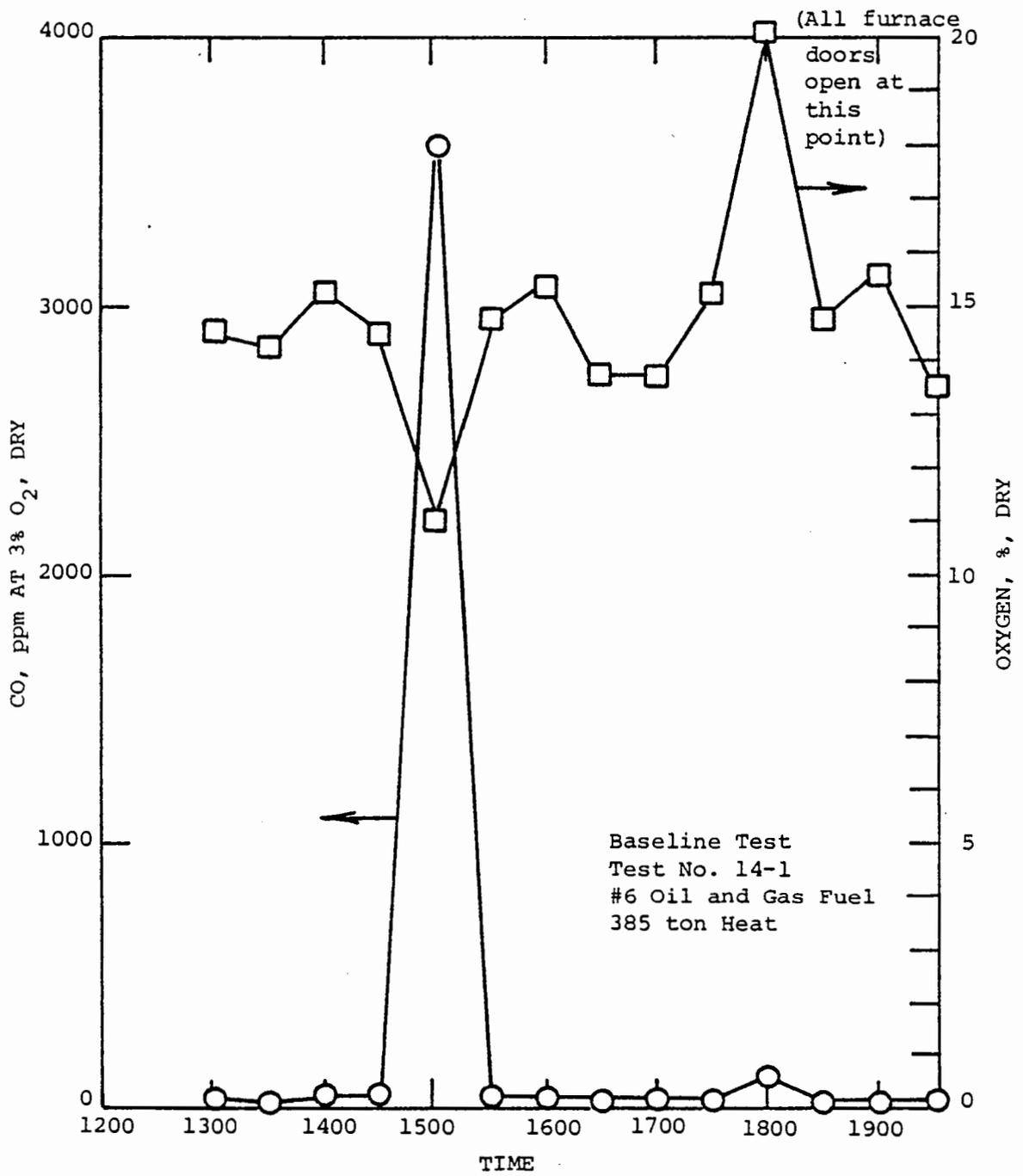


Figure 4-29. CO emission and flue gas O<sub>2</sub> as a function of time for an open hearth furnace, Test No. 14-1.

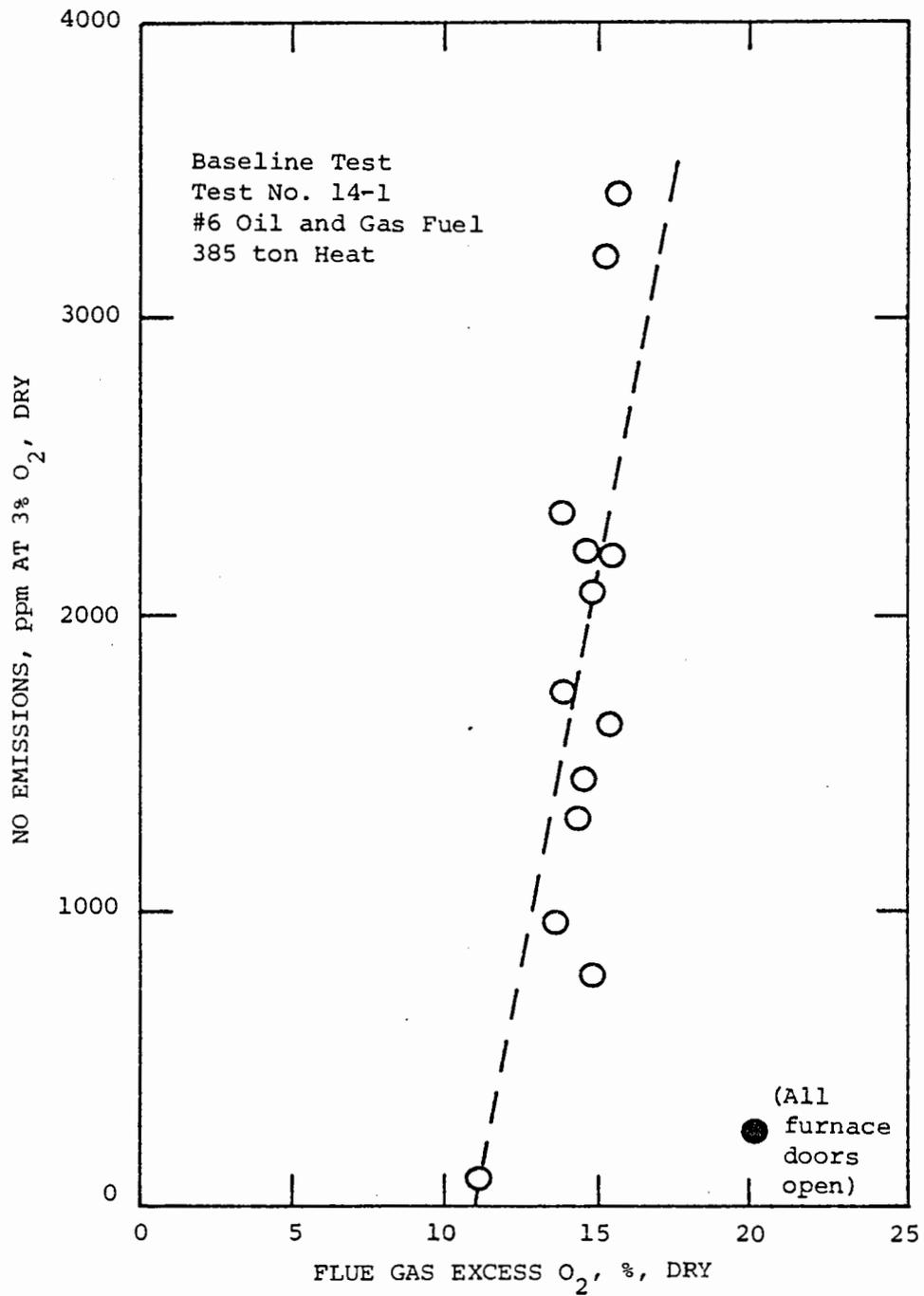


Figure 4-30. NO emissions as a function of flue gas excess O<sub>2</sub>, Test No. 14-1.

all charging doors were open) is 0.7089. While NO is a strong function of O<sub>2</sub> level, the linear correlation is not particularly good indicating that there are other significant variables or that there is a fairly high uncertainty in O<sub>2</sub> measurement due to duct stratifications, dilution or process fluctuations.

The relation between NO and O<sub>2</sub> indicates NO drops to near zero at about 10% O<sub>2</sub>. The O<sub>2</sub> readings were taken downstream of the air preheat checkers in which there is a large amount of air leakage and O<sub>2</sub> measurements are not representative of furnace exit O<sub>2</sub>. The NO data indicate that for a measured O<sub>2</sub> of about 10%, the furnace O<sub>2</sub> is close to zero. The same trends previously noted are evident in these curves and the linear regression is nearly the same. If all data points are combined into a single scatter diagram and the least squares curve calculated, the slope is 546.9 ppm NO per % O<sub>2</sub> with a correlation coefficient of 0.701 indicating a weak but significant correlation. Reduction of excess air had been planned to follow the first baseline test. However, the open hearth process proved to have a wide variation in excess air because constant changes in fuel flow are made to control steel temperature. Several discussions were held with the plant operators before and during the test to examine possible means of excess air limitation. The operators insisted that they need complete flexibility to make rapid changes to control steel temperature and any restriction on control might cause a loss of product. It was therefore not possible to impose any restraints during the first test period to attempt to limit peak NOx conditions.

The results of the tests were later discussed with the operators, concentrating on the points during the cycle when NOx peaks, to more specifically define the reasons for occurrence of high excess air. The fact that NO varied so strongly with excess air indicated the possibility that small changes could be made that would still be acceptable to the operators, but result in significant NO reduction. The test crew then returned to that plant to conduct a second test series. Between the first and second test periods, the furnace was shut down for rebricking and refractory replacement to reduce leakage.

For the second test series a portable O<sub>2</sub> instrument was used in connection with a watercooled probe to obtain flue gas O<sub>2</sub> and combustible readings at the furnace bridge wall just below the end burner (sample point B). The

portable instrument was also used to detect air leakage in the lower level duct work near the cold pass in the checker system and the waste heat boiler superheater (sample point C).

NO<sub>x</sub> emissions as a function of time for the second baseline test are shown in Figure 4-31. The plot also includes the major work steps during the cycle. The variations in NO<sub>x</sub> with time are similar to those observed during the first baseline test, indicating little effect of the furnace overhaul. The CO and O<sub>2</sub> emissions as a function of time at sample point A are shown in Figure 4-32. O<sub>2</sub> and combustible readings taken at the furnace bridge wall (sample point B) are shown as a function of time in Figure 4-33. This sample point is most representative of conditions within the furnace and the results indicate lower O<sub>2</sub> levels varying from near zero up to 9% O<sub>2</sub>.

O<sub>2</sub> readings near the checkers and waste heat boiler superheater (sample point C) varied between 10% and 13% O<sub>2</sub>, dry. These results indicate air leakage in the ductwork. During the furnace overhaul, the furnace was rebricked but no repairs were made to the ductwork.

#### Combustion Modifications, Open Hearth Furnace, Location 14--

Variations in excess air flow were measured during a complete heat cycle. A portable O<sub>2</sub> and combustible instrument was used to monitor the flue gas at the furnace exit. Whenever possible, the O<sub>2</sub> readings were kept near 1.5%. Combustible emissions and excess O<sub>2</sub> are plotted as a function of time in Figure 4-34.

CO and O<sub>2</sub> values versus time as monitored in the mobile laboratory are shown in Figure 4-35. NO emission data as a function of time at this low O<sub>2</sub> test is shown in Figure 4-36.

The low O<sub>2</sub> test showed an overall reduction in NO emissions compared to the baseline test. Baseline average NO emissions were 1094 ng/J (2070 ppm at 3% O<sub>2</sub>, dry) as recorded every 30 minutes. The average NO readings during the modified heat cycle were 660 ng/J (1249 ppm at 3% O<sub>2</sub>, dry) representing a 40% reduction in average emission rate. There were still considerable fluctuations in emissions and high peaks in NO<sub>x</sub>, but the test did verify that excess air can be controlled and NO<sub>x</sub> average emissions can be reduced.

#### Location 14 - Open Hearth Furnace Trace Species Tests--

A test was conducted to sample for trace species and organics at the open hearth furnace. Table 4-25 presents the sampling conditions for the trace species and organics test. The test was planned to terminate when two

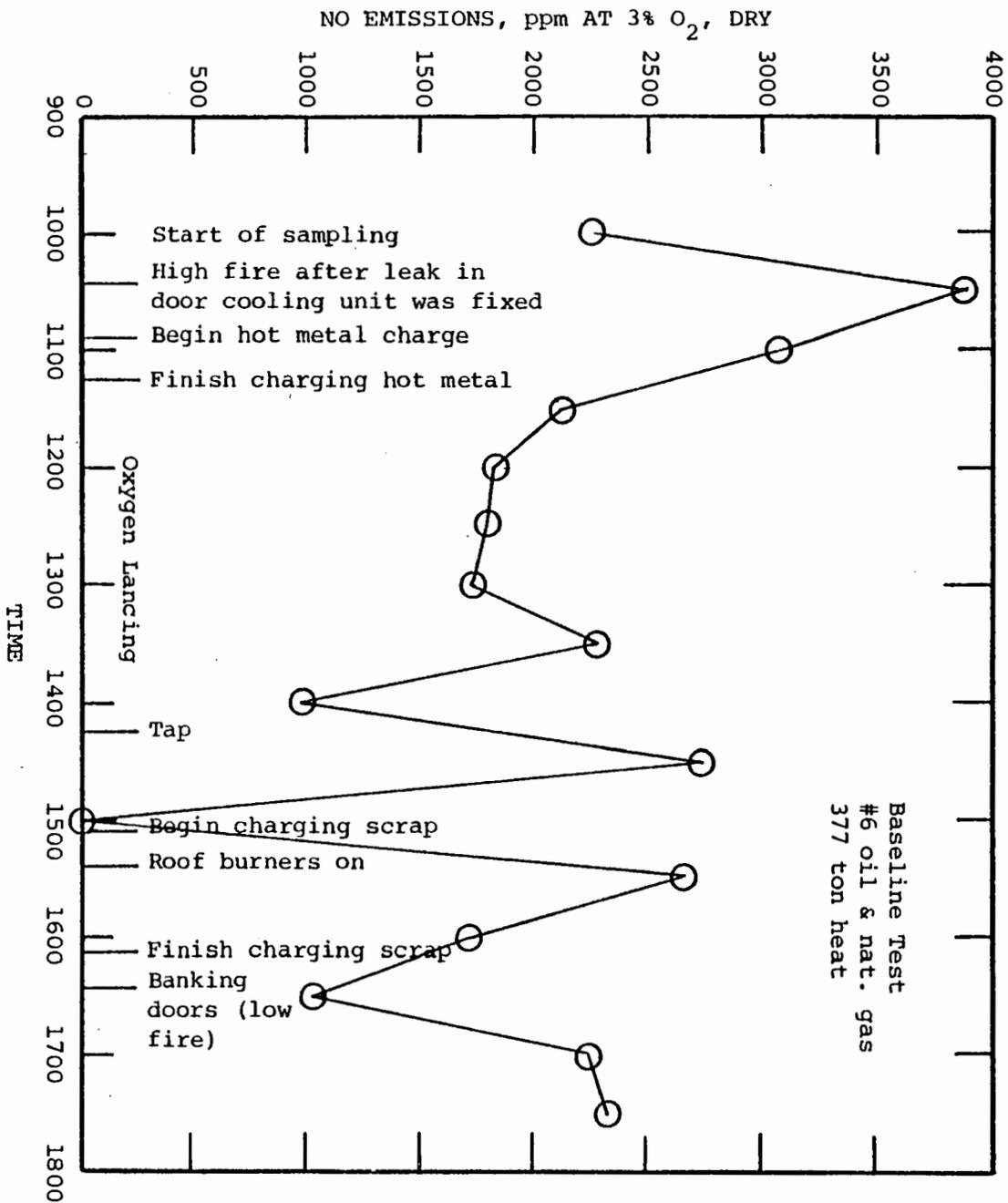


Figure 4-31. NO emissions as a function of time for an open hearth furnace at baseline conditions.

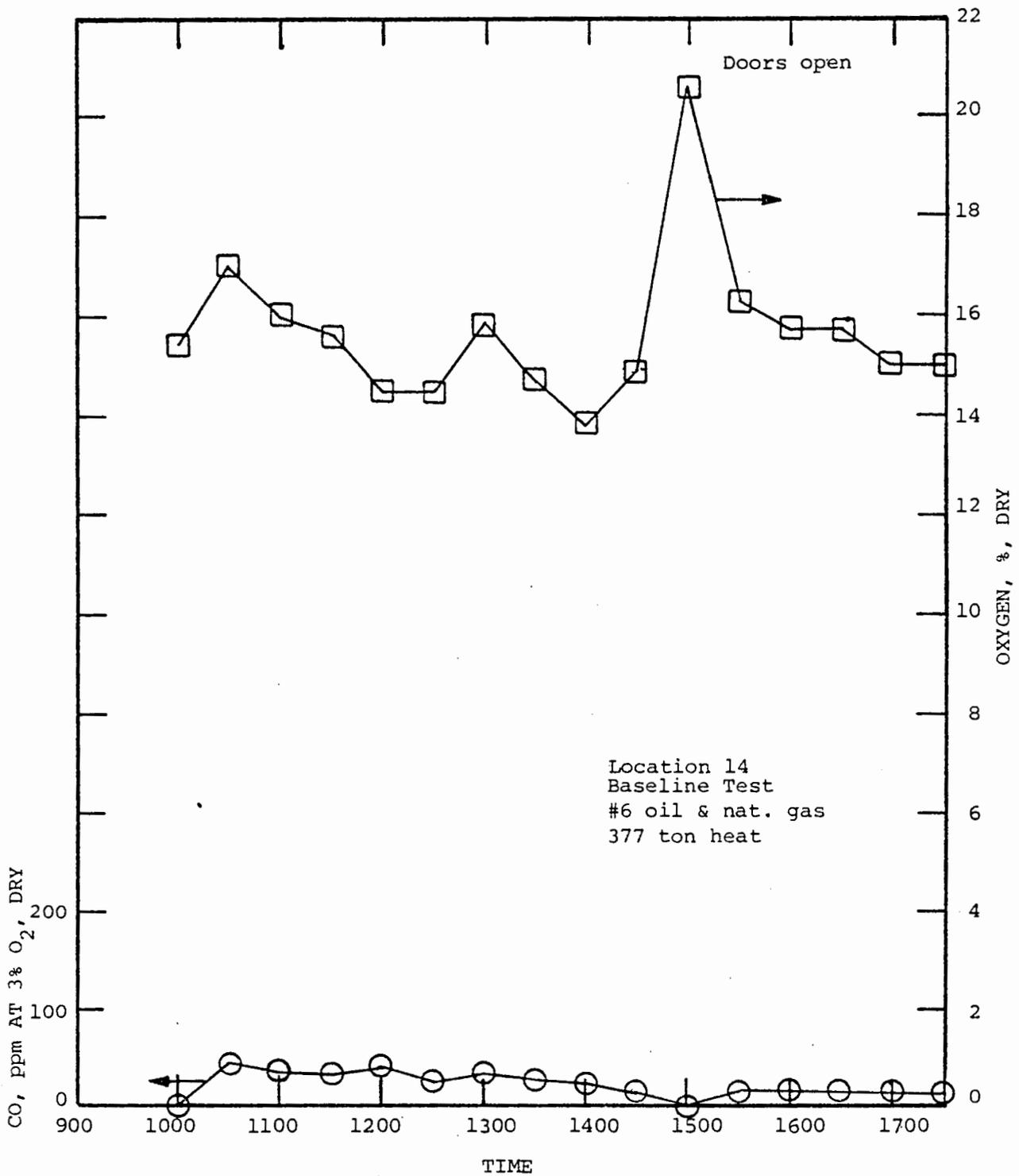


Figure 4-32. CO emissions and flue gas O<sub>2</sub> as a function of time for an open hearth furnace at baseline conditions, measured between the waste heat boiler and the precipitator.

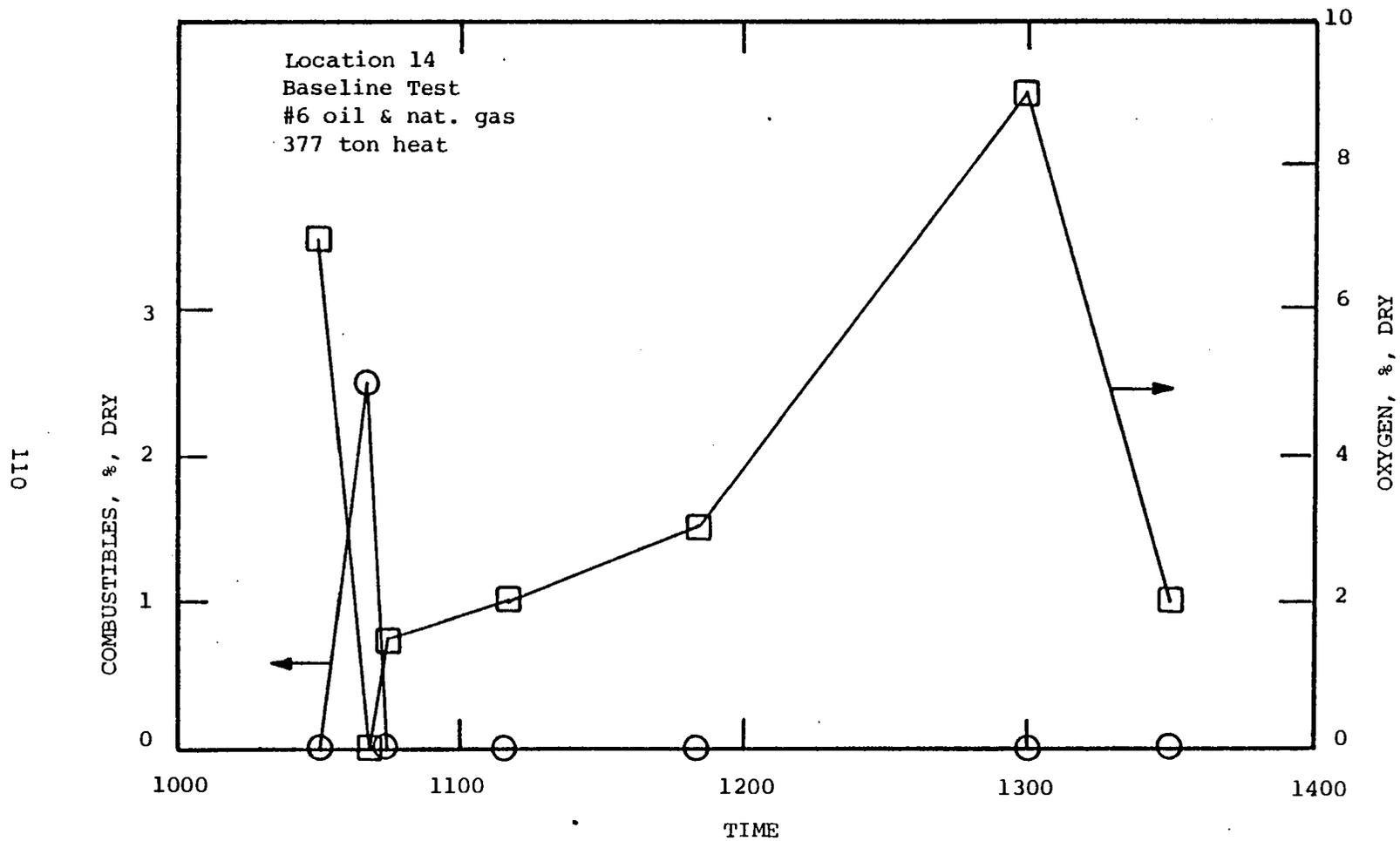


Figure 4-33. Combustible emissions and flue gas O<sub>2</sub> as a function of time at open hearth furnace bridge wall at baseline conditions.

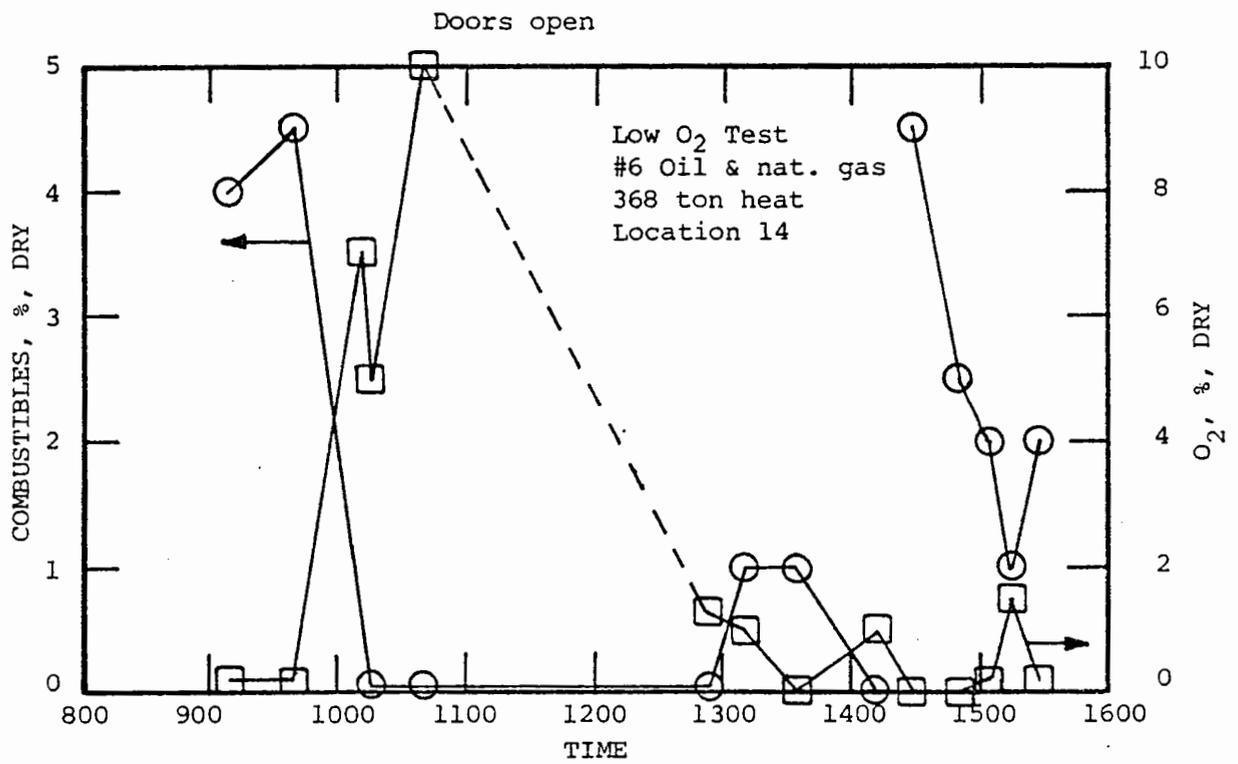


Figure 4-34. Combustible emissions and flue gas as a function of time at open hearth furnace bridge wall at low O<sub>2</sub> condition.

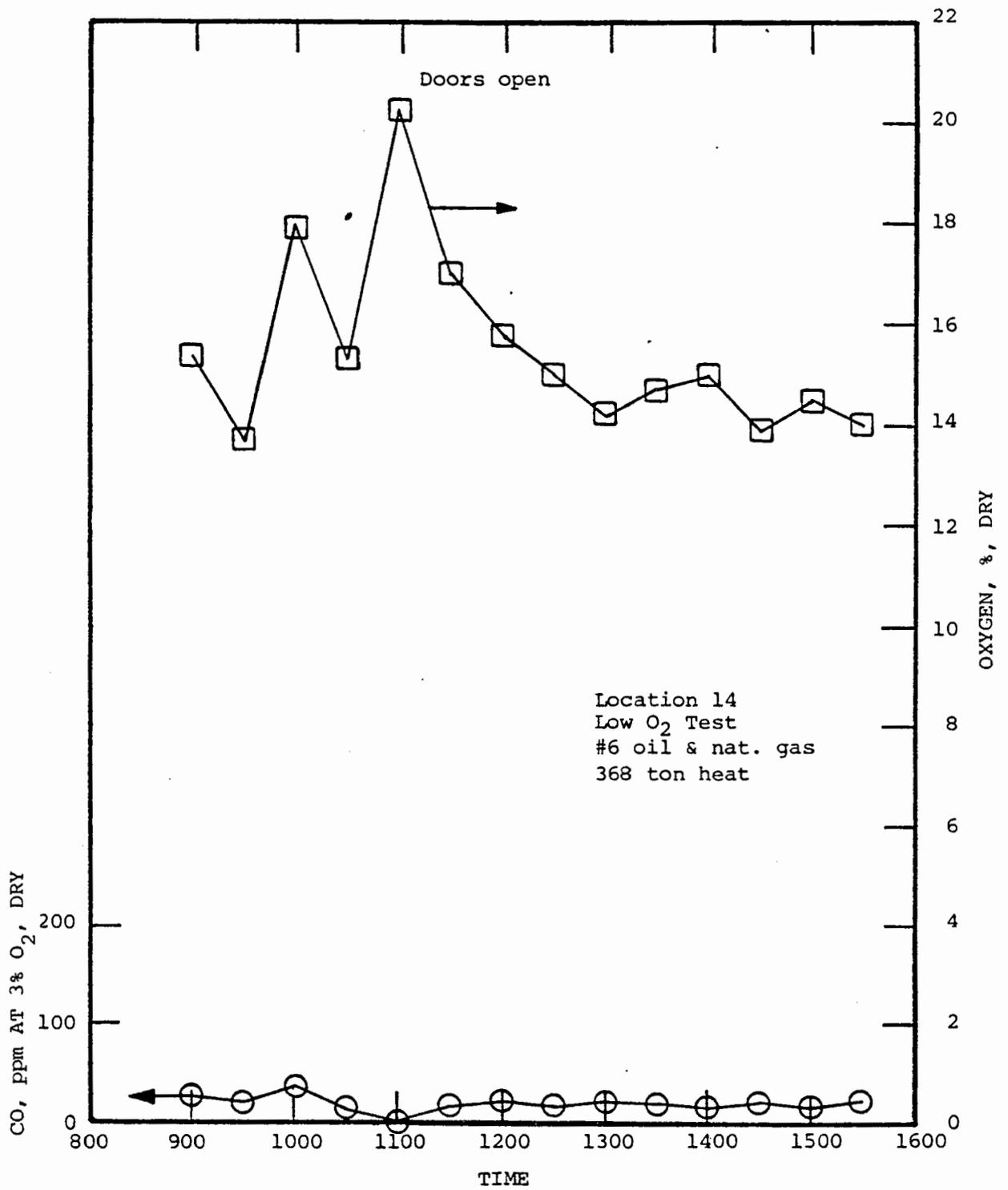


Figure 4-35. CO emissions and flue gas O<sub>2</sub> as a function of time for an open hearth furnace at low O<sub>2</sub> conditions.

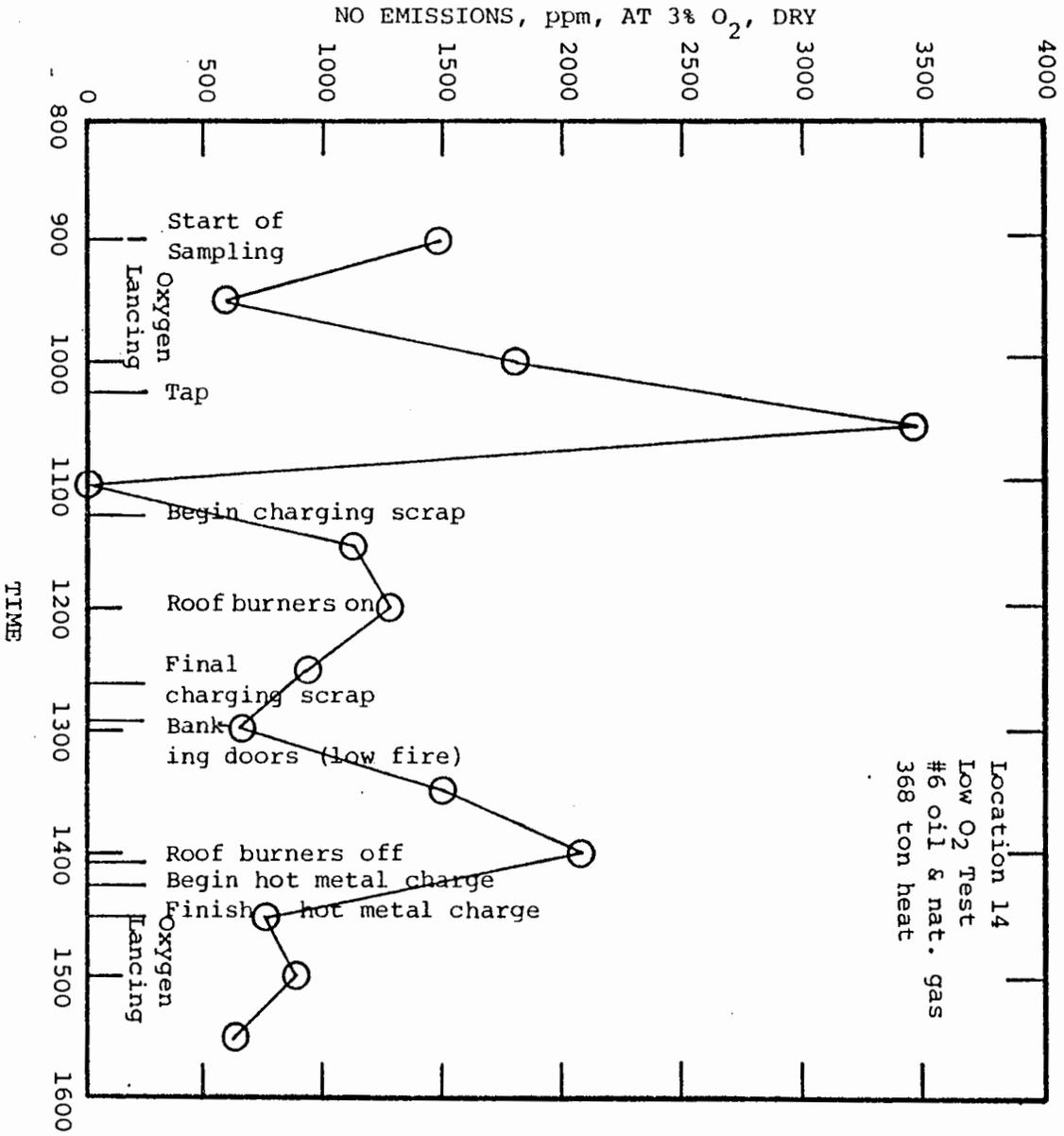


Figure 4-36. NO emissions as a function of time for an open hearth furnace at low O<sub>2</sub> conditions.

filters were plugged or five hours sampling time elapsed, depending upon which occurred first. This test was terminated after two filters plugged at an elapsed sample time of 164.6 min.

TABLE 4-25. TRACE SPECIES AND ORGANICS SAMPLING CONDITIONS  
OPEN HEARTH FURNACE - LOCATION 14

Test Number	14-2
Date	11-18-76
Port Location	ESP Inlet (sample point A)
Velocity, m/s (f/s)	13.96 (45.8)
Stack Temp., K (°F)	522 (480)
Oxygen Content, % dry	13.9
Moisture, %	6.9
Sample Time, min.	164.6
Cyclone Flow, awm <sup>3</sup> /m (awcfm)	0.1226 (4.33)
Isokinetic Rate, %	106
Oven Temp., K (°F)	463 (373)
XAD-2 Temp., K (°F)	295 (71)
Meter Temp., K (°F)	294 (70)
Nozzle Size, mm (in.)	14.3 (0.562)
No. of Filters Used	2
Sample Flow, dry, DNm <sup>3</sup> /m (scfm)	0.073 (2.56)
Volume Collected, dry, DNm <sup>3</sup> (scf)	11.95 (421.9)
Particulate Collected, g	22.806
Solid Particulates, ng/J (lb/MMBtu)	1372 (3.19)
<u>Unit Conditions</u>	
Test Time, min.	230
Process Rate, tons/cycle	375
Hot Metal/Scrap, %/%	48/52
Fuel	Natural gas and No. 6 oil
Fuel Flow Rate, g/s (lb/hr)	402 (3200)
Stack Flow Rate, Nm <sup>3</sup> /s (SCFM)	48.3 (102300)

A replicate trace species test was not performed because the high degree of fluctuating conditions made it unlikely that a comparative replication could be obtained.

The solid particulate loading by the SASS train was 1221 ng/J (2.84 lb/10<sup>6</sup> Btu). This compares with 2157 ng/J (5.02 lb/10<sup>6</sup> Btu) for EPA Method 5.

This difference is not unreasonable, even though the two samples were taken at comparable points in the operating cycle, because of the inherent process fluctuation.

Figure 4-37 shows the NO emissions during the trace species test and indicates the events that were occurring during the test period.

Specie emission concentrations from the open hearth are given in Table 4-26. More detailed data are given in Appendix F. All species were detected except for mercury and tin. The open hearth process is a batch process. Once the steel charge is loaded there is no material input other than the fuel. Mass balance based only on the fuel input produced overbalances for all species (see Appendix F). The bath of molten steel is undoubtedly the main source of the emissions measured. However, there was no way to determine the process weight loss during the heat.

POM compounds detected were anthracene, phenanthrene, methyl anthracenes, fluoranthene, pyrene, chrysene, and benzo fluoranthenes. Anthracene and fluoranthene were most predominant as shown in Table F-66, Appendix F.

Published data provide an interesting comparison with six of the trace metals measured by KVB with the SASS train (Ref. 9). Six trace metals were measured with an EPA Method 5 train and cascade impactors on the open hearth furnace at Location 14. The previous test occurred about one year prior to the KVB test.

Table 4-27 compares the results for both total particulate and for size ranges. During the previous tests several runs were made to develop a standard deviation, which was about  $\pm 30\%$  of the mean for all elements. The KVB data for total emissions of each element agree very well with the previous results. For cadmium, copper and iron the KVB data are within one standard deviation of the mean for the previous data. For lead and zinc the KVB data are nearly within one standard deviation. For nickel the KVB data are 3.1 standard deviations above the previous results. In view of the highly fluctuating nature of the open hearth process and the one-year time difference, these results are remarkably close.

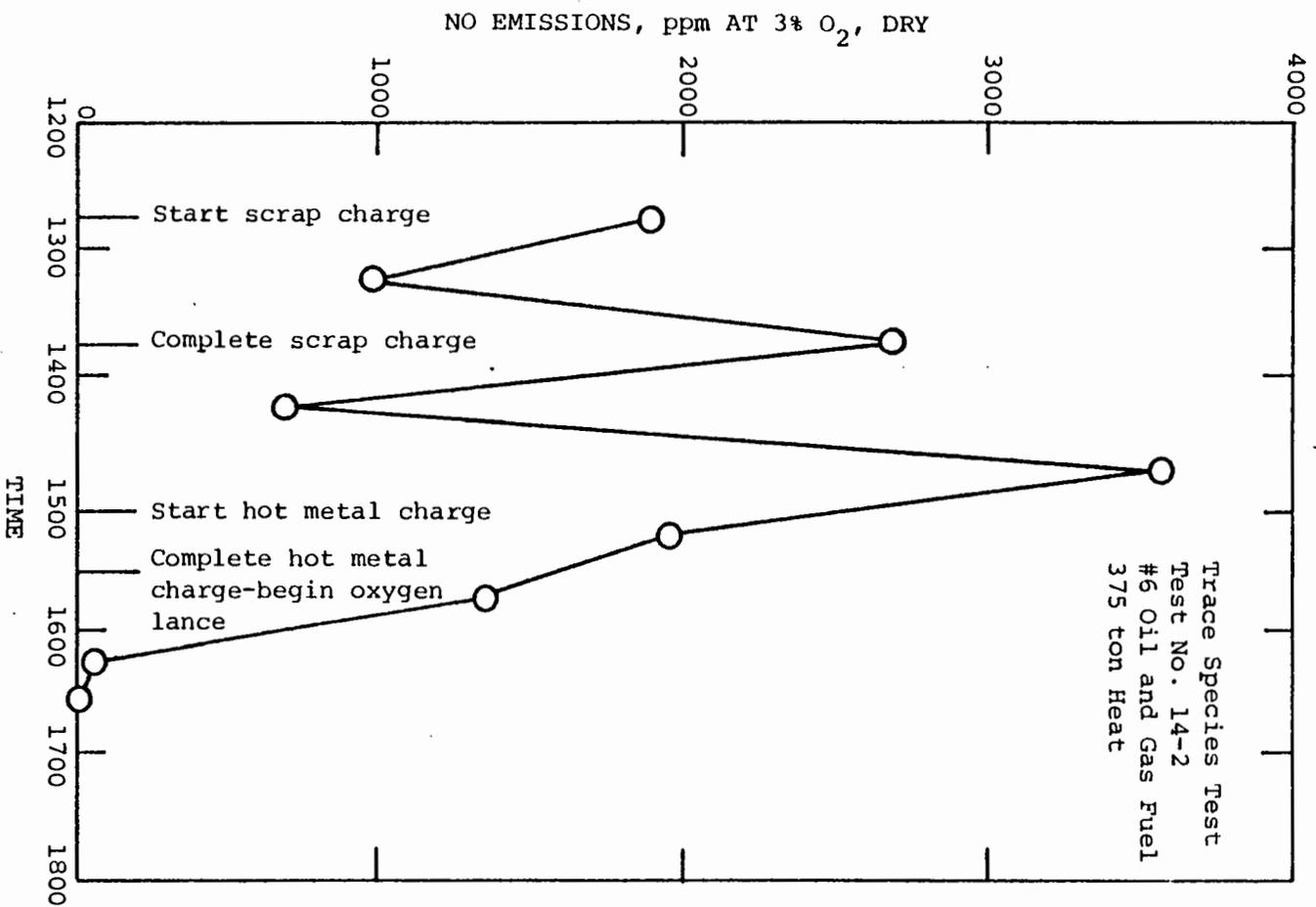


Figure 4-37. NO emissions as a function of time for an open hearth furnace, Test No. 14-2.

TABLE 4-26. TRACE SPECIES AND ORGANIC EMISSIONS  
OPEN HEARTH FURNACE, LOCATION 14

<u>Sampling Location</u>	<u>Species Concentration, <math>\mu\text{g}/\text{Nm}^3</math></u>
	<u>EPS Inlet</u>
<u>Test No.</u>	<u>14-2</u>
Antimony	120 < 1000
Arsenic	150 < 190
Barium	38 < 92
Beryllium	0.4 < 10
Cadmium	570 < 580
Calcium	53000
Chromium	2400
Cobalt	120 < 430
Copper	2700
Iron	530000
Lead	44000
Manganese	3000
Mercury	< 10
Nickel	2100
Selenium	62 < 81
Tellurium	590 < 3500
Tin	< 4400
Titanium	1300 < 1900
Vanadium	110 < 230
Zinc	200000
Chloride	3100
Fluoride	15000
Nitrates	1600
Sulfates	45000
Total POM	1.0
Total PCB	2.4
For additional data, see tables noted in Appendix F.	F -60 to F-66

See Table F-1 for explanation of table values.

TABLE 4-27. COMPARISON OF KVB SASS TRAIN RESULTS  
WITH PREVIOUS DATA FOR  
THE OPEN HEARTH FURNACE AT LOCATION 14

<u>TOTAL EMISSIONS</u>				
<u>Element</u>	<u>Previous Data, ESP Inlet</u>			<u>KVB Test 14-2 at ESP Inlet kg/h</u>
	<u>Mean, kg/h</u>	<u>Stand. Dev. kg/h</u>	<u>One Stand. Dev. Limit, kg/h</u>	
Cadmium	0.128	+ 0.0379	0.090 (-)	0.10
Lead	11.7	+ 3.46	8.24 (-)	7.6
Zinc	51.9	+15.3	36.6 (-)	35.0
Copper	0.452	+ 0.134	0.586 (+)	0.47
Iron	120.	+35.5	84.5 (-)	94.
Nickel	0.187	+ 0.055	0.242 (+)	0.36
Total Particulate	277.	+81.9	358.9 (+)	330.

<u>EMISSIONS BY SIZE RANGE</u>				
<u>Element</u>	<u>Previous Data, ESP Inlet</u>		<u>KVB Test 14-2 at ESP Inlet</u>	
	<u>&lt;2 μm kg/h</u>	<u>≥2μm kg/h</u>	<u>&lt;3μm kg/h</u>	<u>≥3μm kg/h</u>
Cadmium	0.0655	.0625	0.075	.025
Lead	8.89	2.81	5.7	1.86
Zinc	39.7	12.2	22.	13.0
Copper	0.319	0.133	0.31	0.165
Iron	94.2	25.8	53.0	41.0
Nickel	0.0595	0.128	0.31	0.049
Total Particulate	198.	79.	170.	160.

Direct comparison of the size range data is not possible because the previous data are given for less than and greater than 2  $\mu\text{m}$ , while the SASS train separation is at 3  $\mu\text{m}$ . However, the results are similar (within a factor of  $\pm 2$ ) for all elements except nickel. The nickel emission rate by the SASS train for  $< 3 \mu\text{m}$  is higher by a factor of five compared with the previous emission for  $< 2 \mu\text{m}$ . Most of the nickel collected by the SASS train was present in the impingers and condensate (0.28 kg/h).

#### 4.3.2 Steel Billet Reheat Furnace, Location 16/1

##### Equipment Characteristics--

The reheat furnace tested at Location 16 is a continuous type furnace with two-zone firing operating on natural gas fuel. The furnace is divided into a heating and soaking zone as shown in Figure 4-38. About 80% of the fuel is fired in the heating zone. The rated heat input was 35 MW ( $117 \times 10^6$  Btu/hr).

There are 13 dual fuel burners installed in the top firing zone (heating zone) and 14 burners in the bottom zone (soaking zone). The furnace does not have an exhaust heat recuperator; ambient temperature air is used for combustion.

The steel to be heated is charged from the end and moved through the furnace by pushing the last billet charged with a pusher at the charging end. As each cold piece is pushed into the furnace against the continuous line of material, a heated piece is removed. The heated piece is discharged through a side door to the mill table.

##### Emissions Sampling--

Gaseous emissions measured were NO, NO<sub>x</sub>, CO, SO<sub>2</sub>, and O<sub>2</sub>. CO<sub>2</sub> and HC could not be measured due to problems with the instruments. CO<sub>2</sub> values were calculated from the natural gas fuel analysis, Table 4-28.

TABLE 4-28. NATURAL GAS ANALYSIS - LOCATION 16/1

Oxygen, %	0.02
Nitrogen, %	1.27
Carbon Monoxide, %	0.38
Methane, %	93.36
Ethane, %	3.77
Propane, %	0.92
Butane, %	0.21
Pentane, %	0.204
Heating Value, kJ/Nm <sup>3</sup>	39082
Btu/scf	1049

121

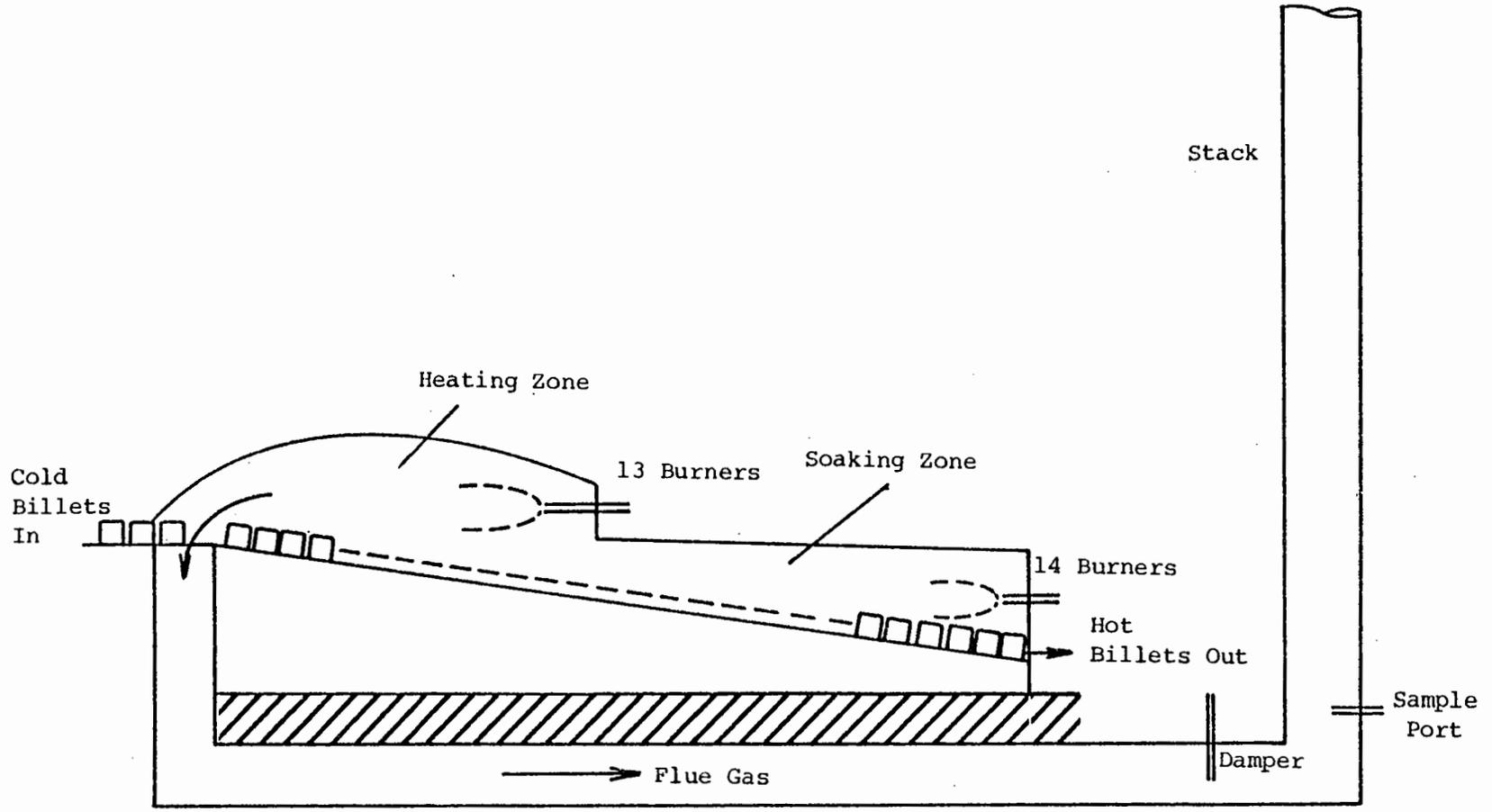


Figure 4-38. Schematic section of reheat furnace at Location 16.

The measurements were made in the stack and a single heated sample line was used to transport the flue gas to the instruments. EPA Method 5 particulate test and wet chemistry  $SO_x$  were conducted at the same sample point.

#### Baseline Tests--

Baseline measurements were made with the furnace firing natural gas with all burners in service. Furnace load changed during the test period from about 90 billets per hour to about 175 billets per hour. All test data are presented in Table 4-29. Total and solid particulates were obtained at a load of about 140 billets per hour. The particulate measurements were 17.3 ng/J ( $0.0404 \text{ lb}/10^6 \text{ Btu}$ ) total particulates and 14.1 ng/J ( $0.0328 \text{ lb}/10^6 \text{ Btu}$ ) solid particulate.

Emissions of  $SO_2$  as measured with the continuous analyzer were consistently very near zero. For natural gas in the area of Location 16, the sulfur content is of the order of 5 ppm by volume of  $H_2S$  (0.31 grains of  $H_2S$  per 100 cu.ft.). Therefore,  $SO_2$  emissions should be approximately 0.5 ppm corrected to 3%  $O_2$ , dry. This is consistent with the continuous analyzer. However, the wet chemistry tests indicated much higher values. Two sampling runs were made resulting in  $SO_2$  values of 109.7 ppm and 110.4 ppm and  $SO_3$  values of 3.1 ppm and 1.4 ppm. The close agreement in the values and the fact that  $SO_3$  is about 3% of total  $SO_x$  indicates that the test was properly conducted. However at very low values of  $SO_x$ , the Shell wet chemistry method is subject to very large uncertainties. Therefore the wet chemistry data presented are not considered to be valid and emissions of  $SO_2$  and  $SO_3$  for this device should be considered as essentially zero.

Figure 4-39 shows  $NO_x$  emissions and  $O_2$  as a function of load at baseline configuration. There is a consistent variation in  $O_2$  with load but no consistency in the  $NO_x$  data.

The  $NO_x$  emissions as a function of  $O_2$  at a heat input of 15 MW ( $51 \times 10^6 \text{ Btu/h}$ ) and 25-30 MW ( $85-100 \times 10^6 \text{ Btu/h}$ ) are presented in Figure 4-40. Fluctuations in  $NO_x$  and  $O_2$  occurred at each load level but there was no apparent trend in  $NO_x$  as a function of  $O_2$ .

TABLE 4-29. SUMMARY OF TESTS FOR 10" REHEAT FURNACE  
AT LOCATION 16/1 - NATURAL GAS FUEL

Test No.	Date 1977	Load Mg/h	Heat Input Load MW	O <sub>2</sub> %	CO <sub>2</sub> <sup>+</sup> %	NO <sub>x</sub> <sup>*</sup> ng/J (ppm)	NO <sup>*</sup> ng/J (ppm)	HC <sup>*</sup> ng/J (ppm)	CO <sup>*</sup> ng/J (ppm)	SO <sub>2</sub> <sup>*</sup> ng/J (ppm)	Wet Chemistry			Total Partic. ng/J (lb/10 <sup>6</sup> Btu)	Solid Partic. ng/J (lb/10 <sup>6</sup> Btu)	Opacity (%)	Comments
											SO <sub>2</sub> <sup>*</sup> ng/J (ppm)	SO <sub>3</sub> <sup>*</sup> ng/J (ppm)					
16/1-1	5/3	16	14.5	16.1	2.8	40.8 (80)	37.2 (73)	---	9 (29)	0						0	Baseline - 60 billets per hour (261 kg/billet)
16/1-2	5/3	16	13.7	15.5	3.1	43.4 (85)	39.8 (78)	---	10.2 (33)	0						0	
16/1-3	5/3	16	16.1	16.2	2.7	45.9 (90)	41.8 (82)	---	14 (45)	0						0	
16/1-4	5/3	16	14.6	15.6	3.1	43.9 (86)	40.8 (80)	---	12.4 (40)	0						0	
16/1-5	5/3	16	13.9	15.7	3.0	43.4 (85)	41.8 (82)	---	8.4 (27)	0						0	
16/1-6	5/4	--	15.8	15.8	2.9	37.2 (73)	35.2 (69)	---	4.3 (14)	0	78 <sup>†</sup> (110)	2 <sup>†</sup> (2)				0	
16/1-7	5/4	25	14.9	15.8	2.9	37.2 (73)	33.7 (66)	---	8.7 (28)	0						0	
16/1-8	5/4	32	15.7	15.6	3.1	39.8 (78)	35.7 (70)	---	8.4 (27)	0						0	
16/1-9	5/4	21	19.1	13.9	4.0	41.3 (81)	38.8 (76)	---	6.2 (20)	0						0	
16/1-10	5/4	21	16.4	14.5	3.7	39.8 (78)	38.3 (75)	---	5.9 (19)	0						0	
16/1-11	5/4	--	14.8	15.0	3.4	42.8 (84)	41.3 (81)	---	5.6 (18)	0						0	
16/1-12	5/5	46	25.6	14.2	3.8	43.4 (85)	41.8 (82)	---	28.8 (93)	0						0	Baseline - 175 billets per hour
16/1-13	5/5	--	24.6	14.0	4.0	42.8 (84)	41.8 (82)	---	23.9 (77)	0						0	Low air setting
16/1-14	5/5	--	28.3	13.5	4.2	35.7 (70)	33.2 (65)	---	29.8 (96)	0						0	#6 and #8 BOOS
16/1-15	5/5	--	28.0	13.7	4.1	32.6 (64)	31.6 (62)	---	32.2 (104)	0						0	#5, 7, and 9 BOOS
16/1-16	5/5	--	28.7	13.5	4.2	32.1 (63)	29.6 (58)	---	29.8 (96)	0						0	#4, 7, 10 BOOS
16/1-17	5/5	31	24.6	14.5	3.7	56.1 (110)	52 (102)	---	25.7 (83)	0						0	Baseline
16/1-18	5/6	39	26.4	14.3	3.8	46.9 (92)	43.9 (86)	---	30.1 (97)	0			17.3 (0.0404)	14.1 (0.0328)		0	Baseline partic - 150 billets/hr
16/1-18	5/6	39	28.6	13.2	4.4	36.7 (72)	34.2 (67)	---	23.6 (76)	0						0	
16/1-18	5/6	39	30.6	13.0	4.5	36.2 (71)	34.7 (68)	---	34.7 (112)	0						0	

123

\*ppm corrected to 3% O<sub>2</sub>, dry

†Calculated from fuel analysis

<sup>§</sup>10<sup>6</sup> Btu/h = 3.413 x MW

†These data are not considered valid.

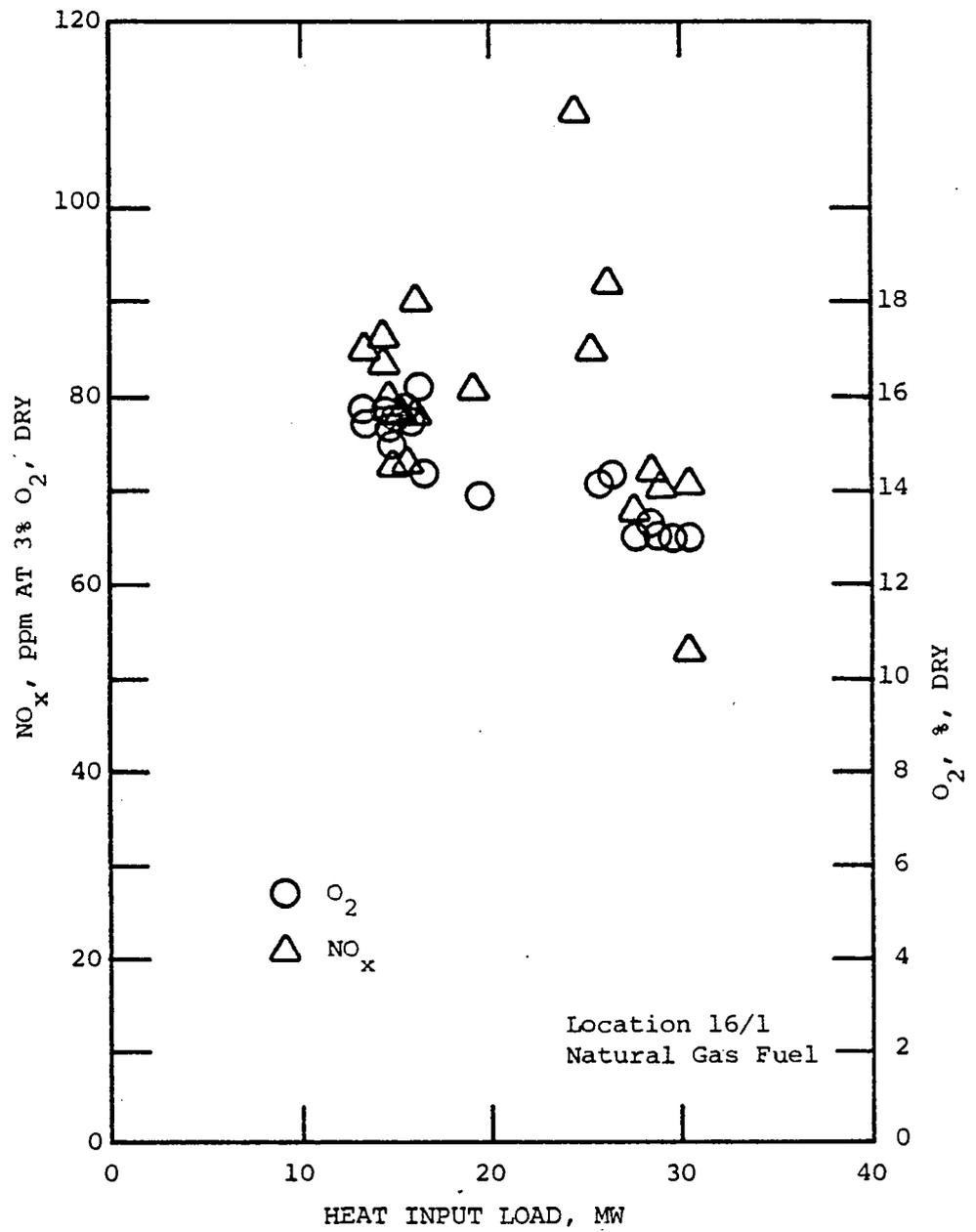


Figure 4-39. NO<sub>x</sub> emissions and O<sub>2</sub> as a function of load at baseline conditions for a reheat furnace.

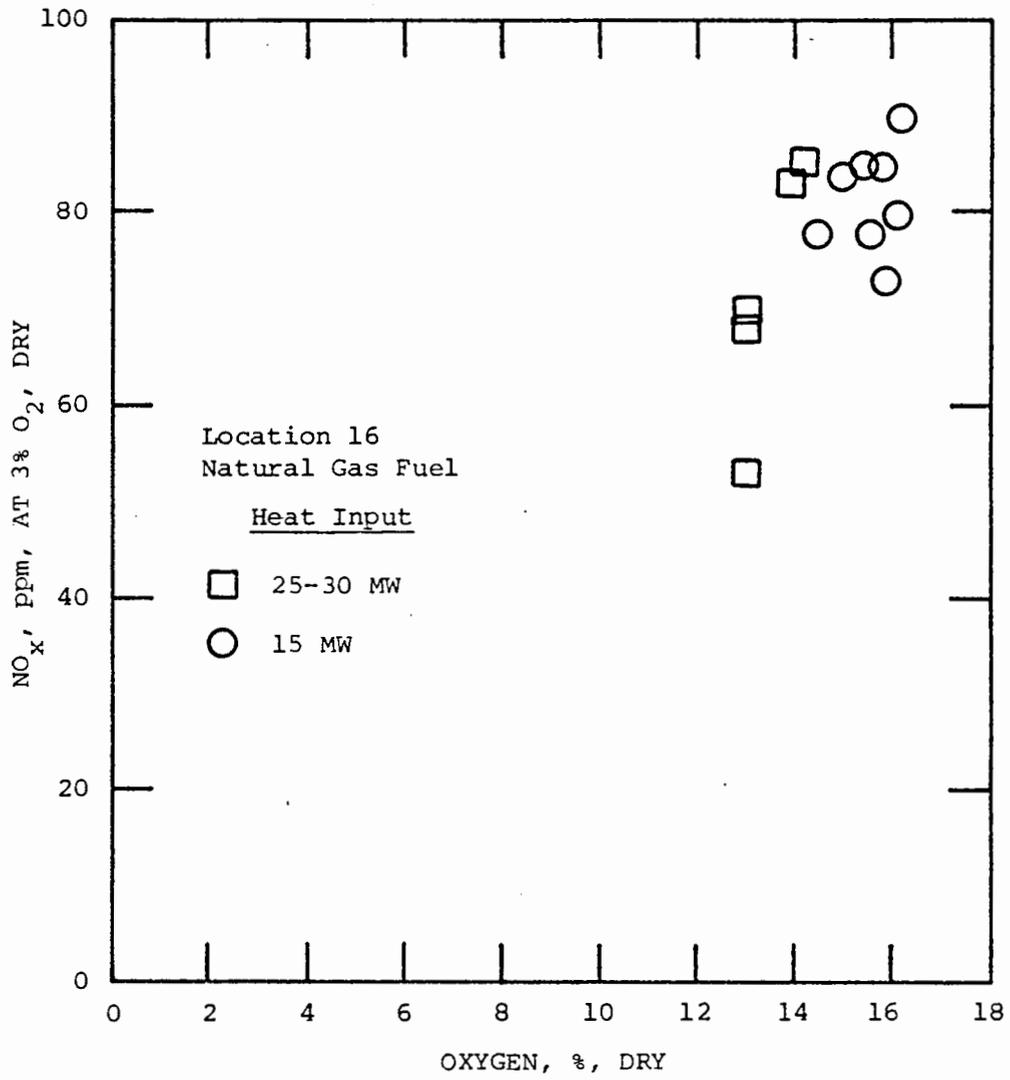


Figure 4-40. NO<sub>x</sub> as a function of O<sub>2</sub> at various loads for a reheat furnace in baseline configuration.

Combustion Modifications, Reheat Furnace, Location 16/1--

One test was run to obtain the effect of low excess oxygen on NO<sub>x</sub> emissions. At a load of 24.6 MW (84x10<sup>6</sup> Btu/h), excess oxygen was reduced from 14.5% O<sub>2</sub> to 14% O<sub>2</sub>. This data point shows a NO<sub>x</sub> reduction of 23% (Test 16/1-13 and 16/1-17). The excess oxygen at the sampling point was believed to be much higher than in the furnace, so that the change in NO<sub>x</sub> when O<sub>2</sub> was reduced from 14.5% to 14% the change in furnace oxygen was a much higher percentage change.

Several tests with burners out of service at the top burner row (in the heating zone) were conducted. The following burner patterns were implemented:

No. Out of Service	1	2	3	4	5	6	7	8	9	10	11	12	13	NO <sub>x</sub> ng/J
0	O	O	O	O	O	O	O	O	O	O	O	O	O	43.4
1	O	O	O	O	O	O	X	O	O	O	O	O	O	--
2	O	O	O	O	O	X	O	X	O	O	O	O	O	35.7
3	O	O	O	O	X	O	X	O	X	O	O	O	O	32.6
3	O	O	O	X	O	O	X	O	O	X	O	O	O	32.1

O = Burners firing

X = Burner with fuel off; air on.

No emission reduction was obtained with the No. 7 burner out of service. The data point was not recorded. The lowest NO<sub>x</sub> emission was obtained with No. 4, 7, and 10 burners out of service, Test 16/1-16.

Stack temperature on this unit was 730 K (855 °F) at 13.5% O<sub>2</sub> during Test 16/1-18. The resultant efficiency is 46%. Because of this very low efficiency no analysis was warranted by the effect of combustion modifications.

Conclusions--

The low O<sub>2</sub> test and the tests with burners out of service show a maximum reduction of 43% in NO<sub>x</sub> emissions compared to the baseline test (Test 16/1-17). No problems were experienced with nonuniform heating of the billets as a result of removing burners from service. Reheat furnace oxygen level at the billets is critical. Too much oxygen will oxidize the steel surface and excessively fuel-rich gas will cause billet sticking. Apparently there was sufficient mixing between the burners and billets so that these problems did not occur.

### 4.3.3 Steel Ingot Soaking Pit, Location 16/2

#### Equipment Characteristics--

The soaking pit at Location 16 is installed in a row of pits under cover of a building adjacent to the entering side of the blooming mill. Figure 4-41 shows a schematic cross-section through a soaking pit furnace building.

The soaking pit is of the one-way fired design without a recuperator as shown in Figure 4-42. It is equipped with one variable heat pattern natural gas burner. The burner has the capability for changing air and gas direction thus allowing an adjustment for flame width as well as flame length. The test unit was rated at a heat input of 2.9 MW ( $10 \times 10^6$  Btu/hr).

The quantity of fuel, the desired fuel/air ratio, and the furnace draft in the pit is controlled automatically. The rate of fuel is controlled by temperature measurement to maintain a preset level. The air is proportioned to the amount of fuel fired at a ratio that will give a slight excess of air. The furnace draft is controlled by automatically raising or lowering the stack damper to maintain the desired positive furnace pressure.

#### Emissions Sampling--

Gaseous emissions measured were NO, NO<sub>x</sub>, CO, SO<sub>2</sub>, HC, and O<sub>2</sub>. CO<sub>2</sub> values were calculated from the fuel analysis, Table 4-30.

TABLE 4-30. NATURAL GAS ANALYSIS - LOCATION 16/2

Oxygen, %	0.02
Nitrogen, %	1.27
Carbon Monoxide, %	0.38
Methane, %	93.36
Ethane, %	3.77
Propane, %	0.92
Butane, %	0.21
Pentane, %	0.204
Heating Value, kJ/Nm <sup>3</sup>	39082
Btu/scf	1049

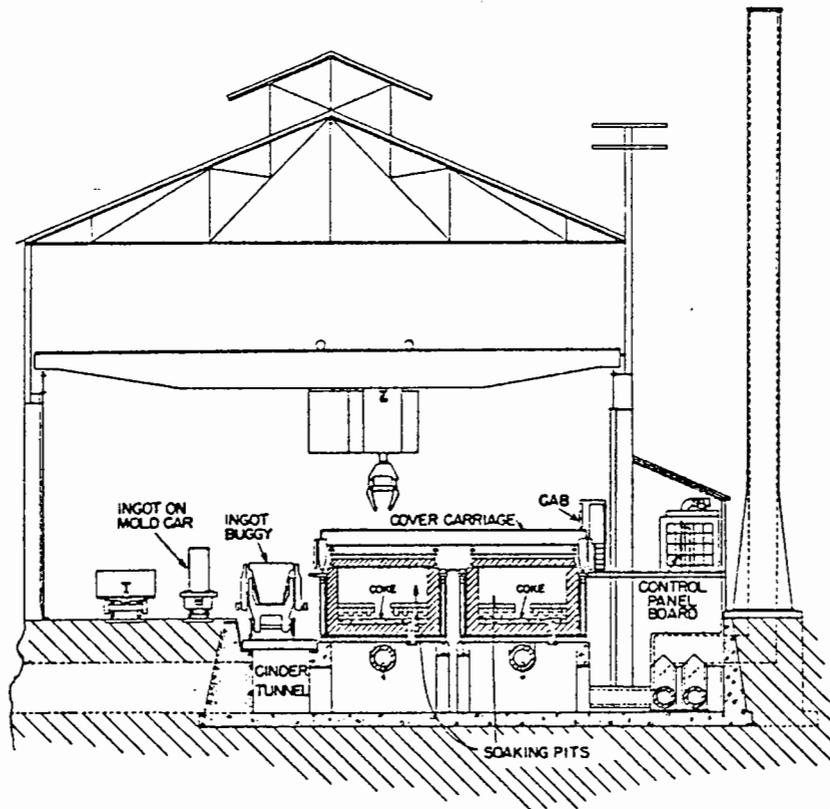


Figure 4-41. Schematic cross-section through a steel ingot soaking pit building.

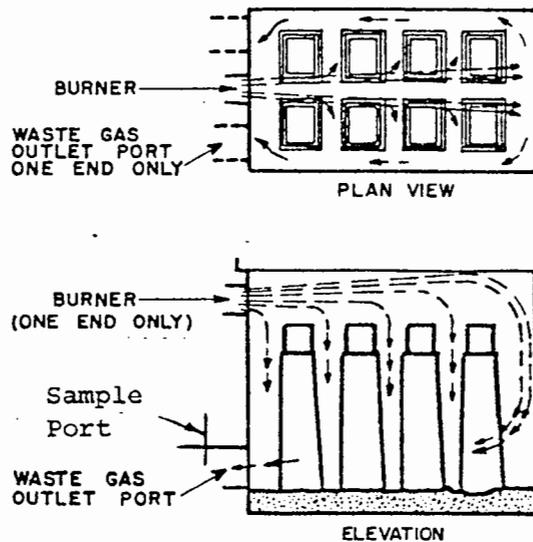


Figure 4-42. Method of heat application in a steel ingot soaking pit.

The measurements were made at the pit outlet just below the burner. The high flue gas temperature of about 1690 K (2400 °F) prevented Method 5 particulate or SO<sub>x</sub> wet chemistry tests due to probe material limitation. All test results are presented in Table 4-31.

C. Baseline Tests--

All measurements were made with the furnace firing natural gas. To maintain the preset pit temperature, heat input load varied during the tests from 1.57 MW (5.36 10<sup>6</sup> Btu/hr) to 2.77 MW (9.45 10<sup>6</sup> Btu/hr). Figure 4-43 shows NO<sub>x</sub> emissions and O<sub>2</sub> as a function of load at baseline conditions. Oxygen and NO<sub>x</sub> are lowest at high load and increase at lower load.

Baseline conditions on each test day were set by different operators. Each operator uses his own discretion to set excess oxygen levels according to flame appearance and heating requirements. There was therefore some fluctuation in baseline emissions.

The high stack temperature (1589 K, 2400 °F) results in a baseline efficiency by ASME heat loss method of less than 10%. At this low level, the effect of combustion modifications on efficiency is not meaningful and no analysis was made.

D. Combustion Modifications--

Several tests with excess oxygen variations were conducted. Reduction of excess air produced a significant NO<sub>x</sub> reduction. The effect of excess oxygen on NO<sub>x</sub> emissions at ~ 2 MW load is presented in Figure 4-44, indicating a 69% reduction in NO<sub>x</sub> by reducing excess O<sub>2</sub> to about 3% from the baseline level of 7%.

Three tests were conducted with an adjustment of flame length. The operator was concerned about uneven heating of the ingots in the pit during tests with a shortened flame. Localized overheating of the ingots close to the burner end could occur and therefore these tests were run faster without giving the furnace sufficient time to stabilize. No significant change in emissions were observed during the flame adjustment tests, as indicated for Tests 16/2-13 to 16/2-16.

TABLE 4-31. SUMMARY OF TEST DATA AT LOCATION 16/2  
STEEL SOAKING PIT - NATURAL GAS FUEL

Rated Load 91 Mg/batch (100 tons/batch); Test Load 77 Mg/batch (85 tons/batch)<sup>†</sup>

Test No.	Date 1977	Heat Input Load MW <sup>§</sup>	O <sub>2</sub> (%)	CO <sub>2</sub> (%) <sup>+</sup>	NO <sub>x</sub> * (ppm) ng/J	NO* (ppm) ng/J	HC* (ppm) ng/J	CO* (ppm) ng/J	SO <sub>2</sub> * (ppm) ng/J	Comments
16/2-1	5/9	2.35	7.0	7.9	51.5 (101)	51 (100)	15.2 (86)	1.6 (5)	0	Baseline
16/2-2	5/9	1.89	6.5	8.2	51.5 (101)	50.5 (99)	--	1.9 (6)	0	↓
16/2-3	5/9	2.07	7.0	7.9	53 (104)	52.5 (103)	--	1.9 (6)	0	
16/2-4	5/9	2.07	6.7	8.1	50.5 (99)	49 (96)	55.4 (313)	1.9 (6)	0	
16/2-5	5/9	1.94	7.1	7.9	52.5 (103)	52 (102)	15.4 (87)	2.8 (9)	0	
16/2-6	5/10	2.77	5.2	8.9	27 (53)	26.5 (52)	1.2 (7)	2.5 (8)	0	
16/2-7	5/10	2.67	5.4	8.8	29.6 (58)	28.6 (56)	1.1 (6)	2.8 (9)	0	
16/2-8	5/10	2.49	6.2	8.4	36.2 (71)	35.2 (69)	1.2 (7)	3.1 (10)	0	
16/2-9	5/11	2.07	4.4	9.4	28.6 (56)	27.5 (54)	4.2 (24)	3.1 (10)	0	Baseline
16/2-10	5/11	1.98	5.3	8.9	28.6 (56)	28.6 (56)	4.6 (26)	3.4 (11)	0	High O <sub>2</sub>
16/2-11	5/11	1.89	3.8	9.7	24 (47)	23.5 (46)	6.5 (37)	3.7 (12)	0	Low O <sub>2</sub>
16/2-12	5/11	1.57	2.7	10.3	16.3 (32)	16.3 (32)	6.0 (34)	5.0 (16)	0	Low O <sub>2</sub>
16/2-13	5/11	1.94	3.6	9.8	28.1 (55)	27.6 (54)	4.1 (23)	3.7 (12)	0	Baseline
16/2-14	5/11	1.94	3.9	9.7	32.1 (63)	30.1 (59)	4.4 (25)	4.0 (13)	0	Short Flame
16/2-15	5/11	1.94	4.0	9.6	33.2 (65)	32.6 (64)	4.2 (24)	1.9 (6)	0	Short Flame
16/2-16	5/11	1.94	4.9	9.1	29.1 (57)	28.6 (56)	2.3 (13)	1.2 (4)	0	Long Flame
16/2-17	5/11	1.89	5.0	9.0	31.6 (62)	31.1 (61)	2.1 (12)	2.8 (9)	0	Baseline

\*ppm corrected to 3% O<sub>2</sub>, dry

+Calculated from fuel analysis.

§10<sup>6</sup> Btu/h = 3.413xMW

† Batch time averages 15 hours.

Stack opacity was zero for all tests.

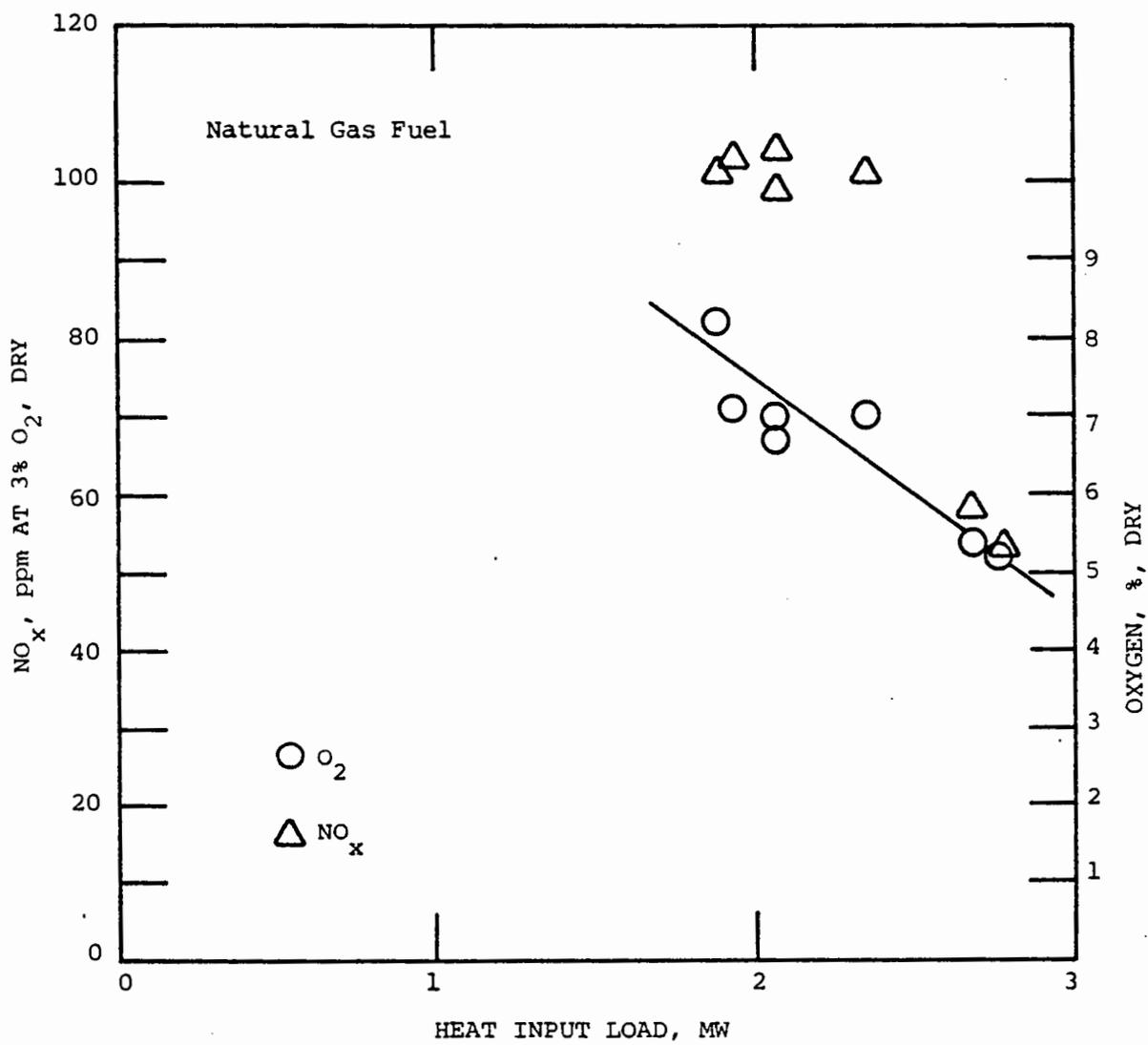


Figure 4-43. NO<sub>x</sub> emissions and O<sub>2</sub> as a function of load at baseline conditions for a soaking pit.

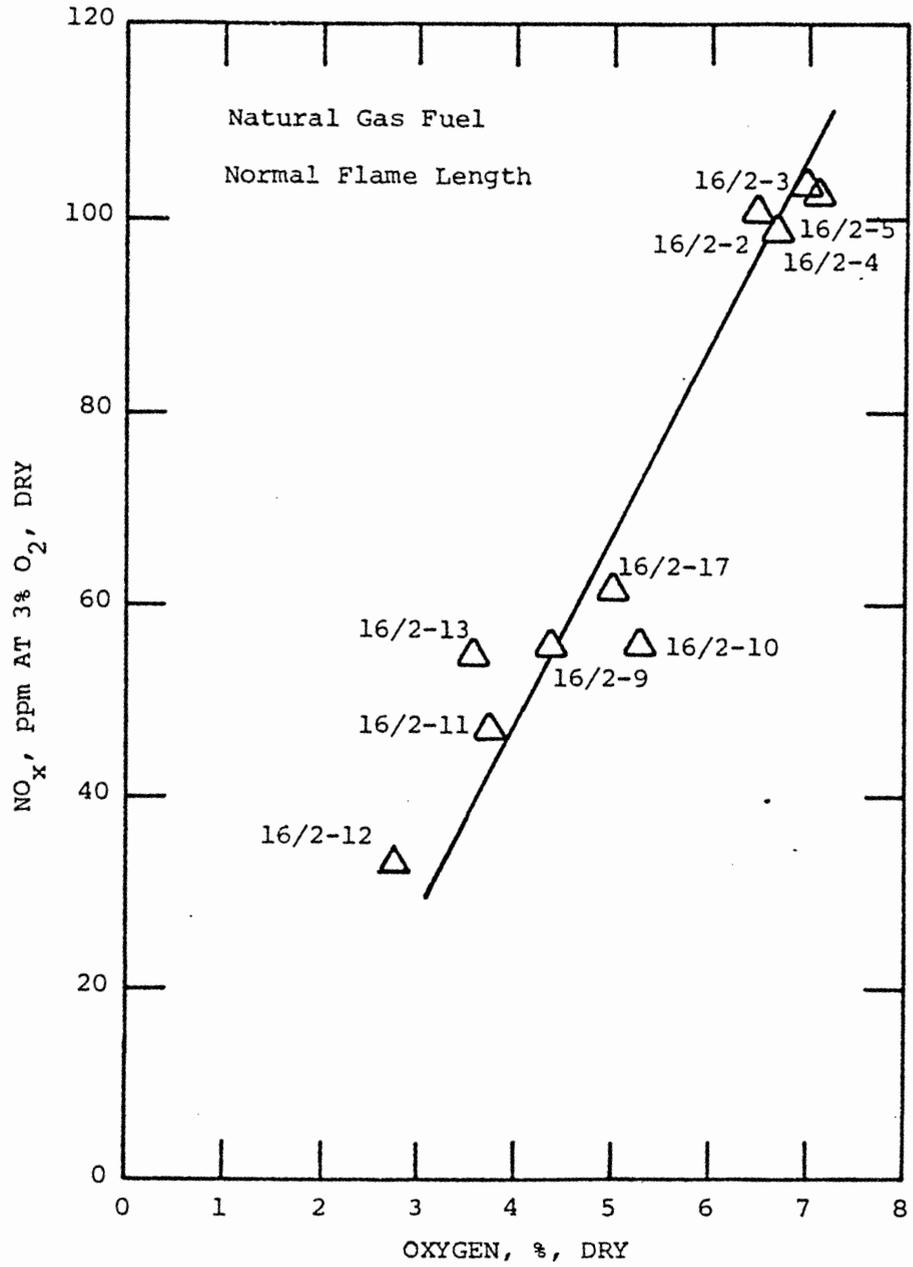


Figure 4-44. NO<sub>x</sub> as a function of O<sub>2</sub> at 2 MW load for a soaking pit at Location 16.

#### 4.3.4 Aluminum Melting Furnace, Location 6

##### Equipment Characteristics--

One metal furnace was tested at Location 6. This furnace was used for scrap aluminum melting and while the process is primarily a batch-type process, it is typical of a large number of installations.

The furnace was a 39 Mg aluminum melting furnace with two combination gas-oil burners located on opposing sides of the furnace. The furnace normally fires natural gas, with No. 2 oil used for standby. The rated total heat input was 10.6 MW ( $38 \times 10^6$  Btu/hr). Each burner had a fuel valve and air damper linked together mechanically. Each burner could be adjusted independently of the other by changing mechanical linkages. The furnace shown schematically in Figure 4-45 was 5 m wide x 7.3 m long x 4.6 m high (16.5 ft x 24 ft x 15 ft) and lined with refractory brick. Charging scrap and ingot was accomplished through a door at one end of the furnace while the molten aluminum was withdrawn at the opposite end of the furnace by siphoning. The exhaust stack was located at the metal discharge end of the furnace. The stack contained a damper and a tempering air entrance above the damper. A sample port was installed in the stack upstream of the damper. Normal instrumentation for the furnace consisted of fuel flow rate, furnace temperature, and gas supply pressure.

The temperature in the stack where the emission sampling was performed was 1200 K (1700 °F) which required a different probe than normally used. Ceramic probes were made from mullite tubing which has a maximum service temperature of 1922 to 2033 K (3000 to 3200 °F) and excellent thermal shock resistance. No problems were encountered with the probes.

##### Baseline Emission Results--

Baseline tests were conducted with the furnace operating in the "as-found" condition. Baseline  $\text{NO}_x$  measurements were 48 ng/J (96 ppm) with the furnace operating at 4.6%  $\text{O}_2$ . Hydrocarbon, CO, and  $\text{SO}_2$  emissions were negligible.

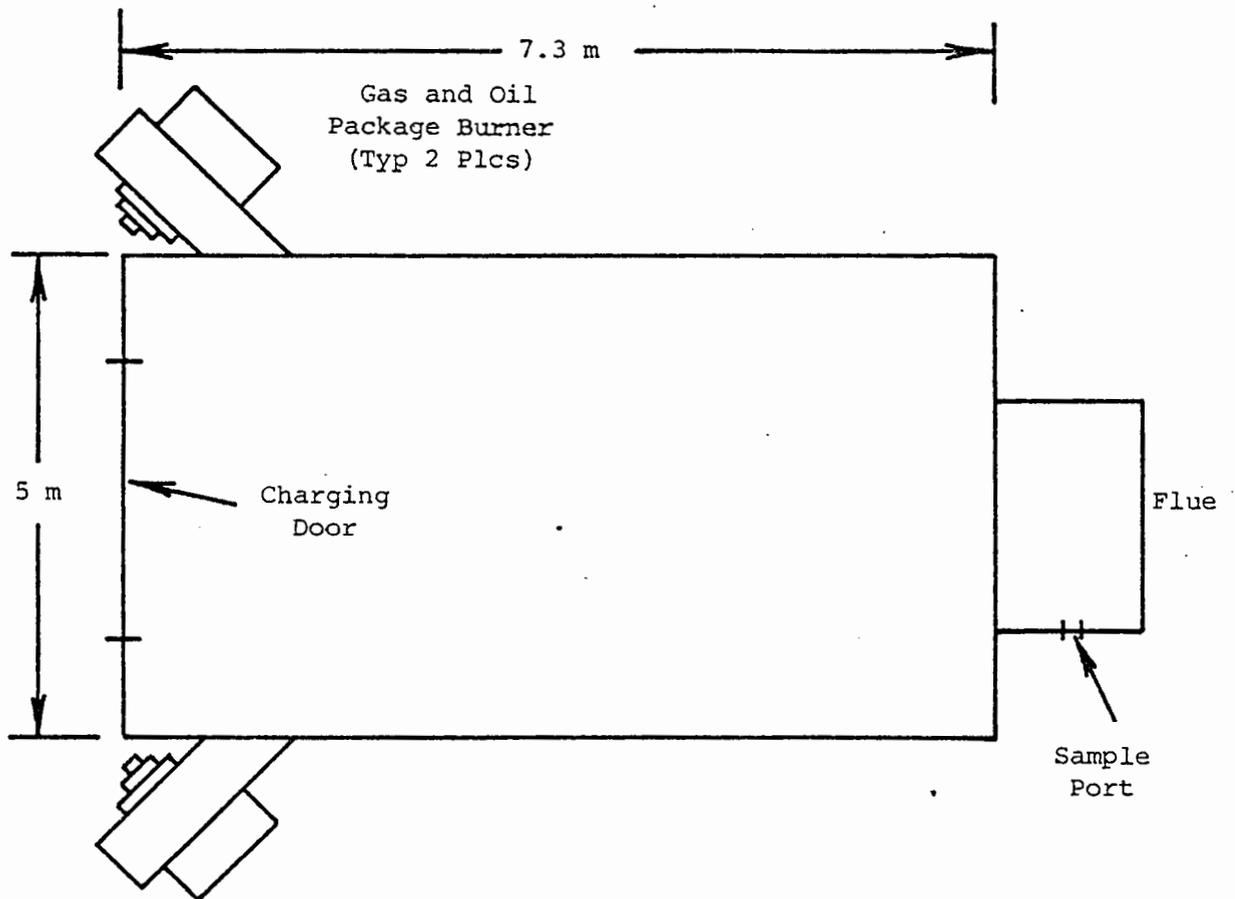


Figure 4-45. Plan view of aluminum melting furnace.

The baseline condition when firing No. 2 oil was 104 ng/J (185 ppm)  $\text{NO}_x$  with the furnace operating at 7.2% excess  $\text{O}_2$ . The fuel oil analysis is given in Table 4-32. HC and CO emissions were negligible on oil firing but  $\text{SO}_2$  measured 136 ng/J (174 ppm) for No. 2 oil firing. No particulate measurements were possible on this furnace because of sample port limitations.

#### Combustion Modifications, Aluminum Furnace, Location 6--

Combustion modification testing at this location consisted of lowering the excess  $\text{O}_2$ . Since there are only two burners located on opposite sides of the furnace, staged or off-stoichiometric firing is not possible. When firing natural gas, the excess  $\text{O}_2$  was lowered from the baseline value of 4.6% to 3.5%. The  $\text{NO}_x$  emissions increased to 57 ng/J (112 ppm), or about 17%. On oil firing, the excess  $\text{O}_2$  was reduced from the baseline value of 7.2% to 5.1% which resulted in an increase in  $\text{NO}_x$  emissions to 108 ng/J (193 ppm) or a 4% increase. Table 4-33 is a summary of the emission measurements for this location. The increase in  $\text{NO}_x$  with reduced  $\text{O}_2$  is characteristic of premixed flames. However, there was no particular reason for this furnace to perform as a premixed system.

#### Efficiency--

The stack gas losses for the aluminum furnace were calculated to be 54% of fuel input for natural gas and 60% for No. 2 oil. Since the process is a batch-type process, the fuel input and stack flow conditions are intermittent and the stack losses are not constant over the heating cycle.

TABLE 4-32. FUEL ANALYSIS, LOCATION 6

---

Test No.	6
Date	6/30/76
Fuel Type	No. 2 Distillate
Carbon, % wt.	86.40
Hydrogen, %	13.12
Nitrogen, %	0.040
Sulfur, %	0.25
Ash, %	0.062
Oxygen (by difference), %	0.13
API Gravity at 60 °F	34.5
Heat of Combustion	
Gross, kJ/kg	45,330
(Btu/lb)	(19,490)
Net, kJ/kg	42,540
(Btu/lb)	(18,290)

---

TABLE 4-33. SUMMARY OF GASEOUS EMISSIONS DATA  
LOCATION 6 - ALUMINUM MELTING FURNACE

Test No.	Date 1976	Heat Input MW	Batch Load <sup>+</sup> Mg/batch	O <sub>2</sub> (%)	CO <sub>2</sub> (%)	NO* (ppm)	NO (ng/J)	NO <sub>x</sub> * (ppm)	NO <sub>x</sub> (ng/J)	HC* (ppm)	CO* (ppm)	SO <sub>2</sub> * (ppm)	Comments
6-1	6/28	9.75	104.5	4.6	10.8	94	48	96	49	1	7	2	Nat. gas baseline
6-2	6/29	9.75	165.0	3.5	11.4	110	56	112	57	0	10	1	Nat. gas - low excess air
6-3A	6/30	8.16	82.5	7.2	11.6	184	103	185	104	0	8	174	No. 2 oil - baseline
6-3B	6/30	8.16	82.5	5.1	12.6	192	108	193	108	0	8	180	No. 2 oil - low excess air

\*Dry, corrected to 3% O<sub>2</sub>.

<sup>+</sup>Three hours per batch.

Stack opacity was zero for all tests.

#### 4.4 BOILERS

Four boilers were tested: two wood/bark boilers (Location 13 and 10/1), a black liquor recovery boiler (Location 10/2) and a petroleum refinery carbon monoxide boiler (Location 11).

##### 4.4.1 Location 13 Tests - Wood/Bark Boiler

###### Equipment Characteristics--

The wood/bark boiler at Location 13 was rated at 45,360 kg/hr (100,000 lb/hr) steam flow firing coal. The boiler was built in 1966 by Wickes Boiler Company and is equipped with an overfeed traveling grate stoker which feeds bark and coal continuously. The wood/bark was injected into the furnace pneumatically through a port located above the overfire air ports. The boiler is equipped with a multiclone dust collector.

The boiler operators were directed to maintain bark flow rate constant during the tests but flow was occasionally interrupted for periods of up to 30 minutes due to bark duct plugging. This occurs from time to time and is considered normal operation. There were no coal or bark scales installed at this unit so no fuel flow rates could be recorded. The percentage of bark heat input was estimated from the steam chart when bark flow is interrupted. The test boiler was encountering high superheater metal temperature when burning wood/bark. The boiler burned bark until the superheater metal temperature reached 706 K (810 °F). The design temperature is 672 K (750 °F). This temperature can be maintained when burning coal only.

Combustion modifications which were evaluated include excess air adjustments and overfire air variation. Total particulate, particulate size distribution, wet chemical SO<sub>x</sub> and trace element tests were conducted on this unit.

###### Emissions Sampling--

Gaseous emissions measurements were made in the stack downstream of a multiclone dust collector. The heated sample line was used to sample all

gaseous emissions. A single sample port downstream of the multiclone was used to sample for particulate,  $\text{SO}_x$ , and trace species and organics. No access was available for measurements upstream of the dust collector.

#### Baseline Tests--

Baseline emission measurements were made with the boiler in the "as found" condition firing about 20% wood/bark and 80% Kentucky coal. Results of all tests are presented in Table 4-34. Fuel analyses are given in Table 4-35. Boiler load at baseline conditions was 41,300 kg/hr steam flow (approximately 90% of rated capacity). Boiler load was relatively constant ( $\pm 6\text{-}1/2\%$ ) throughout the entire test series. Boiler  $\text{NO}_x$  emissions at as-found baseline conditions were 168 ng/J (0.39 lb/10<sup>6</sup> Btu), 266 ppm at 3%  $\text{O}_2$ .  $\text{NO}_x$  emissions increased from 168 to 232 ng/J as wood/bark flow decreased. Highest  $\text{NO}_x$  emissions occurred when only coal was burned.

Solid particulate emissions were 105 ng/J (0.244 lb/10<sup>6</sup> Btu) at 8.5%  $\text{O}_2$  with the boiler at approximately 87% of rated capacity. Particulate size distribution was also measured using a cascade impactor. Data on the size distribution are shown in Figure 4-46 for test number 13-8, where particle diameter as a function of cumulative proportion of impactor catch is plotted. Approximately 40% of the particulate is below 3  $\mu\text{m}$  aerodynamic diameter.

#### Combustion Modifications--

Combustion modification testing included variation of excess air and variation in overfire air. Load variations were not possible as the boiler output was committed to the process and there was no reserve capacity available. Load variations indicated in the summary data table are the result of normal fluctuations in load for a boiler in this type process.

A test series (Tests 13-9 through 13-14) was conducted to evaluate the effect of excess oxygen on emissions. The overfire air was left constant - 100% open (normal position) for these tests. Excess  $\text{O}_2$  was controlled by adjusting the damper on the forced draft fan. The baseline condition for the  $\text{O}_2$  variation tests was 7.75%  $\text{O}_2$  and the  $\text{NO}_x$  emissions were 196 ng/J. The

TABLE 4-34. SUMMARY OF EMISSIONS FROM LOCATION 13 WOOD/BARK BOILER

141

Test Run No.	Date 1976	Nominal Steam Load (Mg/h)	Heat Input: MW	O <sub>2</sub> (%)	CO <sub>2</sub> (%)	NO <sub>x</sub> * ng/J (ppm)	NO* ng/J (ppm)	HC* ng/J (ppm)	CO* ng/J (ppm)	SO <sub>2</sub> * ng/J (ppm)	Wet Chemical		Total Part. ng/J (10 <sup>6</sup> lb/Btu)	Solid Part. ng/J (10 <sup>6</sup> lb/Btu)	Stack Temp. K (°F)	Eff. (%)	Comments
											SO <sub>2</sub> ng/J (ppm)	SO <sub>3</sub> ng/J (ppm)					
13-1	11-2	42.2	33.4	7.7	10.4	168 (266)	163 (258)	7 (33)	--	994 (1130)	---	---	---	---	483 (410)	81.1	"As found boiler test ap- parent high bark flow
13-2	11-2	41.3	32.7	6.9	↑	177 (280)	166 (263)	4 (16)	15 (38)	1504 (1710)	---	---	---	---	482 (408)	81.6	Boiler "as found" - lower bark flow
13-3	11-2	40.8	32.3	8.5	↑	232 (367)	232 (367)	0	3 (9)	1800 (2047)	---	---	---	---	478 (400)	80.8	No bark flow - Kentucky coal only
13-4	11-2	40.4	31.9	7.8	↑	176 (278)	183 (290)	0	12 (30)	1159 (1318)	875 (995)	34 (39)	---	---	486 (415)	80.9	SOx test - baseline conditions
13-5	11-2	42.5	33.7	7.5	↑	187 (296)	184 (291)	0	12 (32)	1186 (1349)	1008 (1146)	26 (30)	---	---	482 (408)	81.4	SOx test - baseline conditions
13-6	11-3	39.4	31.2	8.5	↑	209 (331)	209 (331)	0	53 (138)	1165 (1325)	---	---	166 (.387)	105 (.244)	479 (402)	80.8	Baseline particulate - 35% opacity
13-7	11-3	40.8	32.3	8.4	↑	172 (272)	170 (269)	2 (11)	26 (69)	1055 (1200)	---	---	---	---	489 (420)	80.2	
13-8	11-3	40.8	32.3	7.9	↑	189 (299)	177 (280)	0	25 (66)	1151 (1309)	---	---	---	---	489 (420)	80.6	Cascade impactor - baseline condition
13-9	11-4	41.3	32.7	7.8	↑	196 (310)	193 (306)	2 (10)	16 (43)	1161 (1320)	---	---	---	---	484 (411)	81.1	Baseline for O <sub>2</sub> variation tests
13-10	11-4	41.3	32.7	9.6	↑	250 (395)	257 (407)	1 (6)	39 (101)	1460 (1661)	---	---	---	---	480 (405)	79.9	O <sub>2</sub> variation - high O <sub>2</sub>
13-11	11-4	39.9	31.6	8.8	↑	214 (338)	214 (338)	2 (11)	25 (65)	1329 (1509)	---	---	---	---	483 (409)	80.2	O <sub>2</sub> variation
13-12	11-4	44.0	34.8	5.3	↑	170 (269)	169 (267)	1 (4)	5 (12)	1546 (1758)	---	---	---	---	486 (415)	82.3	O <sub>2</sub> variation - low O <sub>2</sub>
13-13	11-4	38.5	30.5	6.8	↑	160 (254)	160 (254)	1 (5)	6 (15)	1441 (1639)	---	---	---	---	484 (412)	81.5	O <sub>2</sub> variation
13-14	11-4	38.5	30.5	7.9	↑	204 (323)	204 (323)	0	21 (55)	1614 (1836)	---	---	---	---	483 (410)	80.9	Baseline check & overfire air baseline
13-15	11-4	40.4	32.7	7.4	↑	167 (265)	167 (265)	0	0	1453 (1652)	---	---	---	---	484 (412)	81.3	Overfire air reduced to 30% of capacity
13-16	11-8	38.5	30.5	8.0	↑	198 (314)	190 (300)	0	53 (138)	1243 (1414)	---	---	---	---	483 (410)	80.9	Baseline - 19% bark flow
13-17	11-8	39.0	30.9	6.8	↑	122 (193)	122 (193)	0	37 (96)	853 (970)	---	---	170 (.396)	144 (.335)	489 (420)	81.4	Low O <sub>2</sub> - particulate; 19% bark flow, 43% opacity
13-18	11-9	41.3	32.7	8.4	↑	170 (270)	167 (265)	1 (5)	102 (265)	788 (896)	---	---	---	127 (.296)	491 (424)	80.0	TS&O Test
13-19	11-10	39.4	31.2	8.3	↑	150 (237)	150 (237)	0	82 (212)	1238 (1401)	---	---	---	---	489 (420)	80.4	Erratic wood bark flow-hard wood changing to soft wood
13-20	11-10	39.0	30.9	7.4	↑	133 (210)	130 (205)	0	51 (132)	1249 (1420)	---	---	---	---	503 (446)	80.0	Cascade impactor test
13-21	11-10	42.6	33.7	7.3	↑	145 (230)	145 (230)	0	53 (138)	1308 (1487)	---	---	---	---	494 (430)	80.6	Optimization test softwood bark
13-22	11-10	41.7	33.0	7.3	↑	160 (253)	160 (253)	0	45 (118)	1144 (1301)	---	---	---	---	492 (425)	80.8	Low O <sub>2</sub> - reduced overfire air
13-23	11-10	41.3	32.7	8.6	↑	182 (288)	179 (283)	0	95 (246)	1218 (1385)	---	---	---	---	493 (428)	79.7	TS&O baseline test
13-24	11-11	40.1	31.7	8.5	↓	176 (278)	176 (278)	0	86 (225)	981 (1116)	---	---	---	136 (.316)	494 (429)	79.7	TS&O test - bark flow ~ 21% of load

\*ppm corrected to 3% O<sub>2</sub> dry

TABLE 4-35. LOCATION 13 FUEL ANALYSES

Test No.	13-18	13-24	13-18	13-24
Date	11/9/76	11/11/76	11/9/76	11/11/76
Fuel Type	Coal	Coal	Wood	Wood
<u>Ultimate Analysis</u>				
Moisture, % weight	7.35	7.50	60.91	51.71
Carbon, %	66.93	64.42	18.71	24.40
Hydrogen, %	4.93	4.88	2.20	2.94
Nitrogen, %	1.49	1.33	0.21	0.18
Sulfur, %	2.47	2.80	0.08	0.03
Ash, %	7.66	8.32	3.05	1.85
Oxygen (diff) %	16.52	18.25	14.84	18.89
<u>Proximate Analysis</u>				
Moisture, % weight	7.35	7.50	60.91	51.71
Ash, %	7.66	8.32	3.05	1.85
Volatile Matter, %	46.15	46.26	27.79	36.66
Fixed Carbon, %	38.84	37.92	8.25	9.78
<u>Heat of Combustion</u>				
Gross, kJ/kg	27840	27280	7487	9454
(Btu/lb)	(11970)	(11730)	(3219)	(4065)
Net, kJ/kg	26770	26240	7012	8822
(Btu/lb)	(11510)	(11280)	(3015)	(3793)
<u>Boiler Dust Collector Ash Analysis</u>				
Carbon, %	6.04	2.08		
Heat of Combustion, kJ/kg (Btu/lb)	79 (34)	28 (12)		

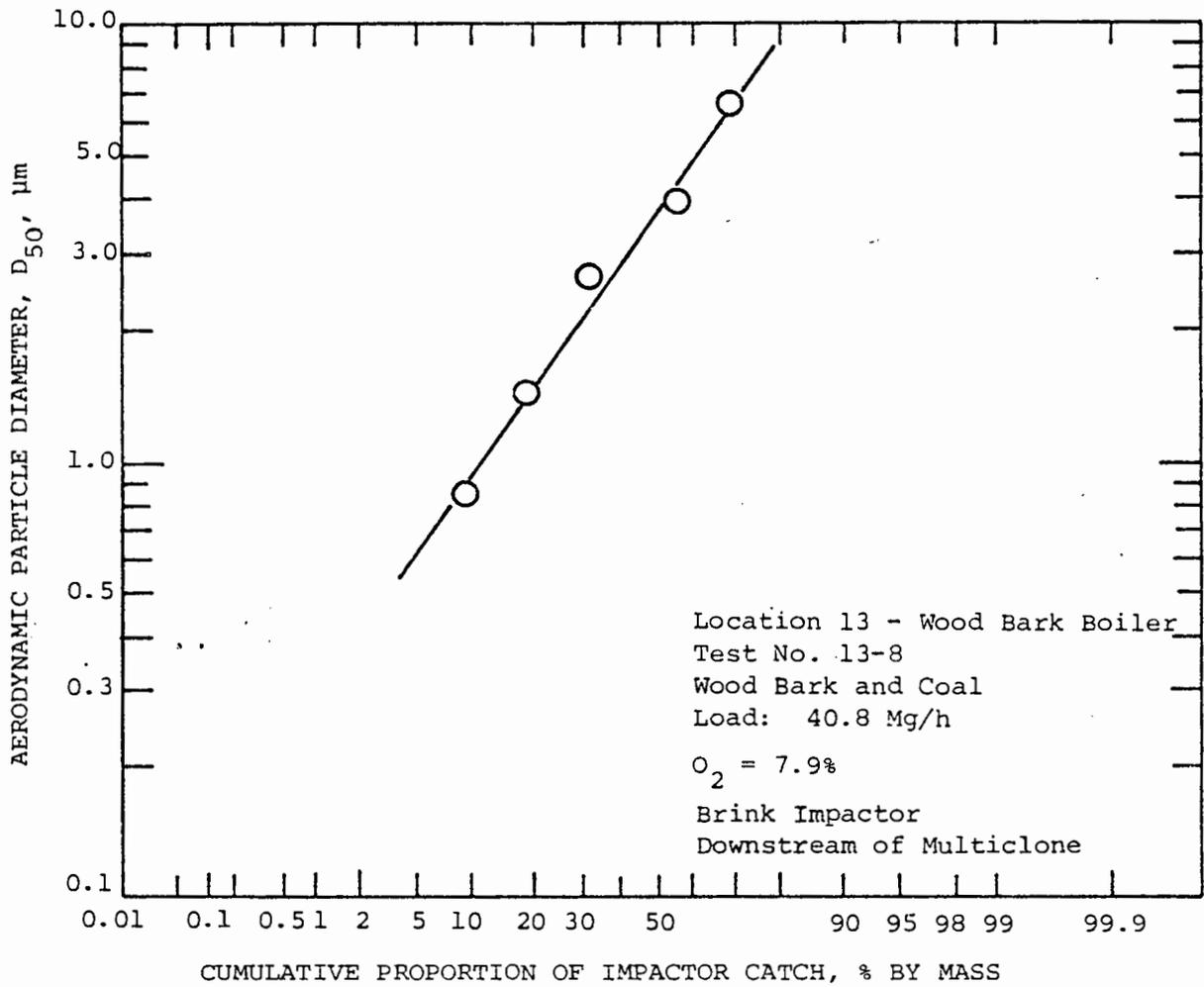


Figure 4-46. Particle size distribution for a wood bark boiler, Test No. 13-8.

excess O<sub>2</sub> for these tests varied from a high value of 9.6% to a low value of 5.3%. The effect of excess O<sub>2</sub> on NO<sub>x</sub> emissions is shown in Figure 4-47 which includes all the test data measured. Lowering the excess O<sub>2</sub> resulted in a decrease in NO<sub>x</sub> from 250 ng/J at 9.6% O<sub>2</sub> to 170 ng/J at 5.3% O<sub>2</sub>. A measurement of 160 ng/J NO<sub>x</sub> at 6.8% O<sub>2</sub> was obtained during this series of tests but load had dropped and grate speed was reduced to maintain the proper bed thickness. During the O<sub>2</sub> variation tests, the grate temperature indicators did not change and it was later verified that the indicators were inoperative. Combustion at the low O<sub>2</sub> (5.3%) condition appeared good and the CO measurement was 5 ng/J.

Following the O<sub>2</sub> variations, the unit was returned to the initial condition for a baseline check and to provide a baseline for the overfire air test. The overfire air damper was normally 100% open for all conditions and all previous tests had been conducted with the overfire air 100% open. The overfire air was changed to 50% open with normal bark flow. No change in NO emissions was observed. The overfire air damper was moved to 30% open. The NO<sub>x</sub> emissions were reduced from 204 ng/J at 7.9% O<sub>2</sub> at the baseline condition to 167 ng/J NO<sub>x</sub> at 7.4% O<sub>2</sub> with the overfire air reduced to 30% open (Test 13-15).

The bark is injected above the overfire air ports. With overfire air ports in the fully open position, much of the bark is burned in suspension and only larger particles fall to the grate. This can lead to incomplete combustion if the smaller particles are carried over to the dust collector before complete combustion. When the overfire air ports are 30% open, all or most of the bark falls on the grate and the moisture in the additional bark on the grate cools the flame which leads to reduced NO<sub>x</sub> emissions. For reduced NO<sub>x</sub> and CO emissions, the boiler should be operated with only 30% overfire air when both wood bark and coal are being fired.

During the test series, it was observed that the SO<sub>2</sub> measurements were varying. The variation in SO<sub>2</sub> concentration is due to fluctuations in wood bark flow. Since the load is fairly stable, when bark flow decreases, more coal is automatically injected to hold the load. This is indicated by an increase in SO<sub>2</sub> concentration.

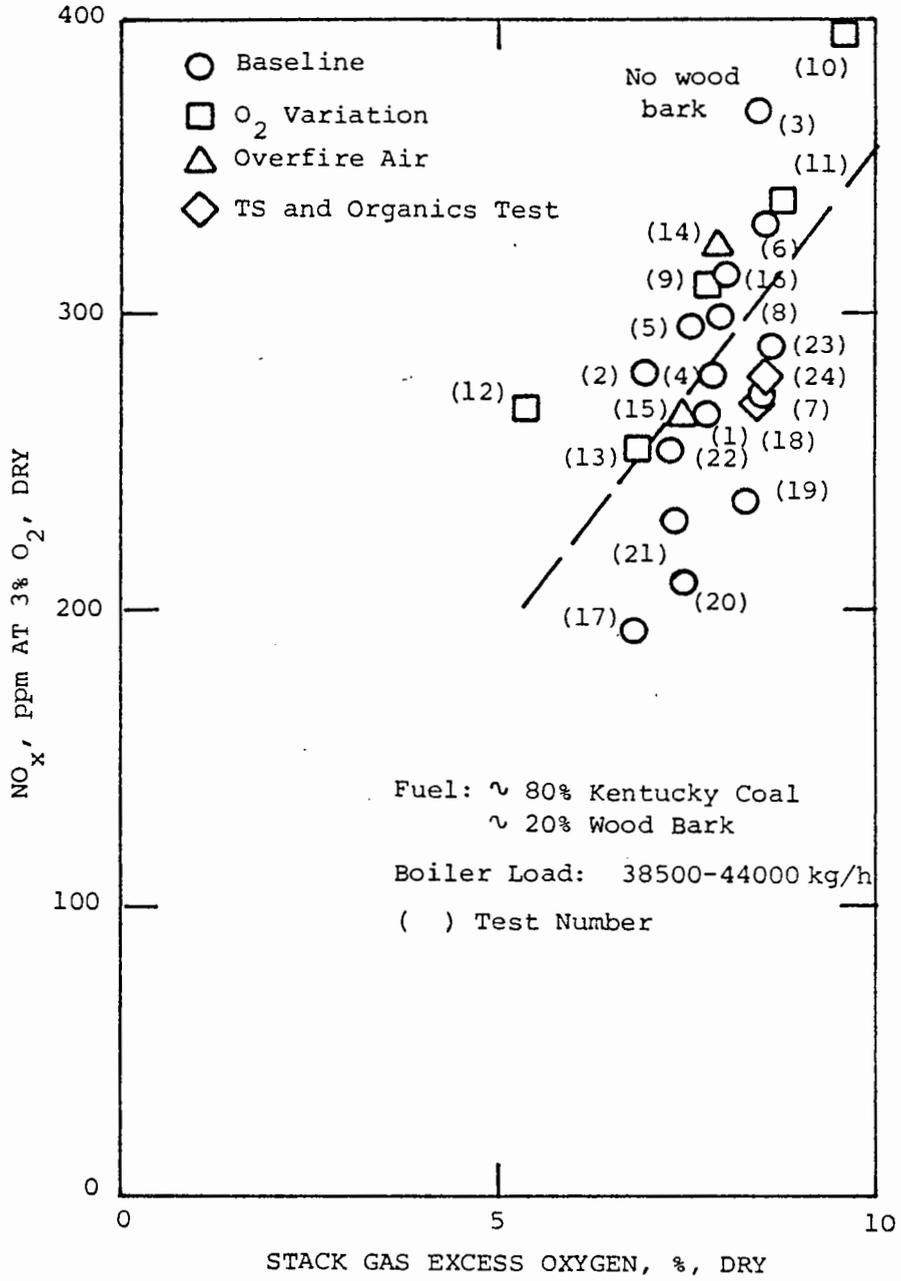


Figure 4-47. NO<sub>x</sub> emissions as a function of excess oxygen for a wood bark boiler.

Total particulate concentration was measured at the low excess O<sub>2</sub> condition. Wood/bark was accounting for 19% of the load at the low O<sub>2</sub> condition. Solid particulate concentration was 144 ng/J (0.335 10<sup>6</sup> Btu) with the boiler operating at 6.75% excess O<sub>2</sub>. NO<sub>x</sub> emission was 122 ng/J at the condition.

A cascade impactor test (Test No. 13-20) was attempted at low O<sub>2</sub> condition. Due to erratic wood/bark flow and wood/bark composition changing, the low O<sub>2</sub> cascade impactor test was conducted at 7.4% O<sub>2</sub>. The O<sub>2</sub> could not be lowered because of surges in bark flow and smoke conditions. During the cascade impactor test, the wood/bark flow accounted for approximately 20% of the load. The results of the low O<sub>2</sub> cascade impactor test are presented in Figure 4-48 where particle diameter as a function of cumulative proportion of impactor catch is plotted. Approximately 30% of the particulate is below 3 μm aerodynamic diameter.

Following the cascade impactor test, a test was conducted (Test 13-21) to try to lower O<sub>2</sub> and reduce superheater tube metal temperature with soft wood/bark accounting for approximately 20% of the load. The overfire air was then adjusted. The rear overfire air ports were reduced to 10% open which resulted in the boiler smoking. No data were taken at this condition. The front overfire air ports were reduced to 10% open with the rear ports fully open and under grate air at 30% open. The conclusions from these tests are that reduced excess air firing can lower NO<sub>x</sub> emissions and improve superheater metal temperature conditions without adversely affecting efficiency or other operating conditions.

#### Efficiency--

Efficiency of the wood/bark boiler was calculated using the heat loss method outlined in ASME Power Test Code PTC 4.1-b. The fuel was assumed to be 20% yellow pine wood/bark and 80% Kentucky coal. Stack gas losses were calculated from the flue gas analyses and radiation loss was estimated from the ABMA Standard Radiation Loss Chart. Combustible loss in the ash was estimated from previous test data on similar units. The estimated efficiency for each test condition is presented in the previous table. Efficiency varied from 82.3% at 5.2% O<sub>2</sub> during Test No. 13-12 to 79.7% at 8.6% O<sub>2</sub> during Test No. 13-23.

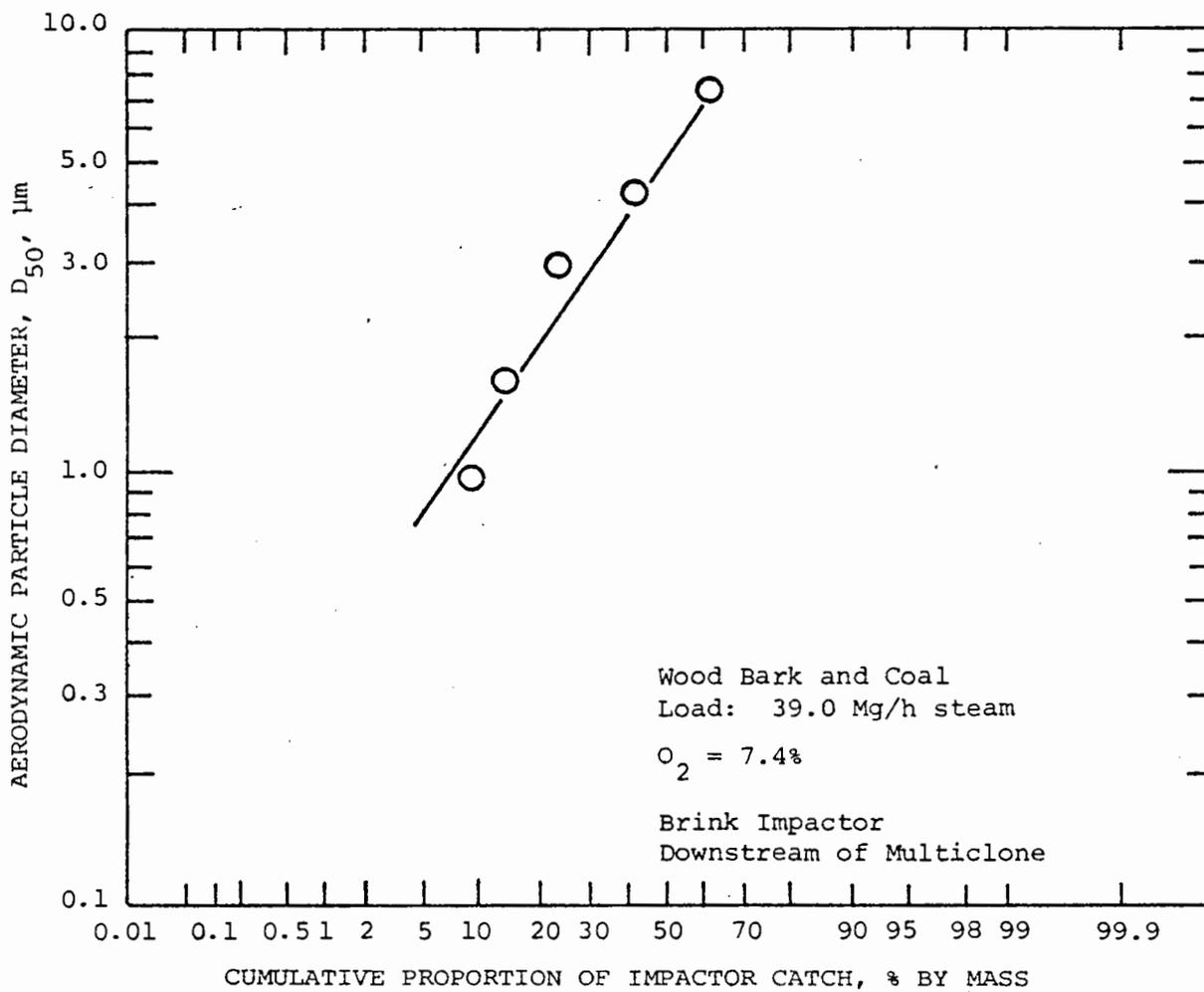


Figure 4-48. Particle size distribution for a wood bark boiler, Test No. 13-20.

Location 13 - Wood Bark Boiler Trace Species Test--

Two trace species and organics tests were conducted on the wood/bark boiler at Location 13. The boiler is fitted with a multiclone dust collector at the outlet. Sampling was conducted only at the dust collector outlet because the inlet to the dust collector was inaccessible.

Table 4-36 presents the sampling conditions for the trace species and organics tests. The tests were planned to terminate when two filters were plugged or five hours of sampling elapsed, depending upon which occurred first. Both tests were terminated after five hours sampling and only a single filter was used for each test.

TABLE 4-36. TRACE SPECIES AND ORGANICS SAMPLING CONDITIONS  
LOCATION 13 - WOOD/BARK BOILER

TS&O Run No.	1	2
Test No.	13-18	13-24
Date	11-9-76	11-11-76
Port Location	Dust Coll. Outlet	Dust Coll. Outlet
Stack Velocity, m/s (f/s)	4.42 (14.5)	4.39 (14.4)
Stack Temp., K (°F)	495 (431)	496 (433)
Oxygen Content, % dry	8.4	8.5
Moisture, %	9.6	7.8
Sample Time, min.	300	300
Cyclone Flow, awm <sup>3</sup> /m (awcfm)	0.065 (2.31)	0.065 (2.31)
Isokinetic Rate, %	93.5	80.3
Oven Temperature, K (°F)	429 (403)	477 (398)
XAD-2 Temp., K (°F)	291 (64)	292 (65)
Meter Temp., K (°F)	285 (54)	278 (41)
Nozzle Size, mm (in.)	19 (3/4)	19 (3/4)
No. Filters Used	1	1
Sample Flow, dry, DNm <sup>3</sup> /m (scfm)	0.372 (1.31)	0.0371 (1.31)
Volume Collected, dry, DNm <sup>3</sup> (scf)	11.25 (397.2)	11.17 (394.3)
Particulate Weight, g	3.0969	3.2690
Solid Particulates, ng/J (lb/MMBtu)	127 (0.296)	136 (0.316)

Solid particulate levels of 127 to 136 ng/J measured with the SASS sampling train are comparable to the EPA Method 5 data of 105 to 144 ng/J.

Results of trace species and organic analysis for the two tests are summarized in Table 4-37. Detailed data are contained in Appendix F, Tables F-50 to F-59. All species were detected except for cobalt, tellurium, tin, and PCB. For most detected species the results for the two tests were in reasonable agreement. However, several species were much higher in the second test (13-24), including manganese, titanium and zinc. Mass balance data, Appendix F, indicate that the value for titanium from the first test is more appropriate. The very high value for the second test was from the condensate and impinger collection and may be due to contamination. For manganese and zinc, the values for the second test gave a better mass balance.

POM compounds were detected in most of the samples collected on these tests. The first test yielded about 44 times as much total POM. Anthracene, fluoranthene and chrysene were detected in the cyclone wash and organic module rinse. These three were also in the XAD-2 resin but the resin also trapped phenanthrene, methylanthracene, pyrene, benzo fluoranthenes, benz (a) pyrene and benz (e) pyrene. This test unit was the only one for which the cyclone wash was analyzed for specific POM by GC/MS because GC analyses indicated a higher total POM concentration in this wash compared with the organic module. However, the concentration of specific POM by GC/MS was higher in the organic module.

TABLE 4-37. TRACE SPECIES AND ORGANIC EMISSIONS  
WOOD/BARK BOILER, LOCATION 13

<u>Sampling Location</u>	Species Concentration, $\mu\text{g}/\text{Nm}^3$	
	<u>Stack Exit</u>	<u>Stack Exit</u>
Test No.	13-18	13-24
Antimony	140<180	130<980
Arsenic	370<420	58<110
Barium	31<55	130<200
Beryllium	<8.6	2.7<13
Cadmium	1.9<9.8	19<26
Calcium	24000	23000
Chromium	270	270
Cobalt	<55	<420
Copper	59	150
Iron	2600	9800
Lead	9.8<28	1600
Manganese	250	1500
Mercury	0.11<52	0.17<11
Nickel	260	230
Selenium	<67	6.2<87
Tellurium	<2700	<3100
Tin	<3600	<4500
Titanium	470	250000
Vanadium	<110	46<180
Zinc	110	1200
Chloride	1200	1100
Fluoride	2700	3000
Nitrates	190	310
Sulfates	21000	22000
Total POM	350	7.9
Total PCB	<14	<1.1
For additional data, see tables noted in Appendix F	F-50 to F-56	F-57 to F-59

See Table F-1 for explanation of table values.

#### 4.4.2 Location 10/1 Tests - Wood/Bark Boiler

##### Equipment Characteristics--

The B&W wood/bark boiler at Location 10 was rated 200,000 lb steam per hour firing gas alone. It was designed to fire wood/bark on an overfed traveling grate and natural gas through four burners, and was equipped with an air preheater.

The design characteristics are given in Table 4-38.

TABLE 4-38. DESIGN CHARACTERISTICS  
OF LOCATION 10/1 WOOD/BARK BOILER

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Maximum Continuous High Pressure Steam Output:
Firing bark and natural gas or natural gas alone:
90 700 kg/h (200,000 lb/h)
Firing bark only: 68 000 kg/h (150,000 lb/h)
Steam Conditions at Superheater Outlet:
Temperature - 714 K (825 °F)
Pressure - 6133 kPa abs (875 psig)
Design Pressure: 7168 kPa abs (1025 psig)
Heating Surface:
Boiler - 1504 m <sup>2</sup> (16,187 ft <sup>2</sup> )
Furnace - 292 m <sup>2</sup> (3138 ft <sup>2</sup> )
Superheater - 338 m <sup>2</sup> (3640 ft <sup>2</sup> )

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The unit was equipped with an electrostatic precipitator.

Combustion modifications included burners out of service, air heater adjustments and air register adjustments. Total particulate and particulate size distribution tests were conducted with the unit firing wood/bark and natural gas.

##### Emissions Sampling--

Gaseous emissions measurements were made at the air heater inlet and outlet. The heated sample line, used for measuring SO<sub>2</sub>, NO<sub>x</sub>, and HC was connected to the air heater outlet.

Particulates were sampled upstream of the precipitator.

#### Baseline Tests--

Baseline emission measurements were made with the boiler firing wood/bark and natural gas. The boiler load could not be held constant because of fluctuating wood flow and swings in load of from 9 to 16 Mg steam per hour were recorded. The nominal load also varied considerably with time. Boiler  $\text{NO}_x$  emission at baseline with high wood flow was 124 ng/J (229 ppm corrected to 3%  $\text{O}_2$ ). With low wood flow  $\text{NO}_x$  dropped to 75 ng/J (138 ppm). Test results are presented in Table 4-39 and the wood fuel analysis is given in Table 4-40.

Solid particulate emissions were 500 to 1334 ng/J (1.2 to 3 lb/10<sup>6</sup> Btu), varying dependent on the amount of wood flow to the boiler. A cascade impactor test was conducted with all burners in service to determine particle size distribution. Figure 4-49 presents particle size as a function of percent cumulative catch for the bark boiler at baseline conditions. These data indicate that only 5% of the particulate leaving the bark boiler are smaller than 3  $\mu\text{m}$  diameter. Opacity was 5%. The wide variation in percentage of particulate below 3  $\mu\text{m}$  which is emitted from wood bark boilers at locations 13 and 10 is due to the removal of larger particulate by the multiclone which preceded the sample port at location 13.

#### Combustion Modifications--

Combustion modification testing included air preheat adjustments and burner-out-of-service tests. Difficulty in maintaining a steady load condition was encountered on all tests. The bark flow to the boiler is not constant or stable. The steam flow fluctuated with bark flow to the boiler with natural gas fuel flow adjusted to attempt to stabilize the steam flow. The  $\text{NO}_x$  emissions as a function of flue gas excess oxygen are presented in Figure 4-50.

Tests 5 to 8 consisted of air preheater adjustment. On the day of these tests, boiler wood flow was high resulting in high levels of HC, CO, and  $\text{SO}_2$  in spite of  $\text{O}_2$  levels that were higher than for baseline. Reduction of air preheat temperature from 550 K to 344 K (530 to 160 °F) did not result in any change in  $\text{NO}_x$  emissions but HC, CO, and  $\text{SO}_2$  were significantly increased.

Tests 9 to 14 consisted of burner shut-off tests. The unit normally operates with the No. 4 burner out of service. Restoring that burner so that

TABLE 4-39. SUMMARY OF EMISSIONS FROM LOCATION 10/1 WOOD/BARK BOILER FIELD TESTS

Test Run No.	Date 1976	Nominal Steam Load Mg/h	O <sub>2</sub> (%)	CO <sub>2</sub> (%)	NO <sub>x</sub> *		NO*		HC*	CO*	SO <sub>2</sub> *	Solid Particulates		Sample † Position	BOOS	Air Preheat Temp. K/(*R)	Temp-ering Air Damper % Open	Gas Fuel Heat MW	Comments
					(ppm)	(ng/J)	(ppm)	(ng/J)				(ppm)	(ppm)						
10/1-1	8/17	67	10.25	8.0	229	124	193	105	54	1993	0	--	--	O	#4	547	0	9.7	Baseline - high wood flow
			9.3	9.9	--		172	93	--	1600	-			I		(525)			
10/1-2	8/18	91	6.5	9.2	138	75	130	70	118	1069	0	--	--	O	#4	549	0	61.7	Baseline - low wood flow
			7.5	8.7	--		127	69	--	373	-			I		(529)			
10/1-3	8/18	85	9.0	9.2	188	102	187	101	0	375	9	1.16	499	O	#4	544	0	61.7	Baseline - part. test, 5% opacity; low wood flow
			9.0	7.4	--		175	95	--	240	-			I		(519)			
10/1-4	8/18	82	9.5	7.7	208	113	196	106	0	376	7	--	--	O	#4	544	0	61.7	Baseline - low wood flow
			8.4	8.0	--		150	81	--	300	-			I		(520)			
10/1-5	8/19	74	10.25	7.8	207	112	194	105	32	1859	0	--	--	O	#4	550	0	13.9	Baseline - high wood flow
			9.5	8.0	--		188	102	--	1393	-			I		(530)			
10/1-6	8/19	45	13.25	5.3	207	112	193	105	805	>2000	322	--	--	O	#4	344	100	13.9	Air heater 100% bypassed
			13.0	5.9	--		236	128	--	>2000	-			I		(160)			
10/1-7	8/19	47	14.00	4.4	258	140	249	135	693	>2000	249	--	--	O	#4	408	50	27.8	Air heater 50% bypassed
			14.25	4.1	--		200	108	--	>2000	-			I		(275)			
10/1-8	8/19	45	13.5	4.5	235	127	221	120	414	>2000	138	--	--	O	#4	528	0	21.7	Air heater 50% bypassed
			13.25	5.5	--		214	116	--	>2000	-			I		(490)			
10/1-9	8/23	57	12.5	5.9	204	111	180	98	48	2626	0	--	--	O	None	529	0	34.4	Baseline - all burners in service
			11.0	8.0	--		180	98	--	1800	-			I		(492)			
10/1-10	8/23	61	9.75	8.0	176	95	176	95	37	1600	74	--	--	O	#1	536	0	36.1	No. 1 BOOS
			10.0	8.2	--		192	104	--	544	-			I		(505)			
10/1-11	8/23	77	8.0	9.9	209	113	190	103	20	554	40	--	--	O	#2	543	0	35.3	No. 2 BOOS
			11.25	8.0	--		185	100	--	1145	-			I		(518)			
10/1-12	8/23	66	10.25	7.4	205	111	193	105	68	1674	5	--	--	O	#3	539	0	34.4	No. 3 BOOS
			11.75	7.1	--		204	111	--	778	-			I		(510)			
10/1-13		78	8.5	9.2	175	95	166	90	18	576	37	--	--	O	#4	546	0	34.7	No. 4 BOOS
			10.0	7.0	--		176	95	--	544	-			I		(522)			
10/1-14	8/23	86	7.4	10.3	242	131	225	122	13	688	16	--	--	O	None	550	0	25.0	All burners in service - air reg. adj.
			7.8	10.5	--		225	122	--	682	-			I		(530)			
10/1-15	8/24	99	7.0	11.0	262	142	251	136	8	746	34	3.108	1334	O	None	560	0	26.1	Particulate test
			3.6	12.0	--		209	113	--	595	-			I		(548)			
10/1-16	8/24	107	4.0	14.4	234	127	228	124	53	1271	29	--	--	O	None	557	0	25.8	Brink impactor test
			4.0	14.8	--		212	115	--	847	-			I		(542)			

153

\*ppm measurements reported on 3% O<sub>2</sub>, dry basis  
 † Sample position, I = inlet, O = outlet of air preheater

TABLE 4-40. FUEL ANALYSIS, WOOD FUEL, LOCATION 10/1

<u>Proximate Analysis</u>	<u>Basis</u>	
	<u>As Received</u>	<u>Dry</u>
Moisture, %	50.69	---
Volatile Matter, T	36.54	74.10
Ash, %	2.27	4.60
Fixed Carbon, %	10.50	78.70
<u>Ultimate Analysis</u>		
Moisture, %	50.69	---
Carbon, %	25.32	51.34
Hydrogen, %	2.73	5.54
Nitrogen, %	0.15	0.31
Sulfur, %	0.05	0.11
Ash, %	2.27	4.60
Oxygen, % (by diff.)	18.79	38.10
<u>Heat of Combustion</u>		
Gross, Btu/lb	4362	8845
Net, Btu/lb	4108	8331

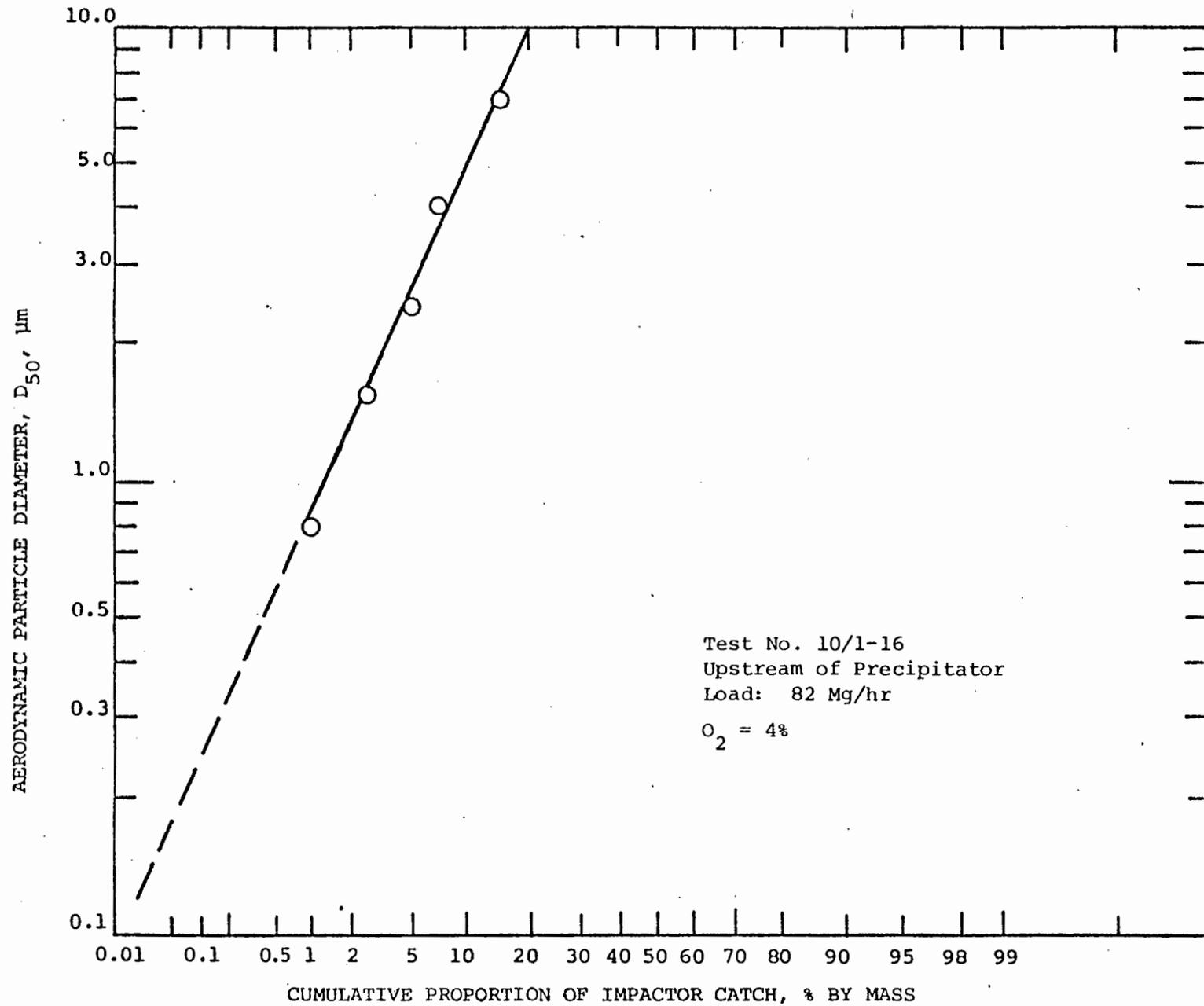


Figure 4-49. Particle size distribution for the wood/bark boiler at Location 10/1.

all four burners were operating yielded NO<sub>x</sub> emissions 12% lower than baseline. However, since wood flow and steam output were fluctuating, comparison between test runs is not valid. The main objective in burner tests was to attempt to reduce high CO and HC levels and that was accomplished primarily by air register adjustments. This, together with Burner No. 4 out of service, yielded the lowest overall emissions.

The conclusion is that reduction of excess air together with burner air register adjustments is the most effective NO<sub>x</sub> control method.

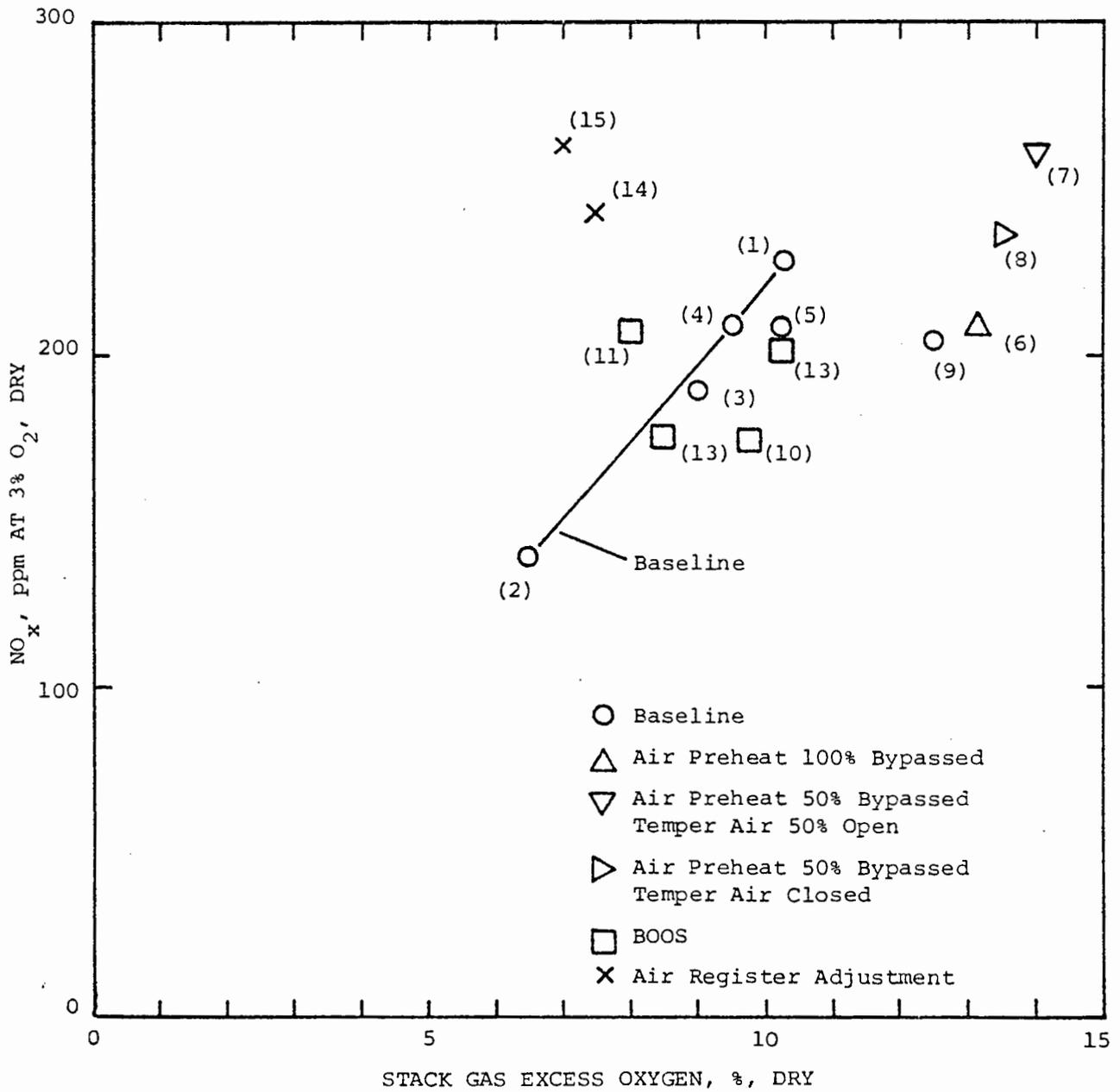


Figure 4-50. NO<sub>x</sub> emissions as a function of excess oxygen for the wood/bark boiler at Location 10/1.

#### 4.4.3 Location 10/2 Tests - Black Liquor Recovery Boiler

##### Equipment Characteristics--

The black liquor recovery boiler at Location 10 was manufactured by Combustion Engineering in 1965. The design performance of the unit is given in Table 4-41. A unit schematic is shown in Figure 4-51. The schematic shows the major components of interest and also indicates the gaseous and liquor flow paths. Weak liquor from the multiple effect evaporator system flows through wet bottom electrostatic precipitators where moisture is removed by the flue gas. In addition, the liquor picks up the solid ESP catch before entering contact evaporators where further moisture is removed. Salt cake ( $\text{Na}_2\text{SO}_4$ ) make-up chemical is added to the strong liquor before the liquor is burned in the furnace. Molten smelt, drawn off from the bottom of the furnace, is mixed with recirculating green liquor in the smelt tank and is then removed for further processing.

Combustion air temperature is raised in a steam preheater and introduced into the furnace as both a primary and secondary stream (to control the relative oxidizing/reducing atmosphere within the furnace). The combustion products are then passed through contact evaporators and wet bottom precipitators where they pick up moisture from the liquor. The I.D. fan and stack complete the gaseous flow path.

Data analysis is complicated by the unusual composition of the black liquor fuel shown in Table 4-42. Complete elemental balances on carbon, hydrogen, sulfur, and sodium are necessary to arrive at expected flue gas composition and heat input necessary for expression of emissions on a heat input basis (ng/J).

Table 4-43 shows a calculation of the elemental distribution for combustion of black liquor. Combustion products include  $\text{SO}_2$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{CO}_3$ ,

TABLE 4-41. DESIGN CHARACTERISTICS  
OF LOCATION 10/2 BLACK LIQUOR BOILER

Dry Solids of Black Liquor	kg/day (lb/day)	680 400 (1,500,000)
Steam Flow	kg/h (lb/h)	97 500 (215,000)
Temperature Steam from Superheater	K (F)	714 (825)
Pressure Steam from Superheater	kPa (psig)	6032 (875)
Feedwater Temp. to Recovery Unit	K (F)	417 (290)
Steam Drum Pressure	kPa (psig)	6349 (921)
Superheater Pressure Drop	kPa (psi)	317 (46)
Gas Temperature from Boiler	K (F)	694 (789)
Gas Temperature from Economizer	K (F)	610 (638)
Gas Temperature from Cascade	K (F)	436 (325)
Air Temperature from Air Heater	K (F)	422 (300)
Draft Loss, Furnace to Econ. Outlet	Pa (in.wg)	374 (1.50)
Draft Loss, Cascade Evaporator	Pa (in.wg)	558 (2.24)
Excess Air from Economizer	%	13
O <sub>2</sub> at Economizer Outlet	%	2.80
Secondary Air Windbox Pressure	Pa (in.wg)	1245 (5)
Primary Air Belt Duct Pressure	Pa (in.wg)	747 (3)
Liquor Solids to Cascade	%	50
Liquor Solids from Cascade	%	68

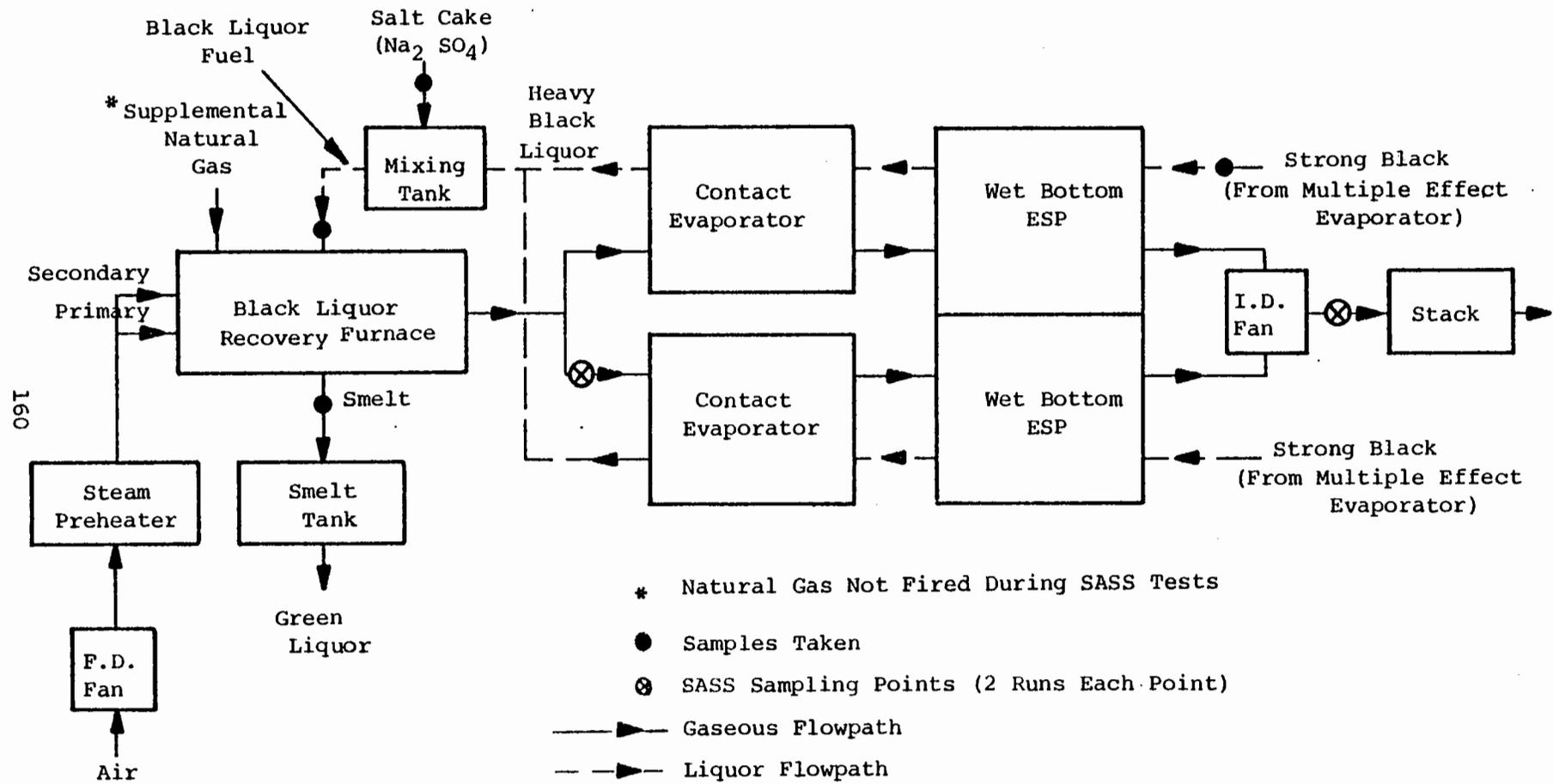


Figure 4-51. Black liquor recovery boiler schematic.

TABLE 4-42. BLACK LIQUOR RECOVERY BOILER,  
LIQUOR AND SMELT ANALYSIS,  
LOCATION 10/2

Test	10/2-2	10/2-10	10/2-10	10/2-16	10/2-16
Material	Liquor	Liquor	Smelt	Liquor	Smelt
<u>Organically Combined Elements</u>					
Carbon	21.07	23.65	---	23.80	---
Hydrogen	2.38	2.36	---	2.55	---
Sulfur	0.19	2.44	---	1.84	---
Nitrogen	0.04	0.06	---	0.06	---
Sodium	7.13	11.56	---	8.56	---
Oxygen (diff)	<u>16.16</u>	<u>8.43</u>	---	<u>15.49</u>	---
Total, Organic	46.97	48.50		52.30	
<u>Inorganic Constituents</u>					
Sodium Carbonate (Na <sub>2</sub> CO <sub>3</sub> )	5.62	14.9	67.68	13.6	88.40
Sodium Sulfate (Na <sub>2</sub> SO <sub>4</sub> )	10.66	4.26	1.68	4.36	0.98
Sodium Chloride (NaCl)	1.25	1.01	2.55	1.09	2.57
Sodium Hydroxide (NaOH)	---	---	21.44	---	---
Sodium Sulfide (Na <sub>2</sub> S)	---	---	---	---	---
Sodium Mercaptan (NaSH)	---	---	1.13	---	8.05
Moisture	<u>35.5</u>	<u>31.33</u>	<u>5.52</u>	<u>28.65</u>	<u>---</u>
Total, Inorganic	53.03	51.50	100.0	47.70	100.0
% Total Sodium	13.52	19.81	43.72	16.31	42.89
% Total Sulfur	2.59	3.40	1.02	2.82	4.82
<u>Gross Heat of Combustion</u>					
kJ/kg	9576	9097	---	9613	---
(Btu/lb)	(4117)	(3911)	---	(4133)	---

TABLE 4-43. COMBUSTION OF BLACK LIQUOR,  
TEST 10/2-10

Liquor Composition	% Weight	Elements, % Weight						
		C	H	S	N	Na	O	Cl
<u>Organic</u>								
C	23.65	23.65						
H	2.36		2.36					
S	2.44			2.44				
N	.06				*.06			
Na	11.56					11.56		
O	8.43						*8.43	
	<u>48.50</u>							
<u>Inorganic</u>								
Na <sub>2</sub> CO <sub>3</sub>	14.9	1.69				6.47	6.75	
Na <sub>2</sub> SO <sub>4</sub>	4.26			0.96		1.38	1.92	
NaCl	1.01					0.40		0.61
Moisture	<u>31.33</u>		3.48				27.85	
	<u>51.5</u>							
	100.0	25.34	5.84	3.40	.06	19.81	44.95	0.61
<u>Combustion Products</u>								
1/2 Org. → S SO <sub>2</sub> Gas	1.62			*0.81			0.81	
2/3 Org. → S Na <sub>2</sub> SO <sub>4</sub> Ash	7.21			1.63		*2.33	3.25	
Bal. Org. Na → Na <sub>2</sub> CO <sub>3</sub> Ash	21.27	2.41				*9.23	9.63	
Bal. Org. C → CO <sub>2</sub> Gas	77.88	*21.24					56.64	
H → H <sub>2</sub> O Gas	21.24		*2.36				18.88	
Mois. → H <sub>2</sub> O Gas			3.48				27.85	
							<u>117.06</u>	(Total O <sub>2</sub> Req'd)
<u>Gaseous Products</u>								
SO <sub>2</sub>	1.62			0.81			0.81	
CO <sub>2</sub>	77.88	21.24					56.64	
H <sub>2</sub> O	<u>52.57</u>	5.84					46.73	
	132.07							
<u>Total Ash (Smelt)</u>								
Na <sub>2</sub> CO <sub>3</sub> (74.4%)	36.17	4.10				15.70	16.38	
Na <sub>2</sub> SO <sub>4</sub> (23.6%)	11.47			2.59		3.71	5.17	
NaCl (2.1%)	<u>1.01</u>					0.40		0.61
	48.65							

\*Values to be used in F<sub>e</sub> equation, Table 4-44.

CO<sub>2</sub>, and H<sub>2</sub>O. Based on information from Combustion Engineering, about one-third of the organic S forms SO<sub>2</sub>; the balance forms Na<sub>2</sub>SO<sub>4</sub> dust which is collected in the dust collector or drops out in the smelt. Part of the C and the balance of the organic Na form Na<sub>2</sub>CO<sub>3</sub> which drops out in the smelt (furnace ash). The balance of the organic carbon forms CO<sub>2</sub>.

Development of the theoretical flue gas composition is shown in Table 4-44, based on the elemental analysis from the previous table. The final result is the dry stack flow per unit heat input, dNm<sup>3</sup>/J (DSCF/10<sup>6</sup> Btu). EPA New Source Performance Standards provide a relationship, called F<sub>e</sub>, that allows calculation of dNm<sup>3</sup>/J (DSCF/10<sup>6</sup> Btu) for fossil fuels. The form of this factor, expanded to include the effect of Na forming Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub>, is given at the bottom of the table. Note that in using the equation for F<sub>e</sub>, the values of %C, %S, and %Na cannot be taken directly from the fuel analysis as is the procedure for fossil fuels. The distribution of C between CO<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub>, S between SO<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub>, and Na between Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> must be determined. Values to be used in the F<sub>e</sub> equation, as developed for test 10/2-10, are indicated with an asterisk in Table 4-43.

Concentrations, in ppm corrected to 3% O<sub>2</sub>, dry, are converted to ng/J as follows. From Table 4-44, stack flow at zero excess O<sub>2</sub> is 3.065x10<sup>-7</sup> m<sup>3</sup>/J (11420 DSCF/10<sup>6</sup> Btu). Therefore:

$$\frac{\text{ng}}{\text{J}} = \text{ppm} \times 10^{-6} \times 3.065 \times 10^{-7} \times \frac{20.9}{29.0-3} \times 41.42 \frac{\text{g-mol}}{\text{g}} \times \text{MW}$$

for NO<sub>2</sub>, MW = 46

$$\frac{\text{ng}}{\text{J}} = \text{ppm} \times 0.6819$$

#### Baseline Emissions--

The black liquor recovery boiler was tested while firing black liquor alone and while firing black liquor and natural gas. Emissions data are presented in Table 4-45. Baseline NO<sub>x</sub> was relatively low, 35 ng/J (52 ppm corrected to 3% O<sub>2</sub>, dry), but HC emission was high, 900 to 2700 ppm, and CO emission was very high, up to 30000 ppm. Particulate emission was 3481 ng/J (8.1 lb/10<sup>6</sup> Btu). Opacity readings were not taken due to the absence of the observer.

TABLE 4-44. FLUE GAS COMPOSITION BASED  
ON BLACK LIQUOR ANALYSIS,  
TEST 10/2-10

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$$\text{Dry Flue Gas} = \text{SO}_2 + \text{CO}_2 + \text{N}_2 \text{ from Comb. Air}$$

$$\begin{aligned} \text{O}_2 \text{ Required} &= 117.06 \text{ kg/100 kg liquor} \\ -\text{O}_2 \text{ in Liquor} &= -8.43 \quad " \\ -\text{O}_2 \text{ in Moisture} &= \underline{27.85} \quad " \\ \text{Net O}_2 \text{ Req'd.} &= 80.78 \quad " \\ \text{N}_2 \text{ from Air} &= \frac{80.78}{.232} - 80.78 = 267.4 \text{ kg N}_2/100 \text{ kg liquor} \end{aligned}$$

Dry Flue Gas

$$\begin{aligned} \text{SO}_2 &= 1.62 \text{ kg/100 kg liquor} \\ \text{CO}_2 &= 77.88 \\ \text{N}_2 &= \frac{267.4}{346.9} \text{ kg dry gas/100 kg liquor} \end{aligned}$$

$$\text{HHV} = 9097 \text{ kJ/kg (3911 Btu/lb)}$$

$$\frac{3.469}{9097} = 381.3 \text{ } \mu\text{g/J (887 lb/10}^6 \text{ Btu)}$$

$$\text{Molec. Wt} = 30.6$$

$$(381.3 \times 10^{-6} \text{ g/J}) \times (.0246 \text{ m}^3/\text{g-mole})/30.6 =$$

$$3.056 \times 10^{-7} \text{ m}^3/\text{J (11420 DSCF/10}^6 \text{ Btu)}$$

Equivalent Form of  $F_e$  Factor:

$$F_e = [1.53 (\%C) + 3.61 (\%H) + .57 (\%S) + .14 (\%N) - .46 (\%O) + .72 (\% \text{ Na as Na}_2\text{SO}_4) + .56 (\% \text{ Na as Na}_2\text{CO}_3)] / (\text{HHV})$$

for  $F_e$  in units of DSCF/10<sup>6</sup> Btu, HHV in Btu/lb

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TABLE 4-45. SUMMARY OF EMISSIONS FROM LOCATION 10/2 BLACK LIQUOR RECOVERY BOILER

165

Test Run No.	Date (1976)	Load (Mg/h)	Heat Input MW	O <sub>2</sub> (%)	CO <sub>2</sub> (%)	NO <sub>x</sub> <sup>*</sup>		NO <sup>*</sup>		HC <sup>*</sup>	CO <sup>*</sup>	SO <sub>2</sub> <sup>*</sup>	Solid Particulates		Fuel	Sec. Air Damper % Open	Black Liquor Solids, %	Sample Position	Comments
						(ppm)	(ng/J)	(ppm)	(ng/J)	(ppm)	(ppm)	(ppm)	(lb/10 <sup>3</sup> Btu)	(ng/J)					
10/2-1	8/26	81	146	4.4	14.4	--	--	--	--	>2000	--	--	--	--	BL	70	65	ESP Inlet	Problems with sample system condensation in sample line
10/2-2	8/27	88	140	3.8	14.4	52	35	48	33	907	>2000	447	8.1	3480	BL	60	65	↓	Baseline - particulate, furn.outlet
10/2-3	8/30	88	147	3.7	15.4	35	24	32	22	2695	>2000	571	--	--	BL	55	65	↓	Baseline
10/2-4	8/31	91	144	3.4	14.4	35	24	32	22	2417	>2000	268	--	--	BL	80	65	↓	Baseline
10/2-5	8/31	88	146	4.7	14.6	39	26	38	26	1398	>2000	280	--	--	BL	100	64	↓	Sec. air damper adjust
10/2-6	8/31	79	155	3.5	15.1	36	25	33	23	2425	>2000	646	--	--	BL	46	63	↓	Sec. air damper adjust
10/2-7	9/1	84	166	3.3	13.3	23	16	21	14	7119	>2000	392	--	--	BL&NG	100	63	↓	Baseline - black liq. & gas
10/2-8	9/1	91	155	3.7	14.0	26	18	26	18	4208	>2000	331	--	--	BL&NG	100	60	↓	Baseline - low solids black liquor
10/2-9	9/1	88	155	4.1	14.4	33	23	31	21	6344	>2000	681	--	--	BL&NG	79	60	↓	Baseline - low solids black liquor
10/2-10	9/15	95	140	4.7	14.0	40	27	36	25	2592	30000	795	9.99	4294	BL	50	65	↓	SASS test, furn. outlet
10/2-11	9/16	--	--	4.1	12.4	33	23	33	23	--	10000	--	--	--	BL&NG	--	--	↓	Baseline, black liq. & gas
10/2-12	9/16	87	93	8.6	11.8	84	57	84	57	10	102	4	7.23	3108	BL	50	69	↓	SASS test, furn. outlet
10/2-14	9/23	95	137	4.5	14.4	41	28	38	26	2160	22000	622	--	--	BL	60	63	↓	Furn. outlet (for SASS test)
				7.2	11.4	--	--	38	26	--	9400	--	0.039	16.8	--	--	--	↓	Outlet SASS test ESP outlet
10/2-15	9/24	97	130	4.4	15.0	36	25	35	24	1400	18000	--	--	--	BL	60	67	↓	Inlet Furn. outlet
				7.1	13.2	--	--	47	32	--	12000	--	--	--	--	--	--	↓	Outlet ESP outlet
10/2-16	9/27	102	124	4.6	14.4	40	27	37	25	1900	18000	--	--	--	BL	65	65	↓	Inlet Furn. outlet (for SASS test)
				7.4	11.7	--	--	41	28	--	17000	--	0.034	14.5	--	--	--	↓	Outlet SASS test, ESP outlet

\*ppm measurements reported on 3% O<sub>2</sub>, dry basis.

Modifications included secondary air damper adjustments and reduction of black liquor solids content. Air damper adjustment reduced  $\text{NO}_x$  by 33% but increased HC by 200%. Reduction of black liquor solids content (increased moisture) had little effect on emissions.

#### Location 10 - Black Liquor Recovery Boiler Trace Species Test--

Four SASS tests were conducted on the black liquor recovery boiler (BLRB). Figure 4-51 shows the sampling points.

The SASS train sampling points were at the entrance to one of the contact evaporators (which passed approximately 80% of the flue gas flow) and in the duct between the I.D. fan and the stack. Samples were taken of the weak liquor, salt cake, strong liquor and solidified smelt. The BLRB is designed to operate on supplemental natural gas fuel during periods of low liquor flow from the pulp digesters, liquor spray nozzle plugging, etc. However, all SASS tests (except a portion of 10/2-14) were conducted with black liquor as the only fuel.

Table 4-46 summarizes the sampling data and Table 4-47 contains the process flow rates. Each test is discussed separately below.

#### Test 10/2-10 - Furnace Outlet--

Test 10/2-10 was conducted with the train positioned at the furnace outlet (inlet to the contact evaporator). The required sampling time to plug two filters was 38.6 minutes.

The significant unit operating parameters (from the control room instruments) for this test are shown in Figure 4-52 and indicate a fairly stable period of operation during the test period.

#### Test 10/2-12 - Furnace Outlet--

Test 10/2-12, a repeat of the previous inlet test, was conducted for 25.8 mins. sampling time when the second filter was plugged. Data analysis indicated that the cyclone flow rate was only 1.6% higher than the desired value and that the sampling was also being conducted at 91.9% of isokinetic conditions. The unit was operating in a somewhat upset condition with large decreases in both steam rate and liquor flow, i.e., -19.1% and -14.9%, respectively. These decreases were due to an agitator gear box failure in one

TABLE 4-46. TRACE SPECIES AND ORGANICS SAMPLING CONDITIONS  
LOCATION 10 - BLACK LIQUOR RECOVERY BOILER

TS & O Run No.	1	2	3	4
Test Number	10/2-10	10/2-12	10/2-14	10/2-16
Date	9/15/76	9/16/76	9/22-23/76	9/27/76
Port Location	Furn. outlet	Furn. outlet	ESP outlet	ESP outlet
Velocity, m/s (f/s)	5.49 (18.00)	7.70 (25.24)	24.10 (79.06)	22.87 (75.00)
Stack Temp., K (°F)	555 (539)	546 (523)	411 (279)	407 (273)
Oxygen Content, % dry	4.7	7.8	7.5	7.45
Moisture, %	25.11	20.99	34.79	31.15
Sample Time, min.	38.6	25.8	300	301
Cyclone Flow, awcmm (awcfm)	0.081 (2.852)	0.115 (4.064)	0.120 (4.224)	0.115 (4.049)
Isokinetic Rate, %	113.6	91.9	97.4	97.7
Oven Temperature, K (°F)	478 (400)	478 (400)	478 (400)	478 (400)
XAD2 Temperature, K (°F)	306 (91)	307 (93)	321 (119)	296 (73)
Meter Temperature, K (°F)	308 (95)	313 (104)	307 (92)	305 (89)
Nozzle Size, mm (in.)	19 (0.75)	19 (0.75)	9.53 (0.375)	9.53 (0.325)
No. Filters Used	2	2	1	1
Sample Flow, dry, scmm (scfm)	0.0424(1.497)	0.0516(1.819)	0.0466(1.644)	0.0472(1.666)
Volume Collected, dry, scm(scf)	1.636(57.74)	1.330(46.92)	13.977(493.2)	14.213(501.5)
Particulate Catch, g	17.7646	8.4520	0.4928	0.4334
Solid Particulate, ng/J (lb/10 <sup>6</sup> Btu)	4294 (9.99)	3180 (7.2)	16.8 (0.039)	14.5 (0.034)

167

TABLE 4-47. BLACK LIQUOR RECOVERY BOILER PROCESS FLOW RATES FOR SASS TESTS

Test	10/2-10	10/2-12	10/2-14	10/2-16
Sample Position	Furn. outlet	Furn. outlet	ESP outlet	ESP outlet
Liquor Vol. Flow, m <sup>3</sup> /s (GPM)	0.0129 204	0.00852 135	0.0124 197	0.0114 180
Liquor Spec. Gravity	1.18	1.17	1.169	1.168
Liquor Mass Flow, g/s	15,185	9,964	14,528	13,263
Sodium in Liquor, %	19.8	19.8	16.3	16.3
Sodium Input, g/s	3,007	1,973	2,368	2,162
95% Smelt Na Output, g/s	2,856	1,874	2,250	2,054
Sodium in Smelt, %	43.7	43.7	42.9	42.9
Smelt Mass Flow, g/s	6,536	4,289	5,244	4,787
Liquor Heat Input, MW (10 <sup>6</sup> Btu/hr)	138 (471)	90.5 (309)	140 (477)	127 (435)
Excess O <sub>2</sub> , %	4.7	7.8	7.5	7.45
Stack Flow, Nm <sup>3</sup> /s, dry* (dscfm)	54.6 115,700	44.3 93,831	66.8 141,600	60.7 128,700

\*stack flow based on  $3.065 \times 10^{-7}$  dNm<sup>3</sup>/J (11420 DSCF/10<sup>6</sup> Btu) at zero excess oxygen

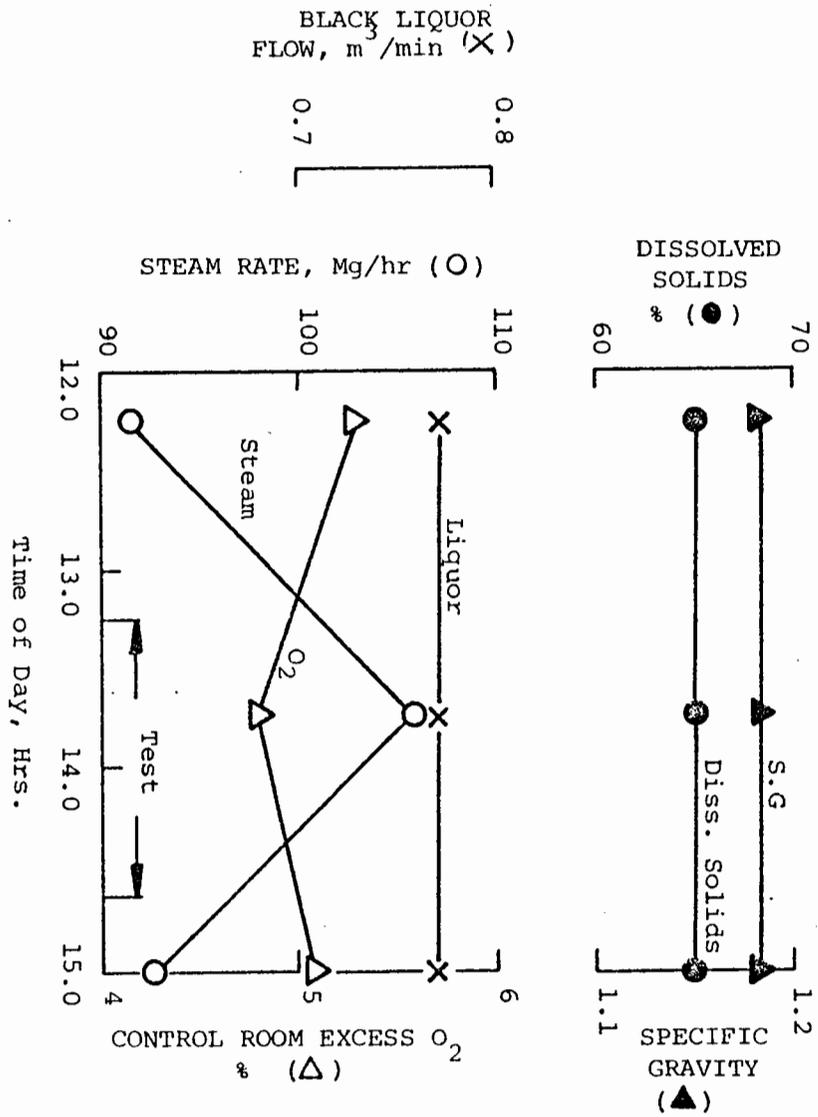


Figure 4-52. Trace species test 10/2-10 boiler conditions.

of the wet bottom precipitators which restricted the liquor flow. Boiler operation prior to the test was nominal but at a slightly lower liquor flow compared with the first test and with only six of eight liquor nozzles in service. Figure 4-53 indicates that a significant upset occurred during the test which was a result of a restriction in the liquor feed to the wet bottom precipitators. As a consequence, the steam rate sharply decayed. Device operation was continued with only four liquor nozzles in service.

#### Test 10/2-14 - Precipitator Outlet--

Test 10/2-14 was performed between the I.D. fan and stack. A full five-hour sampling duration was obtained with one filter. After accumulating 220 min. elapsed time, a problem arose within the oven; the oven heater electrical breaker kept opening. Upon partial disassembly of the oven box, it was found that the insulation on the wires to the circulating fan had failed allowing the wires to weld together. This problem was corrected and the test was concluded the following day.

Unit operation and duct conditions were steady for the split test periods and the sampling rate was within 5.6% of nominal and 2.6% of being isokinetic. During the conclusion of the first hour of the test, the boiler was operating partially on supplemental natural gas due to salt cake plugging of the liquor spray nozzles. The black liquor flow rate had dropped to  $0.4547 \text{ m}^3/\text{min}$  (120 gpm) during the time of natural gas usage. Figure 4-54 shows the process variables required for a system mass and energy balance. Figure 4-55 is a plot of significant process variables for the second part of test 10/2-14. Aside from a modest drop in steam and liquor flow, all other conditions were steady. Seven liquor nozzles were in service.

#### Test 10/2-16 - Precipitator Outlet--

The second BLRB outlet SASS test (10/2-16) was also performed for five hours of sampling time. A procedural change was incorporated for this and subsequent tests and involved forming an ice bath within the XAD2 module top closure. This change reduced the adsorbent temperature. Also as a result of this change, the XAD2 module condensate volume increased with a corresponding decrease in impinger condensable capture. Of note is the

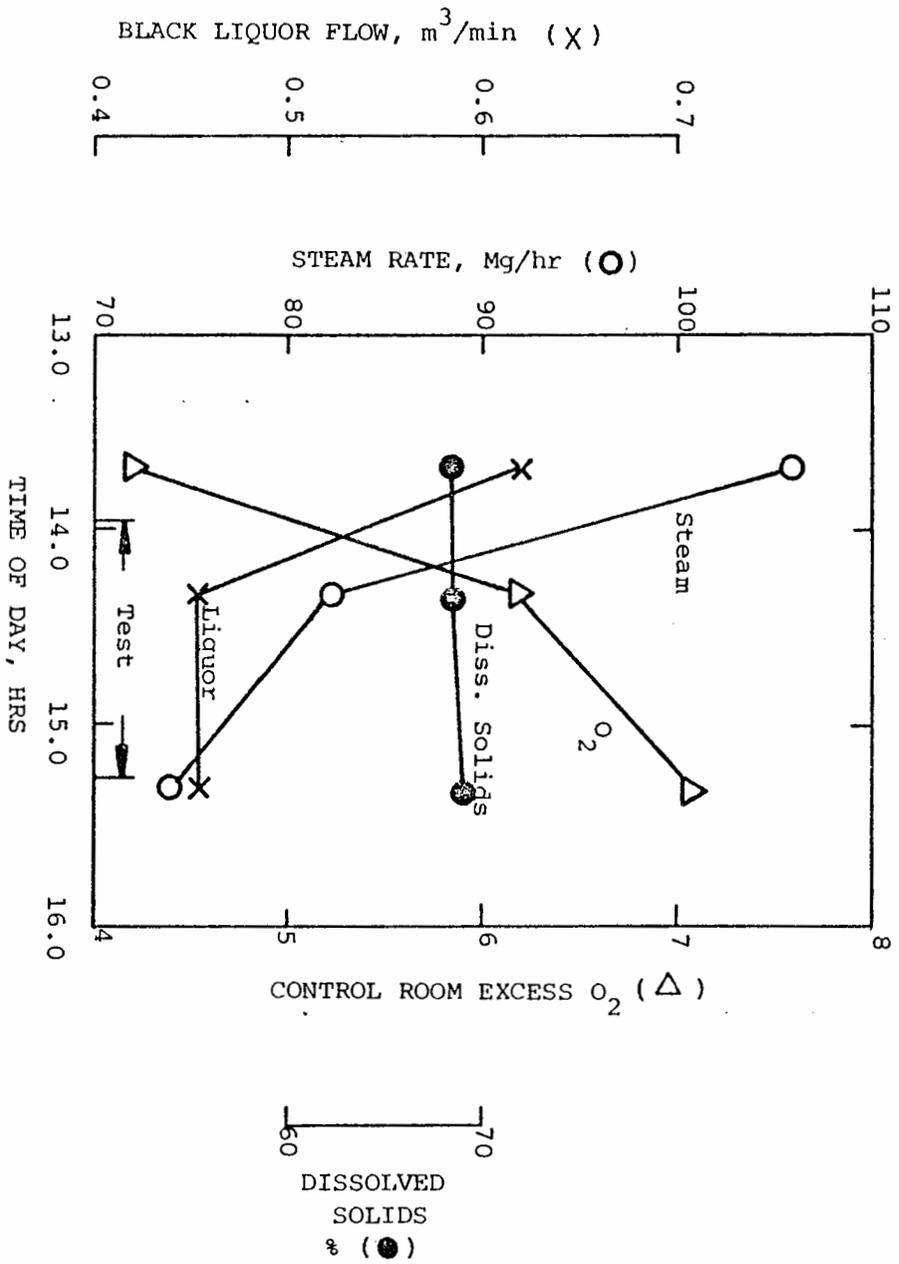


Figure 4-53. Trace species test 10/2-12 boiler conditions.

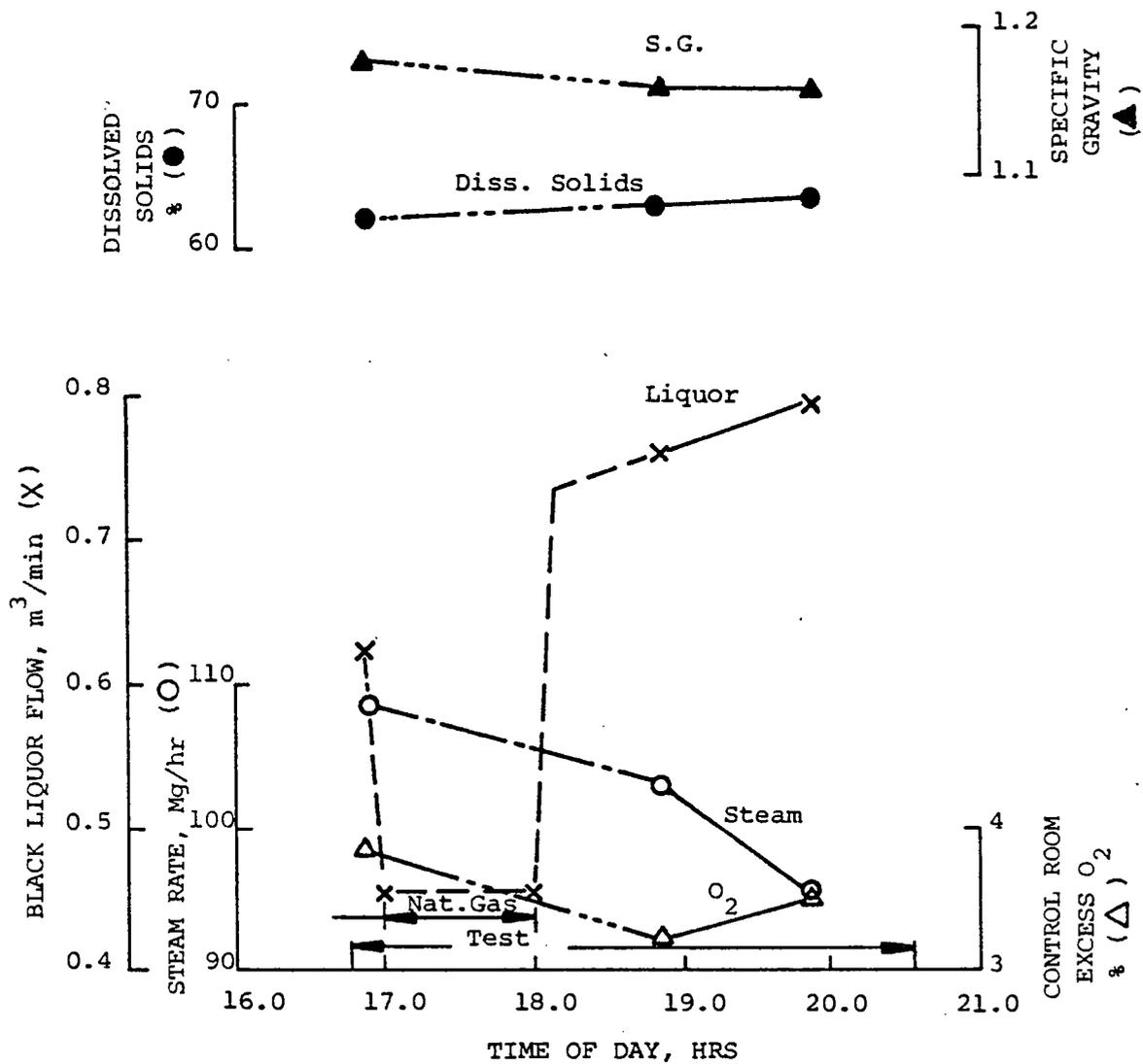


Figure 4-54. Trace species test 10/2-14 (Part 1) boiler conditions.

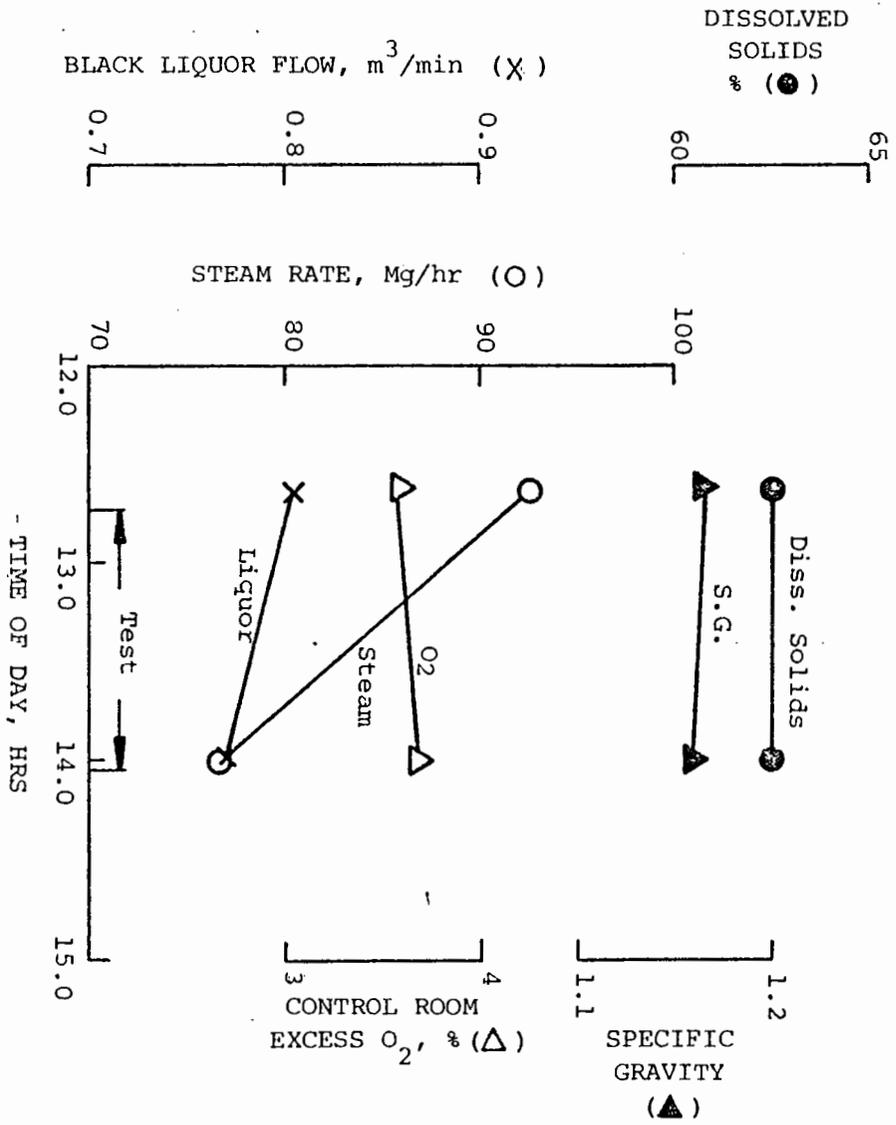


Figure 4-55. Trace species Test 10/2-14 (Part 2.)

marked increase in flue gas moisture content between the inlet to the contact evaporators (23%) and the exit from the wet bottom precipitators (33%). This increase is due to the moisture evaporated from the liquor by the flue gas within these two direct contact devices. The cyclone flow rate was within 1.2% of the nominal value and was sampling at 97.7% of isokinetic conditions. Unit operation, in terms of steam rate and liquor flow to the burners, was nominal during the course of the test as shown in Figure 4-56. However, the unit had been operating without salt cake addition to the liquor as the supply had been exhausted.

Results of the four trace species and organics tests are summarized in Table 4-48. Detailed data are presented in Appendix F, Tables F-21 to F-39. All species were detected except for mercury, tellurium, tin and PCB. Results for duplicate tests at the ESP inlet and at the outlet show good repeatability for cadmium, calcium, chromium, copper, iron, lead, manganese, nickel, selenium, and titanium. At the precipitator inlet, the second test (10/2-12) was conducted with the unit somewhat upset and operating at higher  $O_2$  (7.8%) than for the first test (10/2-10). The increased  $O_2$  appeared to affect two species. For the second test the chloride emissions are much higher but total POM is much lower. Total hydrocarbons were also much lower for the second test (Table 4-45).

The concentrations were reduced by the precipitator for all detected species. Precipitator collection varied from about 65% to over 99% for the data that shows comparable duplicate test results.

As can be seen in Appendix F the mass balances for this unit were consistently high (order of 2 x input) due to species concentrations in the smelt exceeding that of the fuel input. Calculated smelt flow rate may have been too high. Smelt flow could not be measured but was determined from a sodium balance, which should be as accurate a method as practical. The hot smelt sample was removed from the furnace bottom with a steel ladle which could have contaminated the sample. Smelt drops from the furnace floor into a dissolving tank and therefore is not cooled to a temperature for normal ash sampling procedures.

Specific POM compound emissions were highest for anthracene, fluoranthene, chrysene, and benzo fluorantheses (Table F-39). Many other specific POM compounds were present.

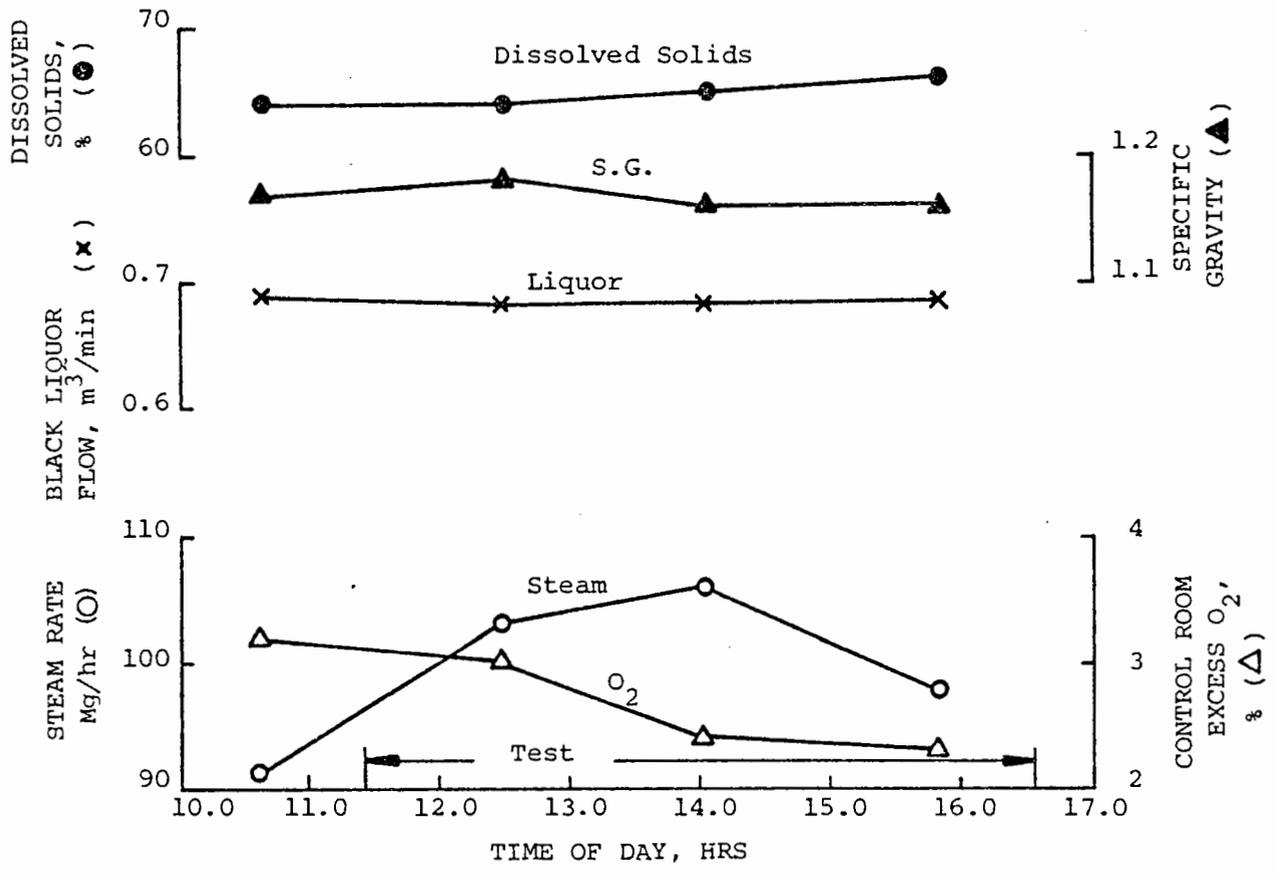


Figure 4-56. Trace species test 10/2-16 boiler conditions.

TABLE 4-48. TRACE SPECIES AND ORGANIC EMISSIONS  
BLACK LIQUOR RECOVERY BOILER LOCATION 10/2

Species Concentration,  $\mu\text{g}/\text{Nm}^3$

Sampling Location	Furnace Outlet		ESP Outlet	
	10/2-10	10/2-12	10/2-14	10/2-16
Test No.				
Antimony	3700 < 4600	< 3400	< 490	< 160
Arsenic	42 < 200	< 200	< 15	< 15
Barium	15000	1400 < 1600	120 < 190	150
Beryllium	0.43 < 19	< 23	0.008 < 3	5.1 < 8.4
Cadmium	130 < 240	130 < 250	30 < 33	18 < 19
Calcium	7300	2000	1200	440
Chromium	750	1700	220	150
Cobalt	500 < 610	160 < 290	48 < 68	300 < 320
Copper	100	71 < 75	7.9 < 10	3.3 < 7
Iron	5200	5600	1400	1700
Lead	180 < 390	170 < 390	2.1 < 69	63 < 130
Manganese	1200	430	51	32
Mercury	< 80	< 80	< 9.3	< 9.9
Nickel	540	500 < 530	93 < 120	69 < 91
Selenium	< 560	1100 < 1600	1.9 < 72	1.9 < 110
Tellurium	< 11000	< 1900	< 2600	< 2700
Tin	< 13000	< 16000	< 2900	< 2800
Titanium	61 < 3900	23 < 4900	7.5 < 930	1900 < 2600
Vanadium	6.7 < 610	< 620	0.09 < 110	< 130
Zinc	1200	560	2.4	84
Chloride	79000	$4.1 \times 10^6$	160000	13000
Fluoride	13000 < 14000	6500 < 8300	2400	330 < 460
Nitrates	200 < 290	7100 < 7300	4600	9.1 < 91
Sulfates	$7.9 \times 10^6$	$4.2 \times 10^6$	14000 < 39000	46000
Total POM	79000	5800	56000	5000
Total PCB	< 7300	< 3300	< 290	< 130
For Additional Data, see Tables Noted in Appendix F	F-21 to F-26	F-27 to F-29	F-30 to F-32	F-33 to F-39

See Table F-1 for explanation of table values.

#### 4.4.4 Location 11 Tests - Carbon Monoxide Boiler

##### Equipment Characteristics--

The CO boiler at Location 11 was designed by B&W to recover the heat discharged from the fluid catalytic cracking unit (FCCU) regenerator that processes 4770 m<sup>3</sup>/d (30,000 bbl/d) in an oil refinery. The boiler was rated at 136,054 kg/hr (300,000 lb/hr) steam flow firing CO rich gases from the regenerator and refinery gas at 135 MW (461x10<sup>6</sup> Btu/hr) heat input.

Analysis of the gas composition of the CO gas from the regenerator and of the refinery gas were provided by the refinery. The total heat input to the boiler was divided approximately 50% to the refinery gas and 50% to the CO gas. The CO rich gas has a low heating value but a large volume at relatively high temperature is consumed. Analyses of the two gases are presented in Table 4-49.

TABLE 4-49. CO BOILER FUEL COMPOSITION

Component	Composition, % Volume	
	Refinery Gas	CO Gas
CH <sub>4</sub>	94.8	--
CO	1.5	9.8
N <sub>2</sub>	1.2	80.0*
H <sub>2</sub>	0.6	--
H <sub>2</sub> O	1.3	--
CO <sub>2</sub>	0.6	9.4
O <sub>2</sub>	--	0.8
TOTAL	100.0	100.0
Heating value		
MJ/m <sup>3</sup>	35.35	1.15
(Btu/cf)	949	30.9

\*By difference

The unit was fired with four B&W spud type gas burners and had NO<sub>x</sub> ports on the right and left sides for introducing air into the furnace away from the primary combustion zone.

Sampling was done in the duct connecting the boiler with the stack. Four sample probes were installed in the duct with the heated line connected to one probe. Particulate measurements were also made at this sample port. A schematic of the FCCU and CO boiler is presented in Figure 4-57.

#### Baseline Emissions--

Baseline emissions were measured with the unit at 136,961 kg/hr (302,000 lb/hr) steam flow firing CO gas and refinery gas. The measured NO emissions at this firing condition were 147 ng/J (126 ppm corrected to 3% O<sub>2</sub>, dry basis). Total particulate emissions at baseline conditions were measured at 129.3 ng/J (0.301 lb/10<sup>6</sup> Btu) using the EPA Method 5 procedure for determining particulate loading. An observer for opacity readings was not available.

#### Combustion Modifications--

Combustion modifications testing included excess air variation, air register adjustments, burner out of service and NO<sub>x</sub> port adjustment. Test results are presented in Table 4-50. Due to fan limitation, large variations in excess air were not possible at full load conditions. The effect of excess air on NO<sub>x</sub> emissions is shown in Figure 4-58 for the CO boiler. The lowest measured NO<sub>x</sub> emissions was with all burners in service, NO<sub>x</sub> ports closed, and air registers adjusted. With the boiler in the baseline configuration, NO<sub>x</sub> varied from 147 ng/J (126 ppm) to 168 ng/J (144 ppm). An air-register adjustment lowered the NO<sub>x</sub> to 130 ng/J (112 ppm). All of these tests were with the NO<sub>x</sub> ports closed.

NO<sub>x</sub> port adjustment (Tests No. 11-6, 7, and 8) showed little influence in NO<sub>x</sub> emissions. Opening the left side NO<sub>x</sub> ports 100% resulted in a reduction in NO<sub>x</sub> from 168 ng/J (144 ppm) to 162 ng/J (139 ppm) or less than 2%. The right side NO<sub>x</sub> ports and combination right and left sides showed even less influence.

Carbon monoxide measurements were much more sensitive to combustion modifications than were NO<sub>x</sub> emissions. The effect of excess oxygen on CO emissions is shown in Figure 4-59 for all tests on the CO boiler. These data show large increases in CO as the excess oxygen is lowered below about 2%. NO<sub>x</sub> port adjustments led to higher CO values. Opening the left side NO<sub>x</sub> ports

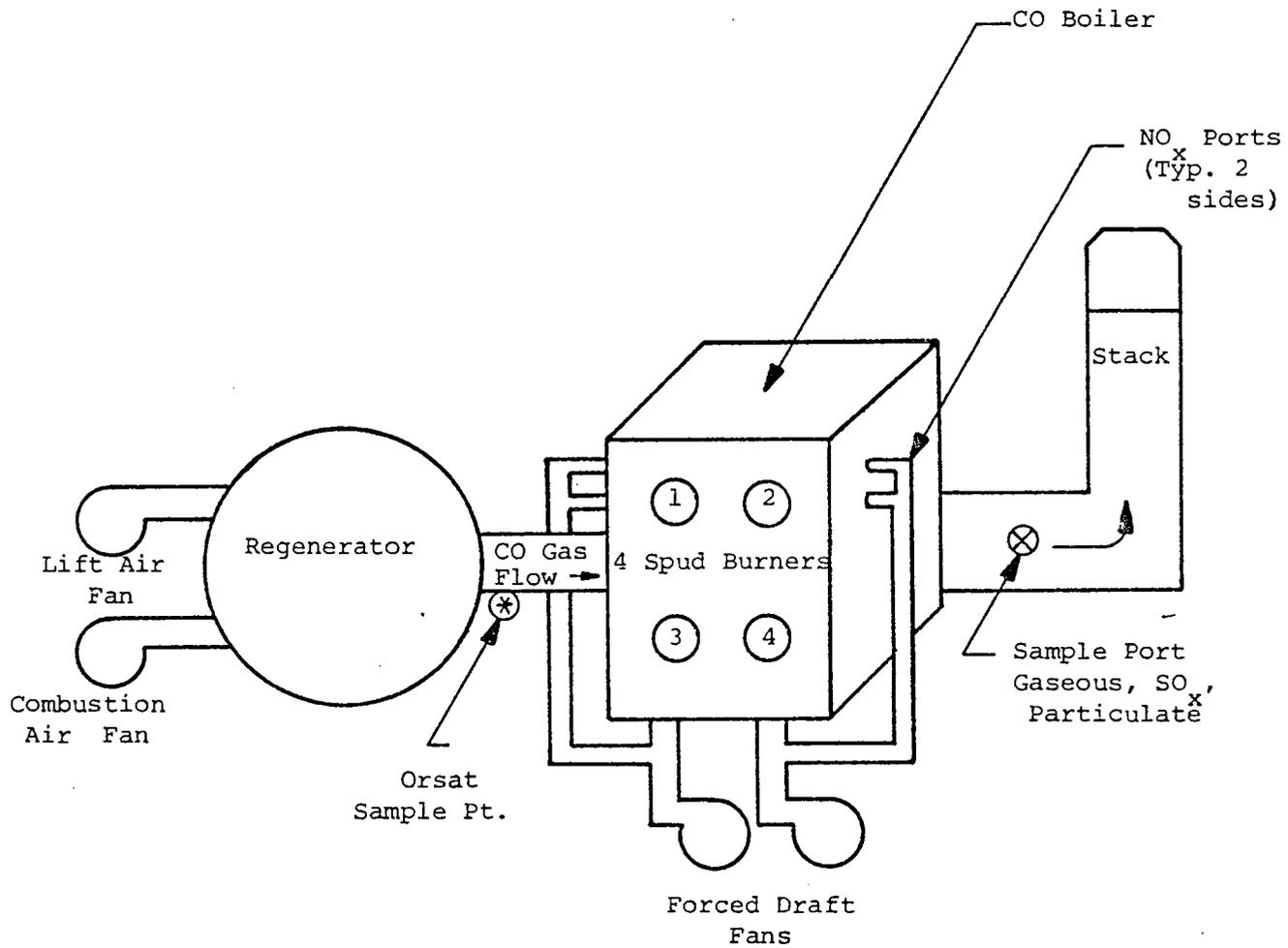


Figure 4-57. Schematic of fluid catalytic cracking unit (FCCU) with CO boiler.

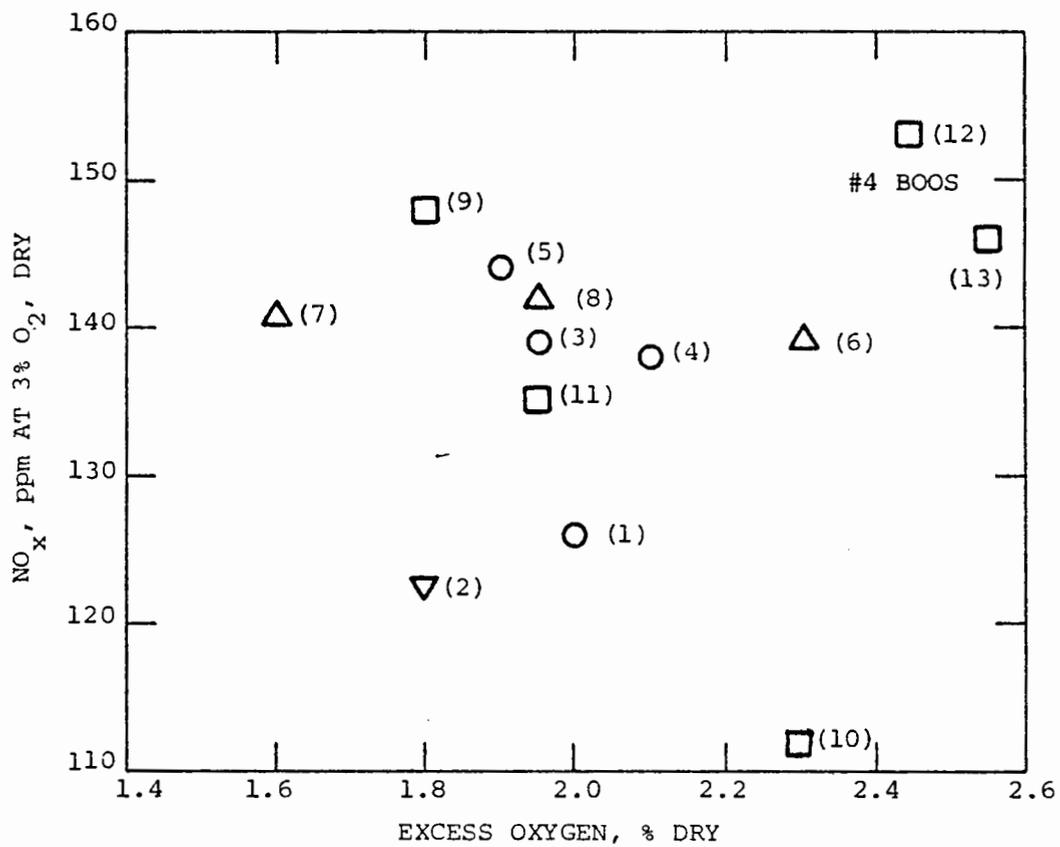
TABLE 4-50. SUMMARY OF FIELD MEASUREMENTS  
LOCATION 11 - CO BOILER

Test Run No.	Date 1976	Load Mg/h (10 <sup>3</sup> lb/h)	Heat Input MM	O <sub>2</sub> %	CO <sub>2</sub> %	NO <sub>x</sub> * ng/J (ppm)	NO* ng/J (ppm)	HC* ng/J (ppm)	CO* ng/J (ppm)	SO <sub>2</sub> * ng/J (ppm)	Wet Chemistry		Total Part. ng/J (lb/MMB)	Solid Part. ng/J (lb/MMB)	Stack Temp. K (*F)	Eff. %	Comments
											SO <sub>2</sub> * ng/J (ppm)	SO <sub>3</sub> * ng/J (ppm)					
11-1	9/7	136.96 (302)	93	2.0	13.8	147 (126)	147 (126)	4 (9)	19 (27)	1165 (720)	--	--	--	--	739 (870)	64.9	Baseline; all BIS, NO <sub>x</sub> ports closed, A/R Config. #1
11-2	9/7	140.59 (310)	93	1.8	14.4	--	142 (122)	--	88 (124)	--	--	--	--	--	744 (880)	64.1	Low O <sub>2</sub> , all BIS, NO <sub>x</sub> ports closed, A/R Config. #1
11-3	9/8	126.08 (278)	88	2.0	13.6	162 (139)	161 (138)	5 (12)	30 (42)	1365 (843)	--	--	--	--	750 (890)	63.8	Baseline; all BIS, NO <sub>x</sub> ports closed, A/R Config. #1
11-4	9/8	124.26 (274)	89	2.1	13.8	161 (138)	161 (138)	5 (12)	21 (30)	1355 (837)	2488 (1512)	66 (41)	129.3 (.301)	107.3 (.250)	754 (898)	63.4	Baseline; partic. & SO <sub>x</sub> , NO <sub>x</sub> ports closed, A/R Config. #1
11-5	9/9	129.70 (286)	90	1.9	13.6	168 (144)	165 (142)	2 (6)	44 (62)	1496 (924)	--	--	--	--	736 (865)	65.0	Baseline; all BIS, NO <sub>x</sub> ports closed, A/R Config. #1
11-6	9/9	126.08 (278)	90	2.3	13.8	162 (139)	162 (139)	5 (12)	23 (32)	1360 (840)	--	--	--	--	728 (850)	65.4	NO <sub>x</sub> port adjust., left side 100% open, A/R Config. #1
11-7	9/9	127.89 (282)	90	1.6	12.0	164 (141)	164 (141)	2 (6)	104 (147)	1337 (826)	--	--	--	--	730 (855)	65.4	NO <sub>x</sub> port adjust., right side 100% open, all BIS, A/R Con. #1
11-8	9/9	126.98 (280)	89	2.0	14.3	165 (142)	165 (142)	5 (13)	107 (151)	1357 (838)	--	--	--	--	733 (860)	65.0	NO <sub>x</sub> port adj., rt. & left sides, 50% open, all BIS, A/R Con. #1
11-9	9/9	126.98 (280)	89	1.8	13.9	172 (148)	172 (148)	4 (11)	11 (15)	1498 (925)	--	--	--	--	736 (865)	64.8	Air reg. adj., A/R Config. #2, all BIS, NO <sub>x</sub> ports closed
11-10	9/10	128.80 (284)	92	2.3	11.7	130 (112)	--	--	11 (16)	795 (491)	--	--	--	--	725 (845)	65.8	Baseline test, NO <sub>x</sub> ports closed, all BIS, A/R Config. #2
11-11	9/10	126.98 (280)	92	2.0	14.4	157 (135)	157 (135)	2 (6)	47 (66)	1480 (914)	--	--	--	--	722 (840)	65.7	#2 BOOS, NO <sub>x</sub> ports closed, A/R Configuration #2
11-12	9/10	128.80 (284)	92	2.5	13.6	178 (153)	178 (153)	2 (5)	6 (8)	1389 (858)	--	--	--	--	728 (850)	65.4	#4 BOOS, NO <sub>x</sub> ports closed, A/R Configuration #2
11-13	9/10	126.08 (278)	92	2.6	13.6	170 (146)	170 (146)	2 (5)	3 (4)	1525 (942)	--	--	--	--	725 (845)	65.6	Baseline, all BIS, A/R Con. #2, NO <sub>x</sub> ports closed

NOTE: \*NO, NO<sub>x</sub>, HC, CO and SO<sub>2</sub> ppm reported on 3% O<sub>2</sub>, dry basis.

Air Register Configuration

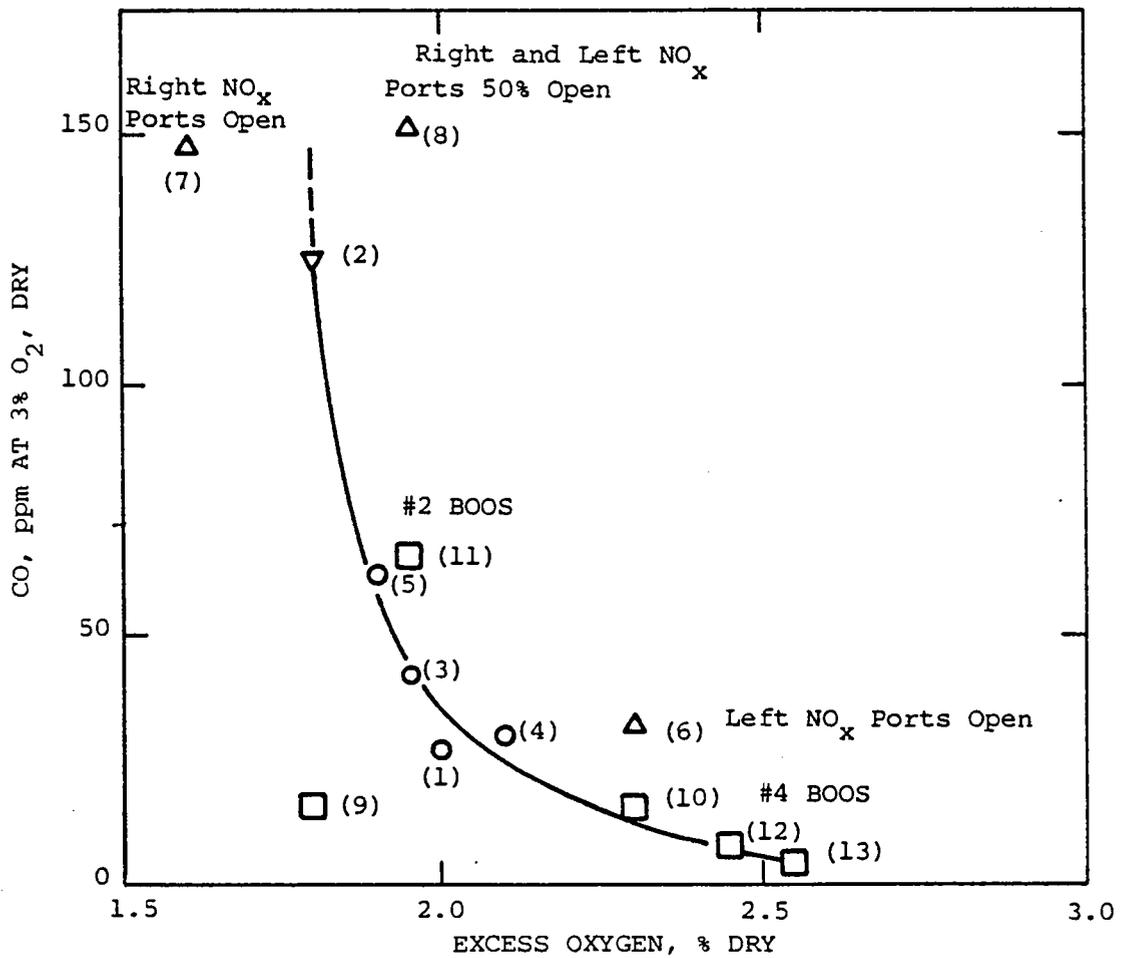
A/R No.	1	2
1	68%	68%
2	68%	68%
3	53%	84%
4	63%	84%



Location 11, Refinery Gas  
and CO Gas Fuel

- ( ) Test Number
- Baseline, A/R Config. 1
- ▽ Excess Air Adjustment
- △ NO<sub>x</sub> Port Adjustment
- Air Register Config. 2

Figure 4-58. NO<sub>x</sub> versus excess oxygen for a carbon monoxide boiler.



Location 11 CO Boiler  
 Fuel: CO Gas & Refinery Gas  
 ( ) Test Number  
 ○ Baseline A/R Config. 1  
 ▽ Excess Air Reduction  
 △ NO<sub>x</sub> Port Adjustments  
 □ Air Register Config. 2

Figure 4-59. CO as a function of excess oxygen for a CO boiler.

reduced CO from 44 ng/J (62 ppm) to 23 ng/J (32 ppm), which was opposite the effect exhibited by opening the right NO<sub>x</sub> ports or a combination of right and left ports. Opening the right NO<sub>x</sub> ports resulted in an increase in CO to 104 ng/J (147 ppm) and opening right and left ports 50% resulted in an increase to 107 ng/J (151 ppm). This effect is attributed to flame pattern variations in the furnace. Air register adjustment, however, allowed the excess oxygen to be lowered without significantly increasing the CO emission. By adjusting the air registers, the O<sub>2</sub> was lowered to 1.8% with the CO measured at 11 ng/J (15 ppm).

Two tests with one burner out of service showed little effect on NO<sub>x</sub>.  
Efficiency--

CO boiler efficiency was calculated using the heat loss method and the analysis of CO gas and refinery gas as furnished by the refinery. High stack temperatures resulted in high dry gas losses for the boiler. Efficiency for the unit ranged from a low of 63.4% to a high of 65.8%. The average efficiency for the unit with the air registers in a modified configuration was about 1.2% higher than in the normal or "as-found" configuration--65.5% versus 64.3%.

#### 4.5 INTERNAL COMBUSTION ENGINES

Two internal combustion engines were tested: a natural gas compressor and a diesel electric generator. The following sections describe the equipment and emissions measurements.

##### 4.5.1 Natural Gas Engine, Location 2

###### Equipment Characteristics--

The test unit was a natural-gas fueled, spark ignited, two-stroke cycle internal combustion engine located in a natural gas processing plant. The eight cylinder engine was a natural aspirated engine made by Clark in 1943, and is rated at 880 hp. Air supply to the engine was controlled by butterfly valves located in each intake manifold. Fuel flow to each cylinder was adjusted with the fuel intake valve. Limited speed control was achieved by means of a governor on the engine. Load changes were made by varying the suction pressure on the compressor which the engine was driving. A schematic of the engine is shown in Figure 4-60.

Engine and compressor instrumentation consisted of eight cylinder exhaust temperature thermocouples, engine tachometer, first stage compressor inlet pressure and temperature, second stage discharge pressure, manifold vacuum, and fuel pressure. These readings were recorded at each engine setting.

An analysis of the natural gas which was fired was obtained from the operating company. The gas analysis is presented in Table 4-51.

TABLE 4-51. NATURAL GAS COMPOSITION, LOCATION 2

Component	<u>Mole percentage</u>
Methane (CH <sub>4</sub> )	89.66
Ethane (C <sub>2</sub> H <sub>6</sub> )	3.30
Propane (C <sub>3</sub> H <sub>8</sub> )	3.05
Iso-butane (C <sub>4</sub> H <sub>10</sub> )	0.87
n-butane (C <sub>4</sub> H <sub>10</sub> )	1.52
Pentane & higher (C <sub>5</sub> H <sub>12</sub> )	<u>1.60</u>
	100.00%

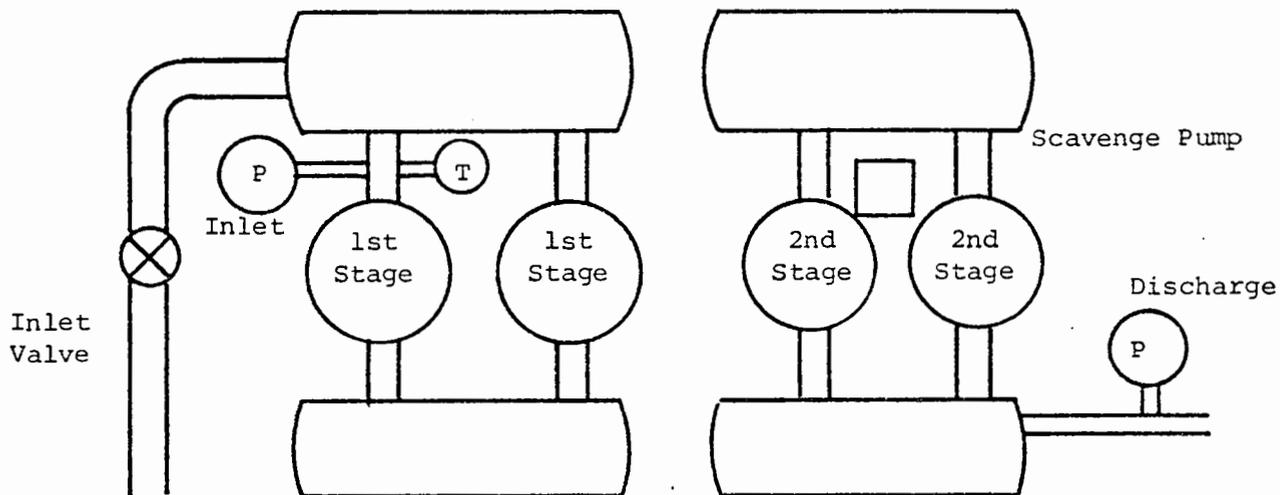
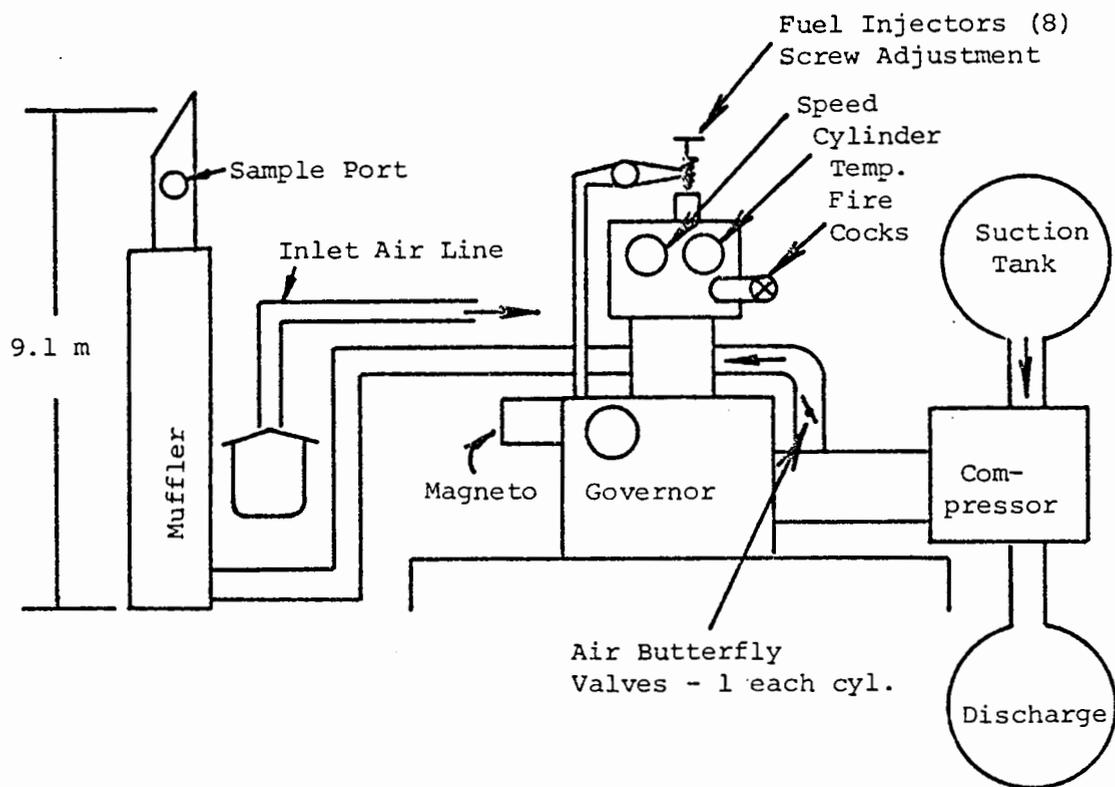


Figure 4-60. Schematic of the natural gas engine at Location 2.

### Special Instrumentation Requirements--

No special instrumentation was required for the testing at this location. The engine tested was instrumented to give most operating parameters. Pressure and temperature gages were installed at the compressor inlet and a compressor discharge pressure was installed to give load characteristics. However, fuel flow, air flow and power were not measurable. Sufficient data were taken to estimate relative power as a percent of baseline.

### Gaseous and Particulate Emission Results--

Baseline tests were conducted on the engine operating in the "as-found" condition.  $\text{NO}_x$  emissions were measured at 976 to 1104 ng/J (1900 to 2150 ppm corrected to 3%  $\text{O}_2$ , dry) with the engine operating at 12.5% to 12.7%  $\text{O}_2$ . Emissions data are presented in Table 4-52. The high volume cascade impactor (eight-stage Andersen) was also run at this engine setting but no measurable particulate was collected so no further particulate tests were scheduled with this unit.

Visual opacity readings were made and the stack was absolutely clear.

### Combustion Modifications--

Combustion modification testing on this unit consisted of load reduction, speed variation, and engine air and fuel flow variation.

1. Load Variation--Gaseous emissions data were taken and a stack gas velocity traverse was conducted at each load condition as the engine load was reduced. The load was varied by reducing the inlet pressure by closing the valve on the compressor inlet. Normal inlet pressure was 13 psig and the load was reduced in 1 psig decrements to 10 psig, the lower limit. Below 10 psig, the engine began to pulsate. After the lower load condition, the engine was reset to the normal operating condition. The effect of load is shown graphically in Figure 4-61. The  $\text{NO}_x$  shows a peak, then drops off sharply as load is increased.

TABLE 4-52. SUMMARY OF TEST RESULTS  
LOCATION 2 - INTERNAL COMBUSTION ENGINE

Test No.	Date 1976	Heat Input MW	O <sub>2</sub> (%)	CO <sub>2</sub> (%)	NO <sub>x</sub> * (ppm)	NO <sub>x</sub> (ng/J)	NO* (ppm)	NO (ng/J)	CO* (ppm)	HC* (ppm)	RPM	Comments
2-1A	4/20	3.14	13.8	4.0	--	--	1670	858	1075	--	260	Baseline + impactor
2-1B	4/20	3.14	12.7	4.5	1988	1021	1626	835	1149	--	260	" "
2-1C	4/20	3.14	12.5	4.9	1908	980	1906	979	995	--	260	" "
2-1D	4/20	3.14	12.5	4.9	1896	974	1800	924	1059	--	260	" "
2-1E	4/20	3.14	12.7	4.8	2118	1088	1746	897	759	--	260	" "
2-1F	4/20	3.14	12.8	4.7	2154	1106	1724	885	785	--	260	" "
2-2A	4/21	3.11	13.0	4.7	2222	1141	1940	996	619	13,500	270	Load variation
2-2B	4/21	3.28	13.3	4.6	2331	1197	1974	1014	639	14,630	270	" "
2-2C	4/21	3.19	13.3	4.4	2283	1172	1917	984	643	14,727	275	" "
2-2D	4/21	3.50	13.3	4.4	2180	1120	1800	924	592	15,330	275	" "
2-2E	4/21	3.17	13.3	4.6	2283	1172	1870	960	608	15,195	275	" "
2-3A	4/22	3.03	13.2	4.8	1941	997	1628	836	654	8,025	270	Speed variation
2-3B	4/22	3.25	12.9	5.0	1785	917	1480	760	685	5,963	300	" "
2-3C	4/22	3.00	13.5	4.6	1927	990	1608	826	576	10,200	250	" "
2-4A	4/22	3.42	13.0	4.7	1783	916	1474	757	675	6,750	295	Air adjustment
2-4B	4/22	3.17	13.2	4.4	1890	971	1500	770	600	8,769	275	" "
2-5A	4/23	3.11	13.3	4.7	1572	807	1180	606	725	11,688	260	Fuel adjustment
2-5B	4/23	2.89	13.3	4.7	1598	821	1309	672	643	9,818	265	" "
2-5C	4/23	3.25	13.3	4.8	1534	788	1216	624	666	8,416	280	" "

\*Dry, corrected to 3% O<sub>2</sub>.

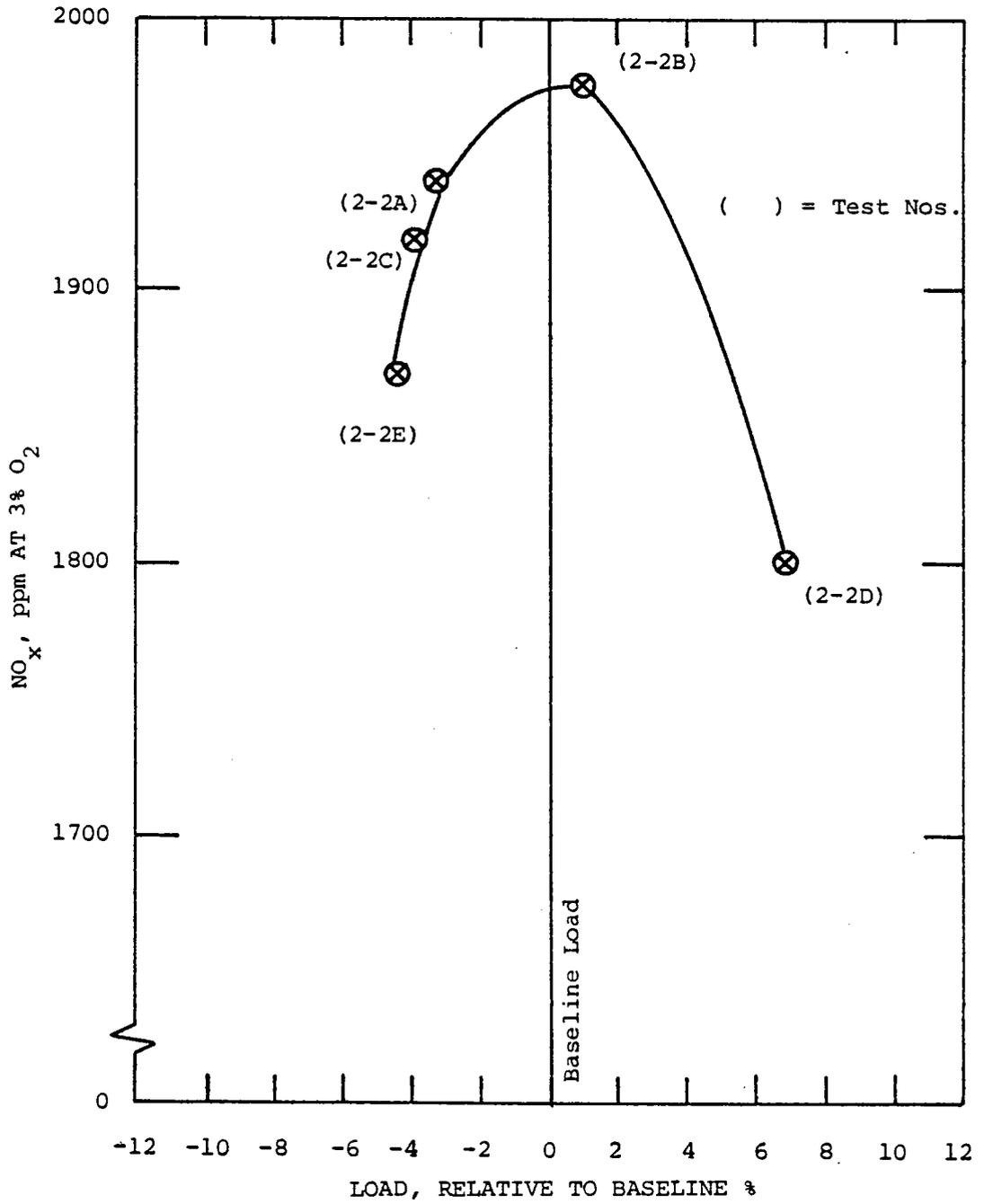


Figure 4-61. Effect of load on NO emissions from the internal combustion engine at Location 2.

2. Speed Variation--Tests were conducted to evaluate the effect of engine speed on emissions by adjusting a governor located on the engine. The initial test of this series was at the "as-found" engine speed, approximately 270 RPM. The speed was then increased to 300 RPM and finally decreased to 250 RPM. Gaseous emissions measurements were made and a velocity traverse by the exhaust stack was conducted at each setting. No appreciable effect on NO emissions was observed but HC emissions exhibited strong dependence on engine speed as shown in Figure 4-62. This is understandable since the major source of unburned hydrocarbons is due to short circuiting during the scavenging process; and the amount of short circuiting should be inversely related to the engine speed.

3. Engine Air and Fuel Adjustment--Tests were conducted to determine the effect of air/fuel ratio on emissions from the engine. For two-cycle engines, the stack level of oxygen is not an indication of the air/fuel ratio in the engine cylinders during the combustion process. In this type of engine the induction and exhaust process occurs in one crankshaft revolution. During a portion of the cycle, both the intake and exhaust ports are open simultaneously and fresh charge scavenges out the remaining combustion products from the cylinder. This short circuiting of fresh mixture during the scavenging process in effect dilutes the combustion products.

A baseline test (2-4A) was conducted with the engine in the "as-found" condition. Air flow to the engine is controlled by eight butterfly valves on each intake manifold. At the baseline condition, six of these eight valves were open. The remaining two valves were then opened completely and measurements were made. This resulted (2-4B) in little change in the gaseous emissions and stack velocity, indicating that there must have been little pressure drop across the valves. Closing the valves to reduce air flow to the engine and decrease the air/fuel ratio from the baseline condition was not attempted because it results in overheating the engine cylinder.

The fuel flow to the engine was then decreased in an attempt to achieve a higher air/fuel ratio. The fuel valve on each cylinder was adjusted until the engine was just able to carry the load. Due to the short circuiting, it is difficult to assess the resulting change in the air/fuel ratio in the cylinders since the stack excess oxygen level is not a direct measure of this

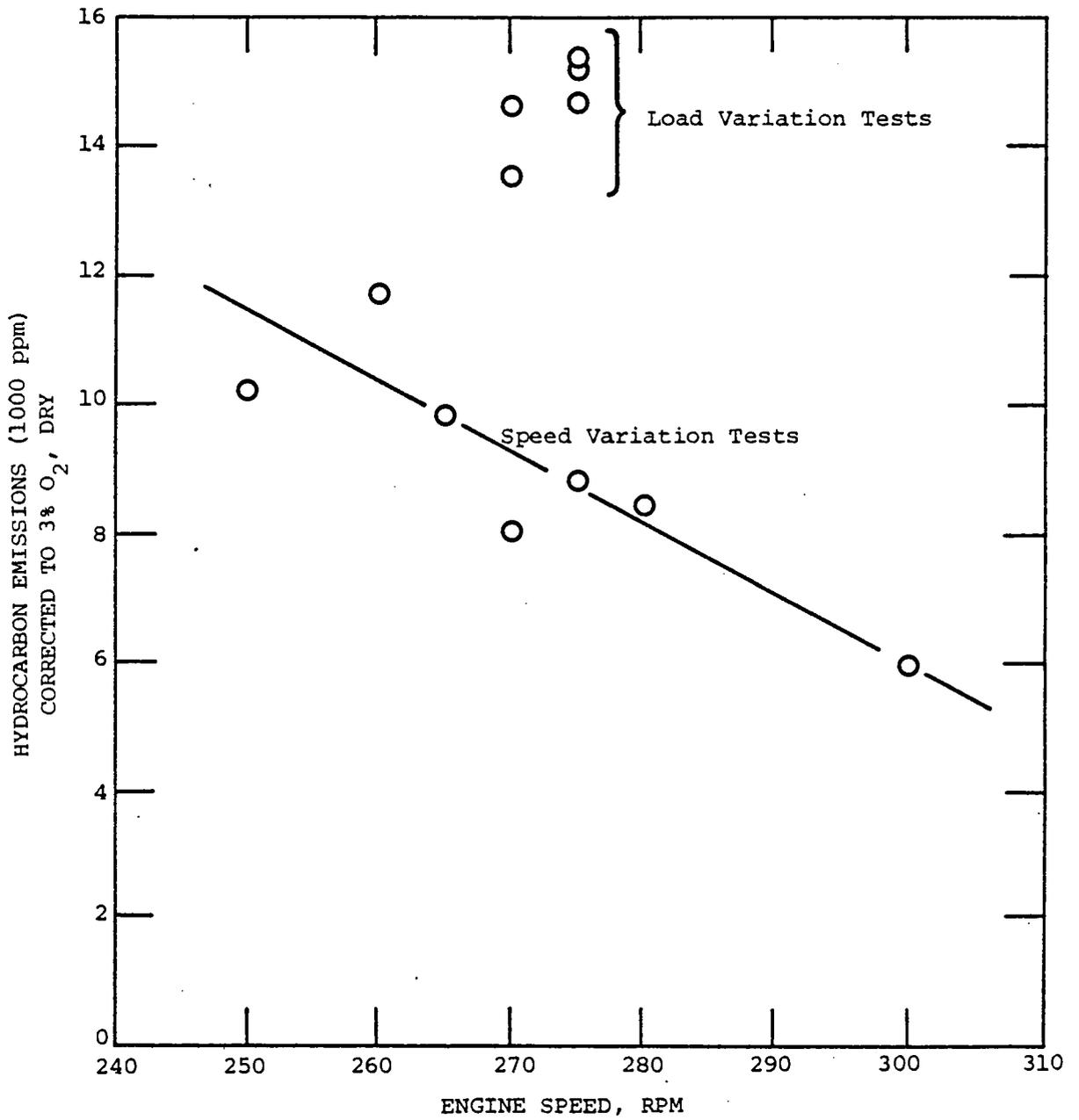


Figure 4-62. Effect of speed on hydrocarbon emissions from an internal combustion engine.

parameter. Since the carbon monoxide and nitric oxide emissions remained essentially constant, it appears that the air/fuel ratio was not greatly altered (see test 2-5B). The fuel valves were then returned to their normal position and an attempt was made to reduce the fuel flow by reducing the gas manifold pressure from the normal setting of 269 kPa (39 psig) to 221 kPa (32 psig). The carbon monoxide and nitric oxide emissions indicated that the air/fuel ratio did not change (test 2-5C). The changes in the unburned hydrocarbon emissions (tests 2-5B and C) appeared to be due to changes in mixture short circuiting with engine speed as opposed to changes in air/fuel ratio.

It is also worth noting that this particular engine is operating with a fairly lean air/fuel ratio in the cylinders. The hydrocarbon emissions originate from two sources (1) unburned hydrocarbons remaining after the combustion process, and (2) "short circuiting" during the scavenging process, with the latter being predominant. The major source of carbon monoxide is the combustion process and thus can be used as an indication of the air/fuel ratio in the chamber. The low carbon monoxide emission levels for this engine indicate that the engine is operating with a fairly high air/fuel ratio relative to stoichiometric.

#### Efficiency--

The efficiency of the internal combustion engine under baseline and modified operating conditions was calculated. No instruments were available for recording fuel and air input flow rates, or compressor power. A velocity and temperature traverse was made across the engine exhaust duct to determine exhaust gas flow rate.

The power delivered by the compressor was taken as  $\int p dV$ . This can be written as  $MEP \cdot \Delta V$  where MEP is the compressor mean effective pressure and  $\Delta V$  is the piston displacement. The time rate of  $\Delta V$ , in turn, is directly proportional to the compressor (and engine) RPM. Reference 7 indicates that the value of MEP is a function of the compressor inlet and discharge pressures, both of which were measured. If it is assumed that the compressor efficiency is constant, then the product  $MEP \cdot RPM$  is a measure of the engine output (load).

Figure 4-63 is the resulting reduced data depicting the variation in engine efficiency (with respect to the baseline) as a function of RPM for a constant load. It is noted that the design RPM (260) yields the highest efficiency for this load.

Figure 4-64 presents engine efficiency as a function of load for constant values of RPM. The trend noted will probably be reversed at larger values of load; i.e., the efficiency will peak and then decrease as the load continues to increase.

#### Conclusions--

NO<sub>x</sub> concentrations for the IC engine tend to be quite high relative to other combustion devices except cement kilns. Fuel adjustment, air adjustment, and speed variation had little effect on the NO<sub>x</sub> emissions from near 2000 ppm for baseline tests to about 1600 ppm for the final fuel adjustment tests. This would appear to be a 20% reduction of NO<sub>x</sub>. However, there appeared to be a day-to-day shift in emissions that could not be attributed to any specific variable, indicating some possible influence other than the parameters measured.

Retarding the spark firing point has been indicated as a means by which NO<sub>x</sub> can be reduced in reciprocating engines. The engine tested at Location 2 had the spark set at 3 to 4 degrees before top dead center. The operators would not allow any adjustment because the engine had two magnetos, one for each four cylinders. Each magneto would have to be adjusted separately. A mismatch in the setting could cause engine operation or maintenance problems not warranted for a temporary test.

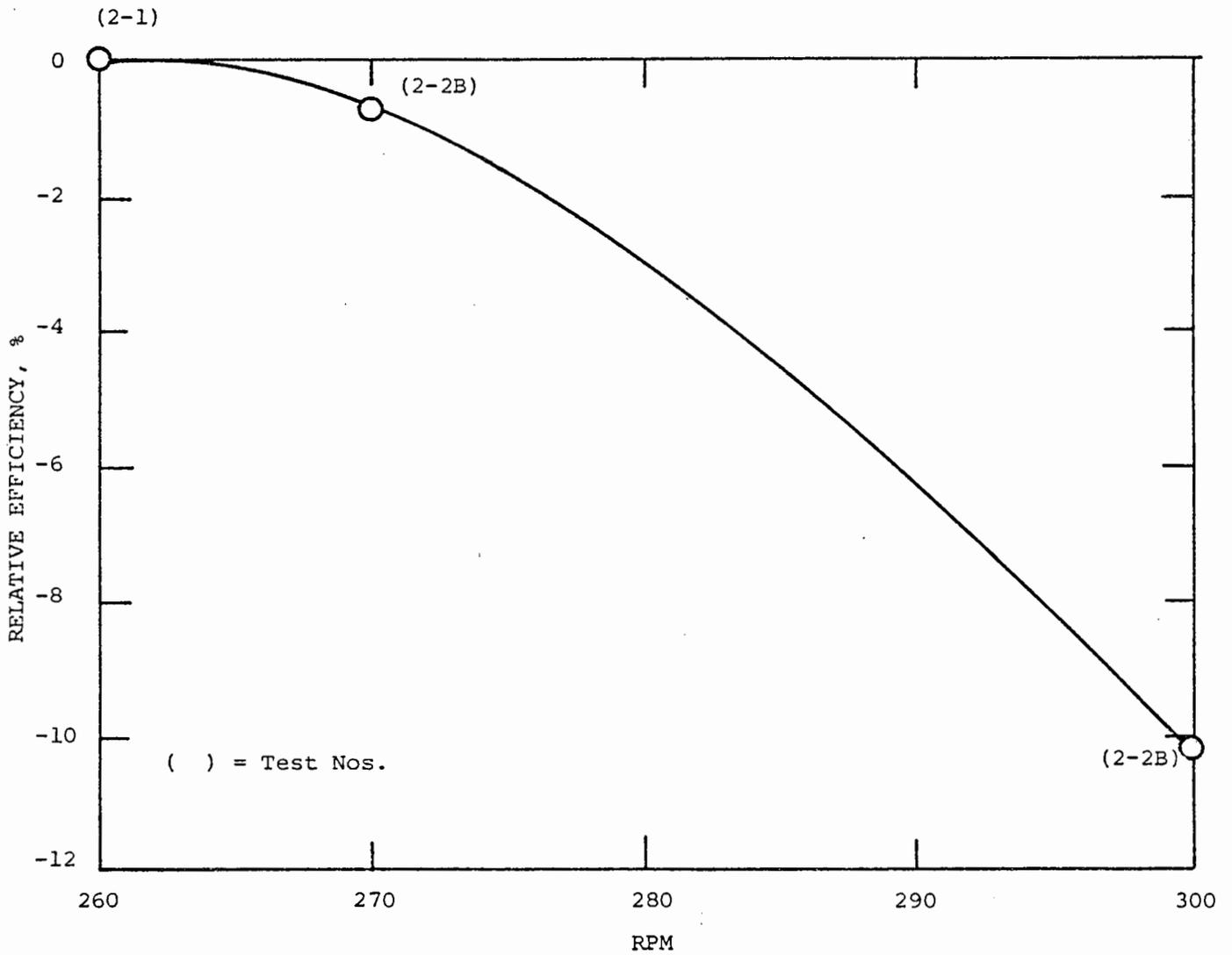


Figure 4-63. Effect of RPM on efficiency at constant load for the natural gas engine at Location 2.

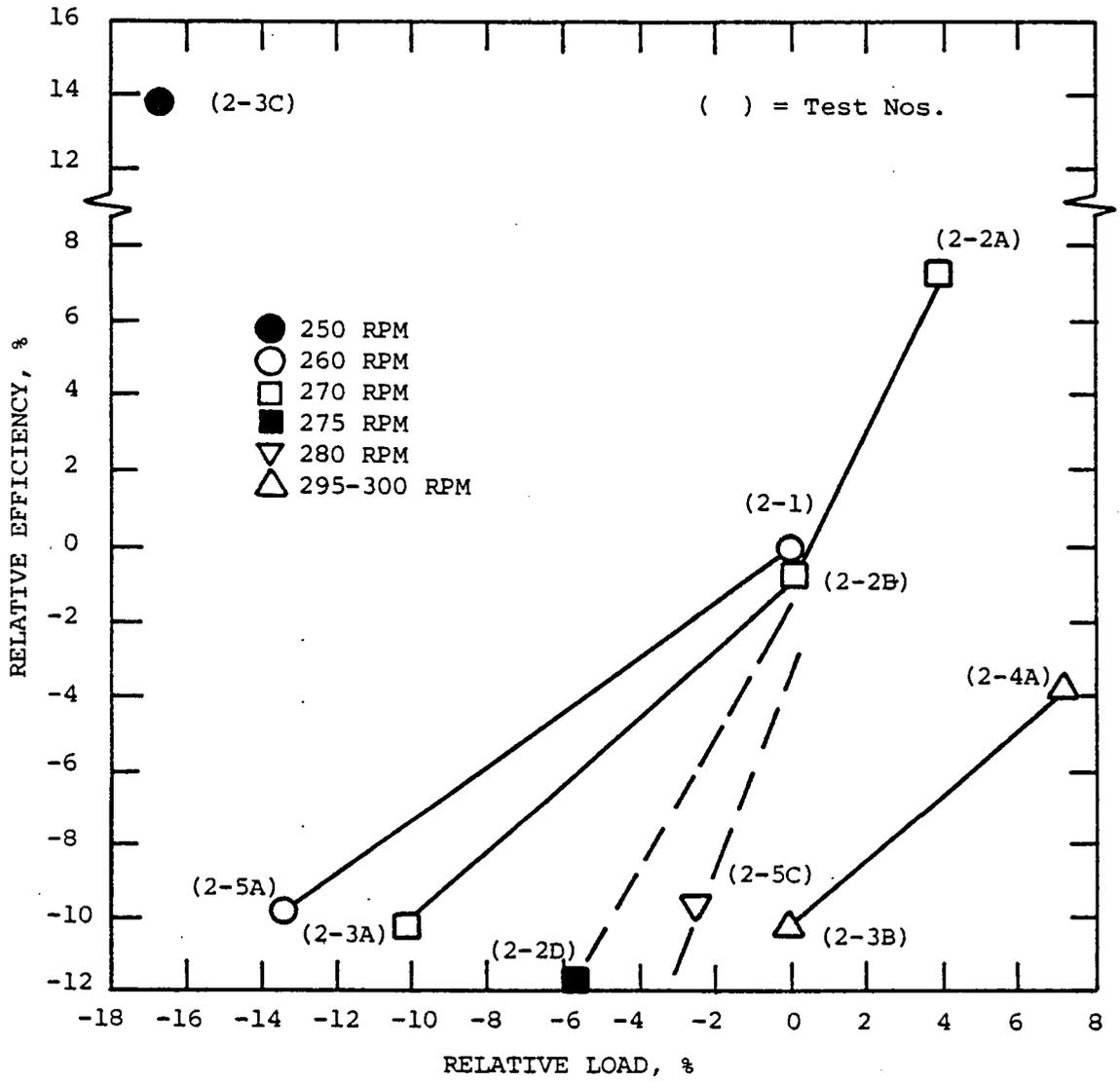


Figure 4-64. Effect of load on efficiency at constant RPM for the natural gas engine at Location 2.

#### 4.5.2 Diesel Engine, Location 15

##### Equipment Characteristics--

The diesel engine tested at Location 15 was a 4-stroke cycle caterpillar turbocharged-aftercooled engine. The engine specifications are:

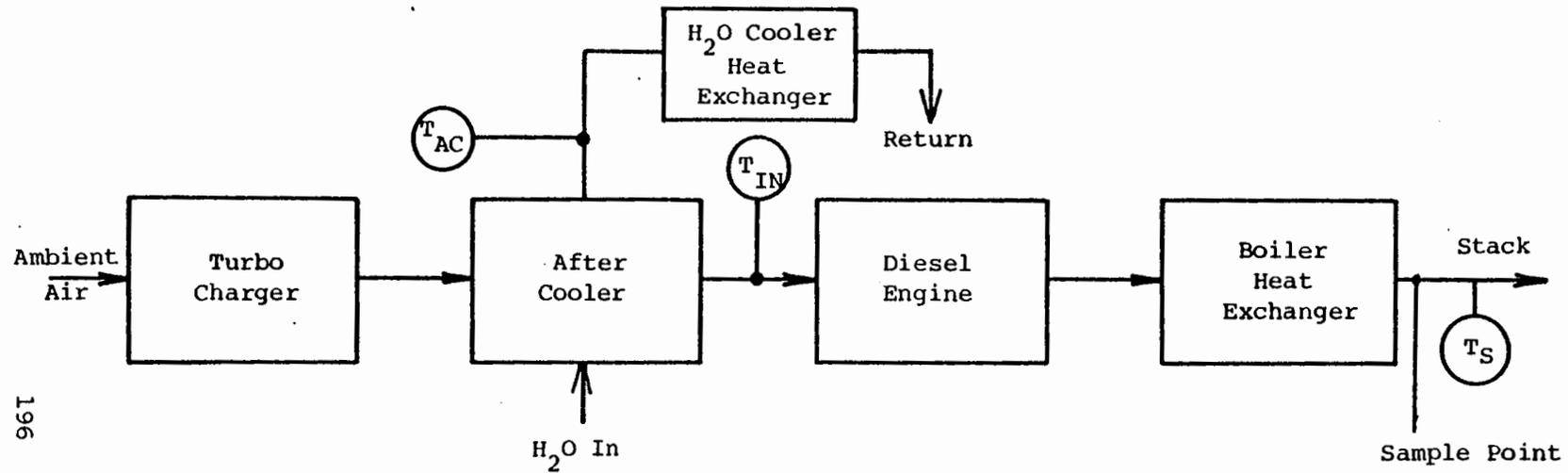
Number of cylinders	V-12
Bore and stroke, mm	159 x 203
inches	6.25 x 8.00
Piston displacement, liters	48.3
cu.in.	2946
Compression ratio	15.5:1
Full load speed	60 Hz, 1200 RPM
Fuel type	No. 2 diesel

The diesel engine drives a generator to supply power to an educational facility. The generator ratings are:

	<u>60 Hz at 1200 RPM</u>
kW at 0.8 P.F. (w/o fan)	600
KVA	750
Voltages available	125/216 230-460 2400
Phase	3
Wire and Connection	10, Wye

##### Emissions Sampling--

Figure 4-65 is a block diagram of the engine inlet air-to-stack flow path. Gaseous emissions measured were NO, NO<sub>x</sub>, CO, HC, SO<sub>2</sub>, and O<sub>2</sub>. The samples were taken in the stack and a single heated sample line was used to transport the sample to the mobile laboratory. Method 5 particulate, cascade impactor, wet chemistry SO<sub>x</sub>, and trace species and organics sampling were conducted at the same point. A summary of the test data is presented in Table 4-53, and Table 4-54 shows the fuel analysis.



196

$T_{AC}$  = After cooler thermocouple  
 $T_{IN}$  = Inlet air temperature thermocouple  
 $T_S$  = Stack gas thermocouple

Figure 4-65. Block diagram of large diesel engine system at Location 15.

TABLE 4-53. SUMMARY OF TEST DATA AT LOCATION 15 - DIESEL ENGINE

Test No.	Date 1977	Heat Input MW	Elec. Output Load MW	O <sub>2</sub> (%)	CO <sub>2</sub> * (%)	NO <sup>†</sup> ng/J (ppm)	HC <sup>†</sup> ng/J (ppm)	CO <sup>†</sup> ng/J (ppm)	SO <sub>2</sub> <sup>†</sup> ng/J (ppm)	Wet Chemistry		Total Partic. ng/J (lb/MMB)	Solid Partic. ng/J (lb/MMB)	Stack Temp. K (*R)	Eff. (%)	Smoke Spot	Comments
										SO <sub>2</sub> <sup>†</sup> ng/J (ppm)	SO <sub>3</sub> <sup>†</sup> ng/J (ppm)						
15-1	4/7	1.2	0.38	10.5	7.9	904 (1611)	10 (54)	33 (96)	93 (119)	--	--	--	--		32.8		As-found - med. load
15-2	4/8	0.2	0.1	15.8	4.2	660 (1177)	220 (1127)	269 (789)	226 (290)	--	--	--	--		26.3	5	Low load
15-3	4/8	0.6	0.19	13.3	5.6	813 (1445)	54 (276)	89 (262)	118 (151)	--	--	--	--		30.2	4.5	Load variation
15-4	4/8	0.9	0.30	11.3	7.3	817 (1456)	8 (41)	40 (119)	97 (124)	--	--	--	--		32.8	3.0	Load variation
15-5	4/8	1.2	0.39	10.6	7.8	838 (1494)	6 (31)	38 (111)	86 (110)	--	--	--	--		33.1	3.0	Load variation
15-6S	4/12	1.5	0.5	9.6	8.6	797 (1421)	13 (67)	29 (85)	130 (167)	97 (124)	9	--	--	664 (736)	33.4	--	SO <sub>x</sub> test
15-6PI	4/13	1.5	0.5	9.4	8.7	805 (1434)	15 (75)	29 (86)	87 (111)	--	--	32.1 (0.0746)	12.3 (0.029)	642 (695)	33.4	2.5	Particulate and impactor
15-7	4/14	1.5	0.5	9.6	8.6	762 (1358)	11 (56)	33 (98)	130 (167)	--	--	--	--	620 (657)	33.4		Maximum aftercooling
15-8	4/14	1.2	0.4	10.1	8.2	732 (1304)	12 (59)	30 (88)	125 (160)	--	--	--	--	618 (652)	33.0		Maximum aftercooling
15-9P	4/15	1.2	0.4	10.0	8.3	735 (1311)	9 (47)	33 (96)	126 (161)	--	--	48.9 (0.114)	12.4 (0.029)	616 (648)	33.0	2.5	Baseline particulate
15-9I,S	4/15	1.2	0.4	10.1	8.2	746 (1330)	11 (58)	30 (89)	128 (164)	124 (159)	12 (16)	--	--	640 (692)	33.0	2.0	Baseline SO <sub>x</sub> , cascade impactor
15-10	4/19	1.2	0.4	10.1	8.2	768 (1369)	12 (64)	30 (88)	137 (175)	--	--	--	6.4 (0.015)	646 (702)	33.0		TS&O Test No. 1
15-11	4/21	1.2	0.4	10.3	8.1	789 (1407)	8 (44)	30 (88)	137 (176)	--	--	--	6.4 (0.015)	650 (710)	33.0		TS&O Test No. 2

\*Calculated based on fuel analysis

†ppm values reported as dry, corrected to 3% O<sub>2</sub>

TABLE 4-54. LOCATION 15 FUEL ANALYSIS

Test No.	15-10	15-11
Date	4/19/77	4/21/77
Fuel Type	No. 2 Oil	No. 2 Oil
Carbon, %	86.95	85.70
Hydrogen, %	12.79	12.65
Nitrogen, %	0.008	0.008
Sulfur, %	0.28	0.24
Ash, %	< 0.001	< 0.001
Oxygen (by difference), %	0.0	0.40
API Gravity at 60 °F	37.4	37.3
Heat of Combustion		
Gross, kJ/kg	45 400	45 120
(Btu/lb)	(19,520)	(19,400)
Net, kJ/kg	42 680	42 450
(Btu/lb)	(18,350)	(18,250)

#### Baseline Tests--

Baseline gaseous emissions were measured with the engine in the "as-found" condition. The baseline load was approximately 0.4 MW. Tests were conducted at up to 0.5 MW but the electrical demand at the facility did not allow steady operation at power outputs in excess of 0.4 MW. Therefore 0.4 MW was selected as baseline. Baseline NO emissions were 905.4 ng/J (1611 ppm). Baseline NO emissions were calculated to be 6.6 g/HP-hr (8.8 g/kW-h) based on engine specifications and actual operating conditions. Data from the engine manufacturer listed NO emissions at 3.7 g/HP-hr (5.0 g/kW-h) at the baseline load condition.

#### Combustion Modifications--

The effect of engine load and inlet air temperature were evaluated and the test results are presented in Table 4-53. The effect of engine load on NO emissions is shown in Figure 4-66. Engine load was reduced from the baseline load of 0.4 MW to 0.1 MW in 0.1 MW increments. At the low load condition (0.1 MW), the NO showed a 27% reduction from the "as-found" condition.

The effect of reduced inlet air temperature on NO emissions is also shown in Figure 4-66 but is shown more clearly in Figure 4-67. NO<sub>x</sub> was found to decrease with reduced inlet air temperature. The decrease in NO<sub>x</sub> was about 8 ppm per K (4.4 ppm per °F) reduction in inlet air temperature with a total 7% reduction over the temperature range tested.

#### Particulate Size Distribution and SO<sub>x</sub> Testing--

Two tests were conducted to measure the total particulate from the diesel engine firing No. 2 diesel fuel at two load conditions. Both tests were performed using the EPA Method 5 to measure total particulate.

At a load of 0.5 MW, the total particulate measured was 32.1 ng/J (0.0746 lb/10<sup>6</sup> Btu) and solid particulate was 12.3 ng/J (0.029 lb/10<sup>6</sup> Btu). When the load was lowered to 0.4 MW, the total particulate measured increased to 48.9 ng/J (0.114 lb/10<sup>6</sup> Btu) and solid particulate was unchanged--12.4 ng/J (0.029 lb/10<sup>6</sup> Btu).

Wet chemistry SO<sub>x</sub> tests were conducted at loads of 0.5 and 0.4 MW using the Shell-Emeryville method. At 0.5 MW, the SO<sub>2</sub> measured was 97 ng/J (124 ppm) and SO<sub>3</sub> was 9 ng/J (12 ppm). The measured SO<sub>2</sub> at 0.4 MW was 124 ng/J (159 ppm) and the SO<sub>3</sub> was 12 ng/J (16 ppm). SO<sub>2</sub> measured with the DuPont Model 400 SO<sub>2</sub> analyzer was 130 ng/J (167 ppm) and 128 ng/J (164 ppm) for 0.5 and 0.4 MW, respectively.

Particulate size distribution was measured at both 0.5 and 0.4 MW loads. An Anderson 2000 high-temperature cascade impactor was used to collect the particulate sample. The particulate size distribution for each load is presented in Figure 4-68. At 0.5 MW load, approximately 53% of the impactor catch was 3 μm diameter or smaller. At 0.4 MW, approximately 82% of the impactor catch was 3 μm or smaller.

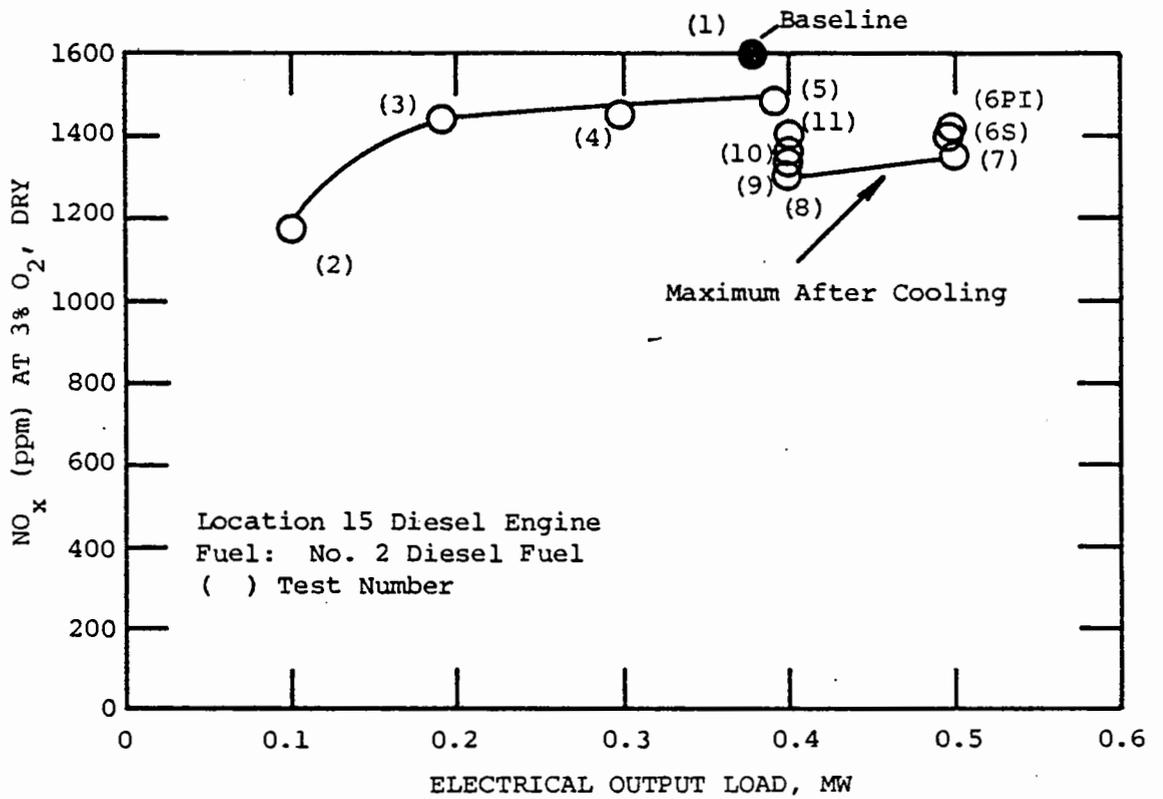


Figure 4-66. The effect of unit load on NO emissions for a diesel engine.

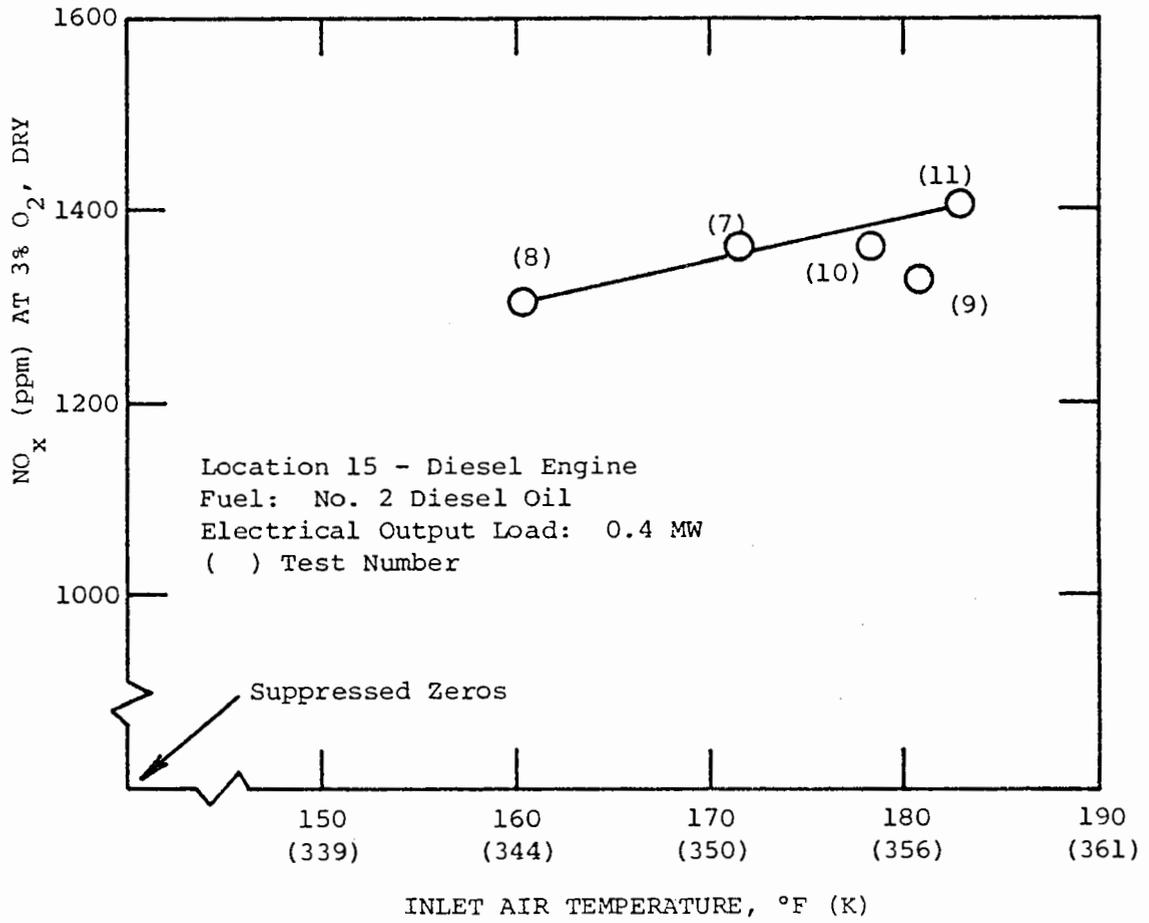


Figure 4-67. The effect of inlet air temperature on NO emissions from a diesel engine.

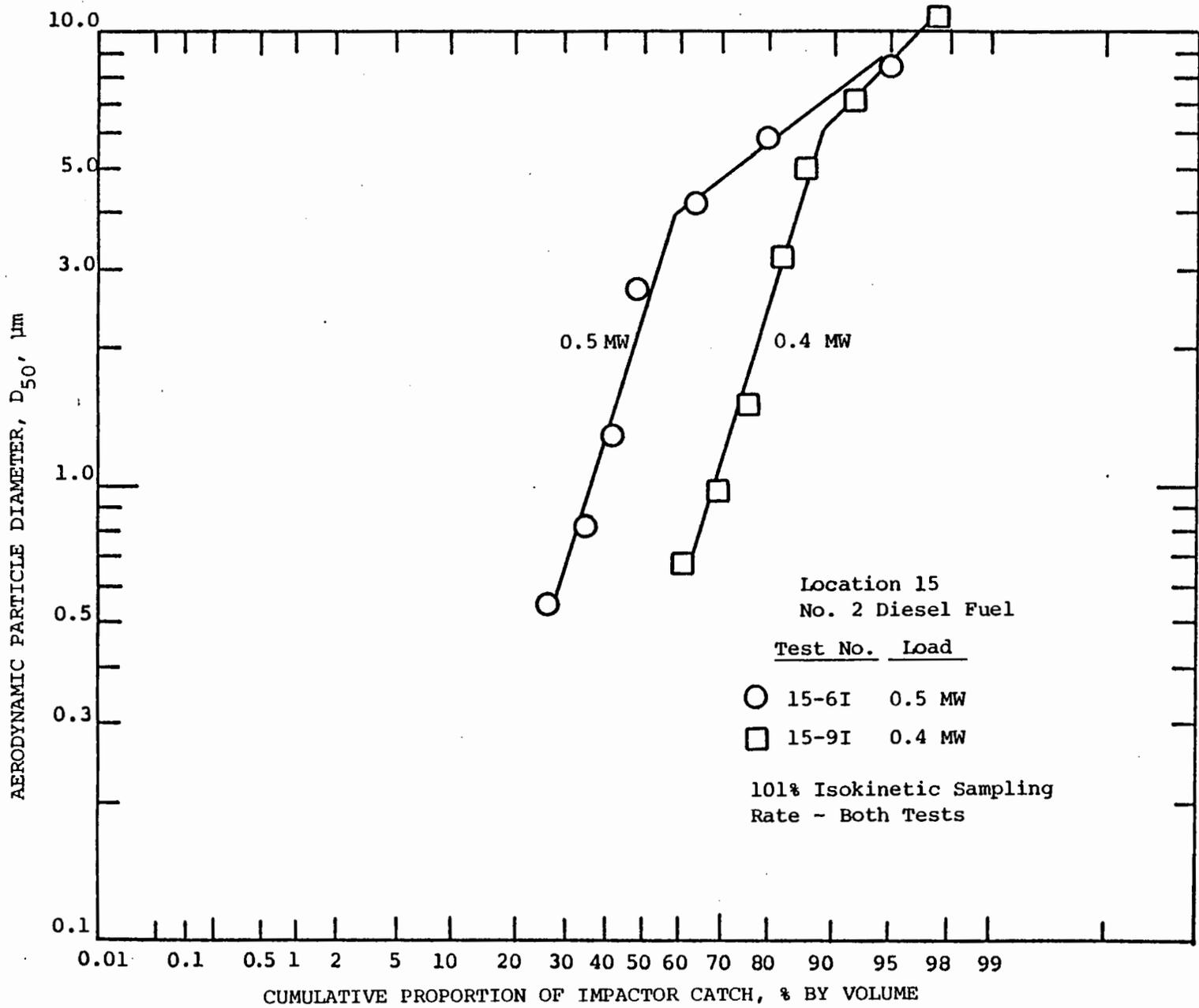


Figure 4-68. Particulate size distribution for a diesel engine firing No. 2 diesel fuel.

### Trace Species and Organics Tests--

Two trace species and organics (TS&O) tests were conducted on the diesel engine at Location 15. The two tests were replicated at the low NO<sub>x</sub> load condition. The TS&O sampling point was in the engine exhaust stack on the centerline. The sampling conditions for the two tests are summarized in Table 4-55.

Results of the sample analysis are summarized in Table 4-56. Detailed data are contained in Appendix F, Tables F-67 to F-76. Of the 26 species to be identified all but antimony, lead and mercury were detected in the exhaust. Only six species could be detected in the diesel fuel: calcium, manganese, zinc, fluoride, nitrates and sulfates. Table 4-57 shows the fuel input and stack output flow rates. The mass balances were less than unity except for nitrates in the first test (15-10). Mass balances were within a factor of two only for calcium (test 15-10) and manganese (both tests). Manganese emissions were higher during the first test; apparent from both the fuel input and SASS measurements. Emissions of zinc were nearly the same for both tests but zinc was below detection in the fuel for the second test.

No solid particulate was collected in the cyclones during the two tests; all material was in the filter, organic module or impingers.

Specific POM's identified (Table F-76) in the XAD-2 resin included anthracene, phenanthrene, methyl anthracene, fluoranthene, benzo(c)phenanthrene, chrysene, benz(a)anthracene, methyl chrysenes, benzo fluoranthenes, benzo(a)-pyrene, and benz(e)pyrene. Anthracene and methyl anthracenes were the predominant compounds. Only four compounds were detected in the organic module wash: anthracene, fluoranthene, chrysene, and benzo fluoranthenes. Of these, chrysene was highest.

TABLE 4-55. TRACE SPECIES AND ORGANICS  
 SAMPLING CONDITIONS - LOCATION 15 DIESEL ENGINE

TS&O Run No.	1	2
Test No.	15-10	15-11
Date	4/19/77	4/21/77
Port Location	Q <sub>L</sub> (6")	Q <sub>L</sub> (6")
Velocity, m/s (f/s)	11.9 (39)	12.8 (42)
Stack Temp., K (°F)	485 (414)	486 (415)
Oxygen Content, % dry	10.1	10.3
Moisture, %	5.6	5.9
Sample time, min.	300	300
Cyclone Flow, awcmm (awcfm)	0.103 (3.64)	0.105 (3.72)
Isokinetic Rate, %	114	108
Oven Temp., K (°F)	479 (403)	482 (408)
XAD-2 Temp., K (°F)	291 (64)	290 (61)
Meter Temp., K (°F)	298 (77)	302 (83)
Nozzle Size, mm (in.)	12.7 (0.5)	12.7 (0.5)
No. Filters Used	1	1
Sample Flow, Dry, scmm (scfm)	0.059 (2.08)	0.060 (2.12)
Volume Collected, Dry, scm (scf)	17.55 (624.1)	18.00 (635.8)
Particulate weight, g	0.2367	0.2364
Solid Particulates, ng/J (lb/MMBtu)	6.43 (0.0149)	6.39 (0.0149)

TABLE 4-56. TRACE SPECIES AND ORGANIC EMISSIONS  
DIESEL ENGINE, LOCATION 15

Species Concentration,  $\mu\text{g}/\text{Nm}^3$

Sampling Location	Stack Exit	Stack Exit
Test No.	15-10	15-11
Antimony	< 360	< 360
Arsenic	4.1	47 < 49
Barium	< 34	830 < 890
Beryllium	3.9 < 5.6	< 5.6
Cadmium	3.6 < 4.1	2.6 < 3
Calcium	1000	160 < 780
Chromium	140	46
Cobalt	0.43 < 68	6.1 < 72
Copper	9.7 < 11	19 < 24
Iron	510	140 < 150
Lead	< 32	< 12
Manganese	30	6.7 < 7.2
Mercury	< 1.8	< 1.8
Nickel	120	3.7 < 56
Selenium	22 < 23	5.4 < 14
Tellurium	< 300	< 290
Tin	< 740	< 720
Titanium	< 1500	< 1500
Vanadium	< 110	< 110
Zinc	74	89
Chloride	1100	1200
Fluoride	68 < 74	47 < 56
Nitrates	480	13
Sulfates	1300	270 < 670
Total POM	< 0.9	< 0.92
Total PCB	< 9	< 9
For Additional Data, see Tables Noted in Appendix F	F-67 to F-72	F-73 to F-76

See Table F-1 for explanation of table values.

TABLE 4-57. TRACE SPECIES MASS BALANCES,  
DIESEL ENGINE, LOCATION 15

	Test 15-10			Test 15-11		
	Fuel Input µg/s	Stack Output, µg/s	Mass Balance, out/in	Fuel Input µg/s	Stack Output, µg/s	Mass Balance, out/in
Calcium	790	580	0.73	790	93 < 450	0.12
Manganese	26	17	0.65	7.9	3.9 < 4.2	0.49
Zinc	260	43	0.17	< 13	52	> 4
Fluoride	330	39	0.12	360	27 < 33	0.075
Nitrates	52	280	5.4	210	7.6	0.036
Sulfates	1200	450	0.38	1300	160 < 390	0.12

#### 4.6 GAS TURBINES

Two gas turbine combined cycle systems were tested. A combined cycle consists of a gas turbine and a steam boiler. The gas turbine exhaust is used as the combustion air for the boiler. The boiler therefore recovers waste heat from the gas turbine exhaust.

##### 4.6.1 Combined Cycle Gas Turbine, Location 7/3

###### Equipment Characteristics--

The combined cycle unit at Location 7 includes a General Electric 12.5 MW gas turbine supplying combustion air to the windbox of a fired boiler. The boiler is a 150 MW (233,300 kg steam flow/hr or 515,000 lb/hr) B&W unit which is capable of using either gas turbine exhaust or forced draft fans for combustion air. All tests conducted during this program were with combined cycle operation and firing gas fuel. The boiler has eight burners, 2 rows of 4 burners each, which fire refinery gas under normal operating conditions.

###### Emissions Sampling--

Measurements were made in the gas turbine exhaust (boiler combustion air) and in the boiler exhaust duct. The instrumentation laboratory was set up so that simultaneous measurements were taken of the gas turbine exhaust and the boiler flue gas. Gas turbine exhaust measurements were made in the duct connecting the gas turbine with the boiler windbox and boiler flue gas was measured in the duct between the boiler and stack. The heated sample line was connected to the boiler flue gas duct so that HC, SO<sub>2</sub>, and NO<sub>x</sub> are measured only at the boiler exit. The initial traverse of the GT exhaust duct showed no gradients in gas composition across the duct, so a single probe with an unheated sample line was used to sample the GT exhaust. The boiler exhaust, however, showed significant variations in composition across the duct due to windbox design, so six probes were installed (one with heated sample line) to assure a representative sample. Some difficulty was encountered in obtaining stable load conditions due to turbine generator problems.

#### Baseline Emissions--

Table 4-58 summarizes the results of emissions tests on this unit. The fuel analysis is presented in Table 4-59. Baseline NO<sub>x</sub> emissions from the gas turbine at 10 MW were 96.9 ng/J (190 ppm, 3% O<sub>2</sub>) and from the boiler at 91% of rated steam flow were 59.2 ng/J (118 ppm, 3% O<sub>2</sub>). The heat input for "Joules" in ng/J is based only on the gas turbine fuel for gas turbine emissions but is based on the total fuel to both gas turbine and boiler for the boiler exit emissions. The gas turbine fuel heat release was 20.7% of the total fuel heat input. Therefore, the NO<sub>x</sub> mass flow from the gas turbine was increased by 200% in the boiler. Total particulate emissions from the boiler stack were 20.8 ng/J (0.0048 lb/10<sup>6</sup> Btu).

#### Combustion Modifications--

In the as-found condition, all boiler burner registers were 60% open; appreciable amounts of CO were measured. Combustion modifications performed on the boiler consisted of air register adjustments and removal of one of the eight burners from service. Air register adjustment reduced boiler stack CO from 401 ppm at baseline to 12 ppm but increased NO<sub>x</sub> by 8%. Removal of the burner (No. 5) from service decreased boiler stack NO<sub>x</sub> by 14%. These NO<sub>x</sub> changes correspond to a 156% increase in NO<sub>x</sub> mass flow in the boiler. Compared to the baseline test, there was a 22% decrease in NO<sub>x</sub> formed in the boiler.

The combined cycle unit exhibited large gradients in O<sub>2</sub> concentration and high CO levels in the "as-found" condition due to the windbox design. The tests showed that air register adjustment can improve the CO problem at higher loads and eliminate CO at lower loads.

TABLE 4-58. SUMMARY OF GASEOUS EMISSIONS DATA - LOCATION 7  
 PETROLEUM REFINERY COMBINED CYCLE GAS TURBINE

Test No.	Date 1977	Turbine Exhaust Measurements							Boiler Outlet Measurements								SO <sub>2</sub> * (ppm)	Comments		
		Heat Input MW	Elec. Output MW	O <sub>2</sub> (%)	CO <sub>2</sub> (%)	NO (ppm)	NO (ng/J)	CO (ppm)	Heat Input MW	Steam Output Mg/h	O <sub>2</sub> (%)	CO <sub>2</sub> (%)	NO <sub>x</sub> * (ppm)	NO <sub>x</sub> * (ng/J)	NO* (ppm)	NO* (ng/J)			HC* (ppm)	CO* (ppm)
7/3-1	7/26	43.1	10	17.5	1.9	190	96.9	82	159.0	213	5.9	8.5	118	59.2	119	59.7	12	401	0	Baseline-particulate test <sup>†</sup>
7/3-2A	7/27	44.3	10	17.7	1.9	475	242	87	169.9	216	4.9	9.9	122	61.2	118	59.2	4	783	2	Baseline-registers 60% open
7/3-2B	7/27	44.3	10	17.5	2.0	208	106	51	172.7	218	5.0	9.5	106	53.1	104	52.1	0	316	2	Register 5 100% open All others 60% open
7/3-2C	7/27	46.9	11	17.2	1.9	190	96.9	129	178.3	229	4.3	10.1	106	53.1	106	53.1	17	334	2	Registers 1, 5 & 6 100% open Registers 2, 3 & 4 60% open
7/3-2D	7/28	49.6	13	17.0	2.1	220	112	22	150.8	204	5.5	8.2	128	64.2	127	63.7	14	12	0	Registers 1, 5 & 6 100% open Registers 2, 3 & 4 60% open
7/3-2E	7/28	52.8	14.5	16.8	2.1	216	110	21	153.2	205	5.4	8.9	121	60.9	119	59.7	1	115	0	Registers 60% open
7/3-3A	7/29	48.5	12.5	17.0	2.0	207	106	45	169.9	224	4.2	9.2	110	55.0	106	53.1	22	>2000	6	Baseline-registers 60% open
7/3-3B	7/29	50.1	12.2	17.5	1.9	226	116	26	169.9	222	4.5	9.2	135	67.5	129	64.7	6	>2000		No. 5 register 80% open; All others 60% open
7/3-3C	7/29	48.9	12.0	17.0	1.9	202	103	45	158.8	213	4.8	8.6	102	51.0	103	51.6	2	>2000	0	No. 5 BOOS, register No. 5 80% open All others 60% open
7/3-3D	7/29	54.8	12.2	17.0	2.0	193	98.5	45	167.1	224	4.2	9.5	110	55.2	109	54.6	2	300	4	Registers 1, 2 & 5 80% open; 3, 4 & 6 60% open; all burners in service

\*All ppm values reported on dry, corrected to 3% O<sub>2</sub> basis.

<sup>†</sup>Particulate: 0.048 lb/10<sup>6</sup> Btu, 20.78 ng/J test 7/3-1 only, 0% opacity.

TABLE 4-59. SUMMARY OF FUEL GAS CHROMATOGRAPHIC ANALYSES  
FOR COMBINED CYCLE AT LOCATION 7

<u>Test No.</u>	7/3-1	7/3-2	
<u>Date</u>	7/26/76	7/27/76	
H <sub>2</sub>	39.5	38.4	
N <sub>2</sub>	1.8	2.3	
CO <sub>2</sub>	0.7	0.7	
C <sub>1</sub>	38.9	41.0	
C <sub>2</sub>	6.4	6.7	
C <sub>2</sub> =	1.0	1.7	
C <sub>3</sub>	7.5	5.2	
C <sub>3</sub> =	1.7	1.9	
iC <sub>4</sub>	1.0	0.8	
nC <sub>4</sub>	0.9	0.8	
iC <sub>4</sub> =	0.1	0.2	
iC <sub>5</sub>	0.1	--	
nC <sub>5</sub>	--	--	
C <sub>5</sub> =	0.4	0.3	
C <sub>6</sub> <sup>+</sup>	--	--	
Heating Value	MJ/m <sup>3</sup> (Btu/cf)	35.4 (953)	34.2 (919)

Note: All values reported on a volume percent basis.

#### 4.6.2 Combined Cycle Gas Turbine, Location 8

##### Equipment Characteristics--

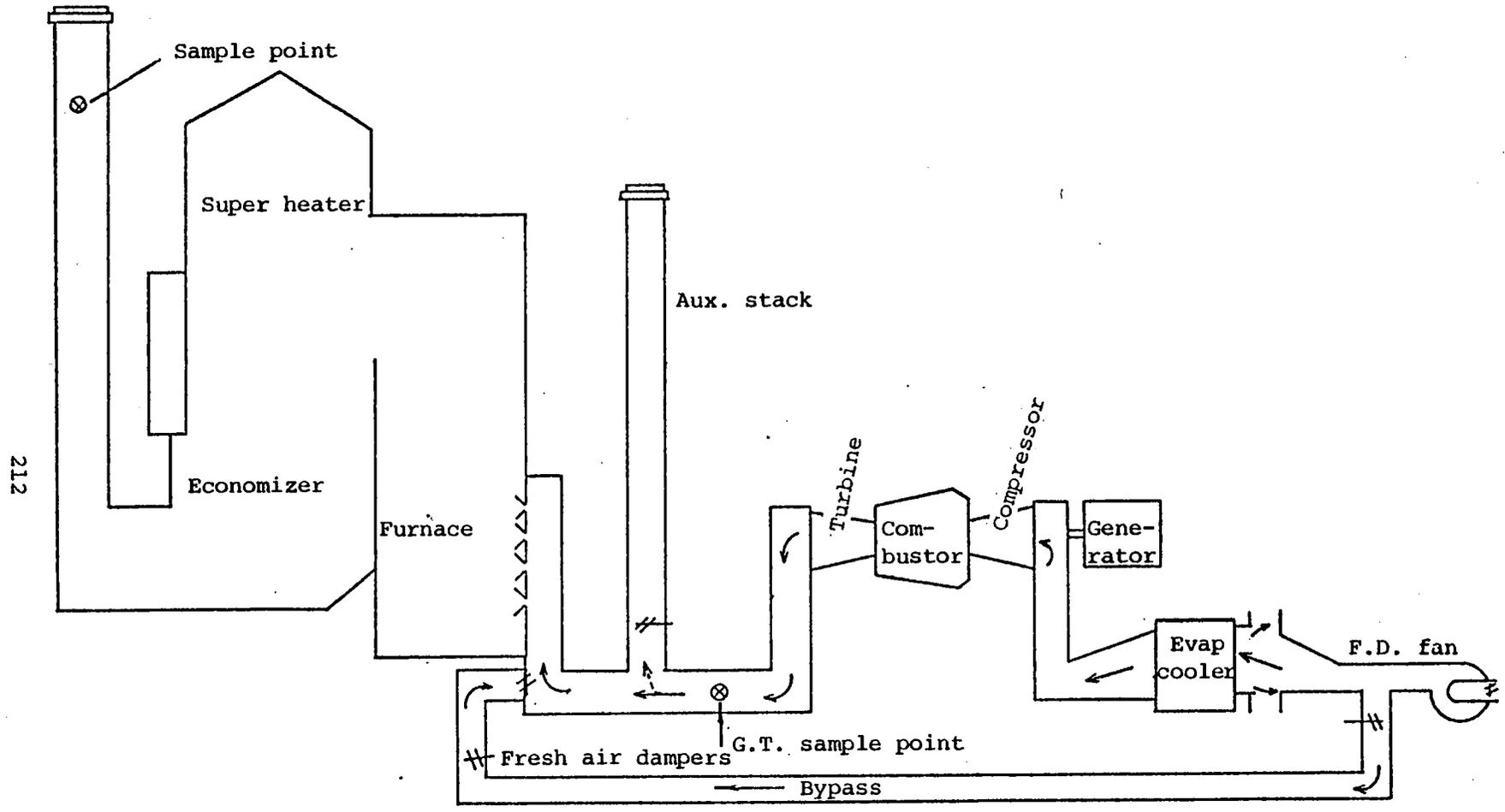
The test unit at Location 8 was a combined cycle gas turbine unit used for plant power generation. The gas turbine was a refinery gas fueled unit made by General Electric and rated at 35.46 MW. The gas turbine exhaust was used for combustion air for the supplementary fired boiler. The boiler was a Babcock & Wilcox unit rated at 200 MW (1,538,000 lb/hr or 697 505 kg/hr). Engineering data for the boiler are presented as follows:

Steam capacity	697 500 kg/hr	(1,538,000 lb/hr)
Design pressure	120.6 MPa	(1,750 lb/in <sup>2</sup> )
Operating pressure	105.1 MPa	(1,525 lb/in <sup>2</sup> )
Furnace volume	1753 m <sup>3</sup>	(61,900 cu ft)
Furnace width	12 m	(39'-0")
Furnace depth	7.3 m	(24'-0")

The boiler has 16 burners, 4 rows of 4 burners each. Combustion air can be supplied by the gas turbine exhaust, forced draft fan or a combination of the two. A schematic of the unit is presented in Figure 4-69.

##### Emissions Sampling--

Measurements were made in the gas turbine exhaust (boiler combustion air) and in the boiler exhaust duct. The instrumentation laboratory was set up so that simultaneous measurements were taken of the turbine exhaust and the boiler flue gas. Gas turbine exhaust measurements were made in the duct connecting the gas turbine with the boiler windbox and boiler flue gas was measured in the boiler stack. The heated sample line was connected to the boiler stack so that HC, SO<sub>2</sub>, and NO<sub>x</sub> are measured only at the boiler exit. The initial traverse of the GT exhaust duct showed no gradients in gas composition across the duct, so a single probe with an unheated sample line was used to sample the GT exhaust. Six sample probes were installed in the boiler stack to assure a representative sample. These lines were unheated.



212

Figure 4-69. Schematic of Location 8 combined cycle unit.

Particulate tests were conducted at the baseline condition with the boiler firing refinery gas and also with 10 of 16 burners firing No. 2 oil. Smoke spot and opacity readings were made when the unit was firing oil. Plume opacity readings indicated a clear stack on oil. Table 4-60 summarizes the results of the emission tests on this unit. Fuel gas samples were taken during the testing and an analysis of the composition is given in Table 4-61.

#### Baseline Tests--

Baseline conditions for the gas turbine at 27 MW, 17.0% O<sub>2</sub> were 83.8 ng/J (166 ppm NO corrected to 3% O<sub>2</sub>, dry basis). Boiler emissions at baseline conditions of 4.9x10<sup>5</sup> kg/hr (1.08x10<sup>6</sup> lb/hr) steam flow, 1.9% O<sub>2</sub>, were 52.0 ng/J (103 ppm, NO<sub>x</sub> corrected to 3% O<sub>2</sub>, dry basis). On a mass flow basis the NO<sub>x</sub> mass flow increased by 195% in the boiler. These levels are nearly identical to the petroleum refinery combined cycle system discussed above. When the boiler was switched to No. 2 oil the total NO<sub>x</sub> emissions increased to 64 ng/J (114 ppm, 3% O<sub>2</sub>) or a 213% addition to NO<sub>x</sub> mass flow over the gas turbine emission rate. Particulate emissions were 4.68 ng/J (0.0109 lb/10<sup>6</sup> Btu) when firing gas and 10.7 ng/J (0.0249 lb/10<sup>6</sup> Btu) when firing oil in the boiler.

#### Combustion Modifications--

The combustion modification tests on the combined cycle unit consisted of air register adjustments and burner out-of-service tests while firing gas fuel. Air register adjustment did not result in lower NO<sub>x</sub> emissions. Several burner patterns were tried with burners out of service. A 12% reduction in NO<sub>x</sub> resulted from two burners out of service with the registers in the normal position. With four burners out of service (no load change) and the fresh air damper closed, the NO<sub>x</sub> was reduced approximately 38%.

The design of gas turbine engines does not allow for field combustion modifications. However, where the gas turbine exhausts through a fired waste heat boiler, the opportunity exists to reduce total emissions through combustion adjustments of the boiler. For this test, the gas turbine generated NO<sub>x</sub> was about 33 kg/h (73 lb/hr). Total baseline NO<sub>x</sub> emission was about 98 kg/h (216 lb/hr) or an additional 65 kg/h (143 lb/hr) added by the boiler. At the low NO<sub>x</sub> condition, gas turbine NO<sub>x</sub> was still 33 kg/h, but total NO<sub>x</sub> was reduced to 61 kg/h (134 lb/hr). While the total NO<sub>x</sub> was reduced by 37%, the boiler-generated NO<sub>x</sub> was reduced by 56%.

TABLE 4-60. SUMMARY OF EMISSIONS FOR LOCATION 8 COMBINED CYCLE GAS TURBINE

Test No.	Date (1976)	Heat Input MW	Gas Turbine							Boiler											Bacharach Smoke Spot	Comments		
			Load MW	O <sub>2</sub> (%)	CO <sub>2</sub> (%)	NO		CO (ppm)	O <sub>2</sub> (%)	CO <sub>2</sub> (%)	NO <sub>x</sub>		NO		HC (ppm)	CO (ppm)	SO <sub>2</sub> (ppm)	Particulate*		Heat Input MW			Load (Mg/h)	Stack Temp (K)
						(ppm)	(ng/J)				(ppm)	(ng/J)	(ppm)	(ng/J)				lb/10 <sup>6</sup> Btu	(ng/J)					
8-1	8/2	114	27	17.0	2.0	166	83.8	9	1.9	10.2	103	52.0	102	51.5	1	5	0	0.0109	4.68	406	490	492	--	Baseline - particulate
8-2	8/3	118	28	17.0	1.9	166	83.8	58	3.3	9.8	108	54.5	105	53.0	1	8	0	-	-	391	470	494	--	Air register adjustment
8-3	8/3	117	27.8	17.0	2.1	157	79.3	36	2.7	10.7	91	45.9	92	46.4	3	4	2	-	-	391	470	492	--	BOOS (1 & 4) Air registers normal
8-4	8/3	114	27.1	17.0	2.0	162	81.8	36	3.0	10.1	96	48.5	95	48.0	3	5	0	-	-	406	490	493	--	BOOS (6 & 7) Air registers normal
8-5	8/3	113	26.9	17.0	2.0	171	86.3	22	6.3	8.0	116	58.6	112	56.5	0	4	0	-	-	383	460	512	--	BOOS (1,4,6 & 7) Fresh air damper 50% open
8-6	8/3	117	27.8	17.0	2.1	166	83.8	54	2.2	10.9	108	54.5	106	53.5	0	7	0	-	-	406	490	493	0	Baseline
8-7	8/4	122	28.9	17.0	2.0	166	83.8	49	2.4	10.4	104	52.5	103	52.0	3	6	0	-	-	414	500	493	--	Baseline
8-8	8/4	117	27.9	17.0	2.0	166	83.8	27	3.5	10.2	104	52.5	102	51.5	2	7	0	-	-	391	470	492	--	BOOS (2 & 3)
8-9	8/5	105	25.0	17.0	1.8	144	72.7	36	6.8	11.2	114	64.0	95	53.3	4	6	7	0.0249	10.7	388	470	507	2.5	Baseline - Cold line only Turbine on gas; boiler on oil
8-10	8/6	118	28.0	16.9	2.1	130	65.6	22	2.0	10.8	101	51.0	100	50.5	6	8	0	-	-	406	490	493	--	Baseline
8-11	8/6	117	27.9	17.0	2.1	157	79.3	36	2.1	10.6	64	32.3	63	31.8	0	6	0	-	-	406	490	493	--	BOOS (1,4,6,7) Fresh air damper closed

NOTES: 1. All tests were with refinery gas fuel except Test 8-9 for which the turbine was still firing refinery gas but the boiler was firing oil.

2. ppm values for NO<sub>x</sub>, NO, CO, HC, and SO<sub>2</sub> are corrected to 3% O<sub>2</sub>, dry basis.

3. Burner pattern:

4	3	2	1
○	○	○	○
8	7	6	5
○	○	○	○
12	11	10	9
○	○	○	○
16	15	14	13
○	○	○	○

\*Opacity was zero during particulate tests.

TABLE 4-61. FUEL GAS ANALYSIS - LOCATION 8

<u>Component</u>	<u>Concentration - Mole %</u>
Methane	77.65
Ethane	1.89
Propane	0.76
Iso-butane	0.16
N-butane	0.24
Pentanes	0.03
C <sub>6</sub> <sup>+</sup>	0.09
Ethane	0.67
Propene	0.11
Nitrogen	0.28
Carbon dioxide	0.81
Hydrogen	17.31
Higher heating value	33.9 MJ/m <sup>3</sup> 910 Btu/CF

Analysis performed by mass spectrometry method.

## SECTION 5.0

### RECOMMENDATIONS

The combustion modification and emission measurement tests conducted in this program have provided a basis for recommendations for the purposes of planning future research. These recommendations concern areas of investigation that were outside of the scope of the current program, but are considered essential to the objective of reduced emissions from industrial combustion equipment. Most of the suggestions are logical extensions of the completed work and are concerned with combustion modifications that require more extensive hardware alterations than were possible in the existing contract.

#### 5.1 AREAS REQUIRING ADDITIONAL WORK

The survey of emissions data and literature (Appendix A) indicates that the major industries with high emissions are petroleum refining, wood products, cement, chemicals, and metals. Not all of these industries are desirable candidates for additional combustion modification work since the total emissions may be fragmented among many individual devices of different design. This is particularly true in the chemicals industry. The most cost effective approach is to concentrate on devices that make up a large segment of their industry's emissions and are somewhat adaptable to combustion control. Consideration should be given to process heaters, wood/bark boilers, cement kilns, and metals producing furnaces. The major emphasis should also be on devices where existing technology is not totally adequate; i.e., where combustion modifications were of limited effectiveness in the current program and where new approaches and technology development are required.

Process heaters were estimated to be highest in annual  $\text{NO}_x$  emissions from the sources considered. Cement kilns are high in  $\text{NO}_x$ ,  $\text{SO}_x$ , and particulates although the latter two emissions are process or fuel related and difficult to control with combustion modifications. Wood boilers are also

high in NO<sub>x</sub> emissions and there is reason to believe that current NO<sub>x</sub> control technology for boilers will be difficult to apply to these devices. The metals producing industry has more fragmented emissions among several devices such as furnaces, smelters, heat treat ovens, etc. However, soaking pits and reheat furnaces are estimated to contribute a major portion of the NO<sub>x</sub> emissions from steel making operations.

The industrial combustion devices requiring the most attention initially are process heaters. Their energy use is large and their emissions, particularly NO<sub>x</sub>, on an annual basis are significant. Most important, the natural draft refinery heaters do not lend themselves readily to conventional combustion modifications where significant emissions reduction can usually be achieved by operational changes that modify the firing practice. Hardware configuration and process constraints have prevented the successful application of fuel-rich firing modes with burners out-of-service or over-fire air ports. Low excess air firing has met with limited success and more sophisticated methods such as flue gas recirculation were not possible since units were not available with these provisions and hardware modifications were outside of the scope of the current study. Natural draft units pose specific constraints in terms of air control mixing and draft requirements that inhibit the application of low-NO<sub>x</sub> modes. However, based on American and Japanese development efforts, significant emissions reductions may be possible in many cases by relatively minor burner hardware modifications.

The success of these low NO<sub>x</sub> and low excess air designs suggests that significant NO<sub>x</sub> reductions may also be possible on a retrofit basis for existing units. Although process heaters are of primary concern, similar conditions exist with kilns and furnaces where minor hardware modifications may well be the most cost-effective approach to emissions control through combustion modification.

## 5.2 RECOMMENDED PROGRAM OBJECTIVES

A Phase II effort is recommended to follow the current industrial combustion devices program with these additional objectives:

1. Define and evaluate combustion modification concepts requiring relatively minor hardware modifications to control emissions on four major combustion device categories.
2. Examine the process constraints that may inhibit the application of these concepts and select the approaches showing the most promise.
3. Demonstrate the feasibility of the concept for retrofit applications by conducting subscale reduced emissions demonstration tests.
4. Establish the cost/benefit factors of candidate combustion modification concepts from an emissions, fuel efficiency, and operations impact standpoint.
5. Conduct full-scale combustion modification demonstration tests in the field on units made available by cooperating industries.
6. Evaluate emissions and operational performance data in combination with cost/benefit analyses to recommend an approach (or priority of approaches) for a given combustion device.
7. Prepare a final engineering report that documents the engineering development of the recommended combustion concepts in a manner that will maximize technology transfer to the relevant burner and process equipment manufacturers.

## 5.3 PROPOSED PROGRAM SCOPE

The recommended Phase II program differs from the completed program by involving hardware modifications that would require more time and funds than are currently available. This is not a fundamental combustion or hardware development program since a majority of the concepts to be examined will fall in the category of retrofit burner modifications. The most complex task proposed is that of instituting flue gas recirculation on a process heater

which admittedly will require some extensive duct modifications. In most cases, the modifications considered will concern optimization of existing design parameters to minimize  $\text{NO}_x$  and can be implemented in most cases with relatively minor equipment substitutions.

The first major element of the recommended program is the feasibility demonstrations at the subscale level which could best be performed in cooperation with a major burner manufacturer. The purpose for these demonstration tests is two-fold. It provides a proving ground for a combustion modification concept prior to its use on a full-scale field unit which is committed to a process. It also allows the engineering personnel and the burner manufacturer to optimize the approach so that they can speak with confidence when approaching industries to provide units for modification. The latter is the key to the success of the program; commercial industry will be more receptive to an emissions reduction concept if it has been proven on a full-scale process. In the same manner, individual industries are more willing to provide a production unit for demonstration of a combustion concept if it has been developed previously on a smaller scale. For these reasons, the subscale feasibility demonstrations are considered a major part of the program. While they are taking place, it will also provide sufficient time to acquaint potential host equipment owners with the objectives of the program and to solicit their cooperation in providing volunteer units.

The second major element of the recommended program is the field demonstration tests to confirm the effectiveness of the candidate  $\text{NO}_x$  control concepts on full-scale operational units. The objective is not only to demonstrate the feasibility of the concept on a specific unit design, but also to show that the concept has a wide range of application by additional tests on other basic combustion device configurations. The added experience with more than one unit will provide a broader base of understanding and emissions data concerning the modification and will also increase industry's ability to adopt new emissions control technology.

## 5.4 TECHNICAL APPROACH

Combustion modification and emission measurement tests are essential to the objective of reduced emissions from the four major categories of combustion devices recommended for the Phase II program. Process heaters were identified as one of the largest contributors and also as one with design configurations that made it difficult to apply existing modified firing practice methods that have proven attractive on industrial and utility boilers. To illustrate the technical approach that should be followed in Phase II, the process heater category was selected for a more detailed discussion of candidate combustion modification concepts. A final technical scope of work should contain a similar attention to concepts attractive for kilns and furnaces. The primary intention is to indicate the type of modified combustion concepts that could be considered, recognizing that these ideas are preliminary in nature.

### 5.4.1 Background on Process Heater Combustion Modifications

The application of combustion modification methods to process heaters for emissions reduction is more difficult than it is on industrial or utility boilers because of several basic differences in design configurations. One of the major limitations in combustion control on process heaters is the fairly widespread use of natural draft designs. Total pressure drops through the heater and across the burner are quite small ( $\sim 125$  Pa,  $0.5''$  H<sub>2</sub>O) and any air flow adjustment or modification, that creates a positive pressure in the top of the heater could result in casing leaks and structural damage to the unit. In addition, process heaters tend to have large numbers of burners to achieve even heat distribution and therefore it is more difficult to implement a burner's out-of-service low NO<sub>x</sub> firing mode. The low velocity, more laminar nature of the air flow tends to inhibit mixing between the fuel-rich in-service burners and the air-only burners, which also tends to produce long flame zones and less even heat distribution. If the process heater firebox is not high enough to permit complete fuel burnout prior to entering the convective passes, an undesirable condition with flame impingement or carryover may occur.

The problems outlined above exist to a lesser extent on most moderate to larger sized boilers where forced draft operation provides the opportunity to control both the air and the fuel, and with more turbulence and mixing. Boilers frequently have fewer burners (for the same unit heat rate) which are easier to control and much larger changes in local air/fuel ratio and flow rate can be made without influencing final steam temperatures and unit performance. In addition, most utility size boilers have very high furnace sections which provide an adequate combustion length to accommodate fuel-rich combustion without flame carryover. For these reasons, some low  $\text{NO}_x$  firing modes which are well suited for boiler applications are less adaptable to process heaters.

The previous discussion has briefly identified some of the limitations encountered in achieving significant emissions reductions in natural-draft process heaters through minor operational combustion modifications in the field. However, significant  $\text{NO}_x$  reductions may be possible through relatively minor component modifications that would be attractive for implementation in the field on a retrofit basis. The purpose of this discussion is to identify these concepts and briefly examine their principle of operation and relative attractiveness for field implementation.

#### 5.4.2 Combustion Modification Approaches

There are two general approaches that initially deserve consideration in performing combustion modifications on process heaters. In natural draft devices, the air flow, mixing, and flame shape are intimately interrelated; air flow adjustments to alter burner stoichiometry have a negative impact on the other parameters. Therefore, consideration should be given to varying burner stoichiometry by adjusting the fuel and air flow parameters that control the mixing. Another approach to limiting  $\text{NO}_x$  formation in the flame zone is to control the local mixing and flame zone intensity by minor burner design modifications to achieve more desirable temperature and stoichiometry conditions.

Low NO<sub>x</sub> burner configurations for process heaters have recently been developed in Japan and the United States for new units. The purpose of the proposed combustion modification study is to examine methods that could be implemented on existing process heaters and compare these methods with burner replacement on a minimum cost retrofit basis. Several approaches recommended for consideration are listed below:

1. Modified fuel injection
2. Controlled entrainment
3. Steam injection
4. Staged combustion
5. Flue gas recirculation
6. Modified atomization
7. Overfire air
8. Controlled heat withdrawal

#### 5.5 SUPPORT AND DISCUSSION OF PROGRAM ELEMENTS

A four-phase combustion modification feasibility task is recommended to examine the range of application and to resolve any possible difficulties at a scale that is less expensive to modify. The initial phase of the recommended task would concern further definition and evaluation of the concepts with analytical examination of the requisite fluid mechanics, heat transfer, etc. This would be followed by an examination of the process constraints, the adaptability to a range of existing heater designs, and any unusual performance requirements. Assuming that the concept still remained attractive, it would be tested on a single burner research test stand over a range of operating parameters that would adequately define its emissions performance and limitations. The support of the burner manufacturers and process heater manufacturers would be a prerequisite for this effort. Prior to the full scale tests, a fourth phase concerning cost/benefit calculations of the combustion modifications from an emissions, efficiency, and operational impact standpoint should be considered. With this background and support of the equipment manufacturers, considerably less difficulty should be encountered in acquiring a full-scale process heater for modification.

The combustion modifications proposed (with the exception of Nos. 5, 7, and 8) are not major burner redesigns but rather are a refinement of existing designs. If the development of a concept requires significant research funding to achieve a significant emissions reduction, it will be considered outside the scope of the present study and will be recommended for individual research support. The primary objective of the study is to identify process operational and design parameters that affect emissions and efficiency and then establish the approximate range of desirable operation for subsequent full scale demonstration tests.

## SECTION 6.0

### REFERENCES\*

1. Cato, G. A., et al., "Field Testing: Application of Combustion Modifications to Control Pollutant Emissions from Industrial Boilers - Phase I," EPA 650/2-74-078a, NTIS No. PB 238 920/AS, October 1974.
2. Cato, G. A., et al., "Field Testing: Application of Combustion Modifications to Control Pollutant Emissions from Industrial Boilers - Phase II," EPA 600/2-76-086a, NTIS No. PB 253 500/AS, April 1976.
3. Carter, W. A., et al., "Emissions Reduction On Two Industrial Boilers With Combustion Modifications," EPA-600/7-78-099a, NTIS No. PB 283 109, June 1978.
4. Hunter, S. C., et al., "Evaluation of Two Industrial Boilers With Combustion Modifications for Reduced Pollutant Emissions," ASME Paper 77-WA/APC-1, December 1977.
5. Bartz, D. R., et al., "Control of Oxides of Nitrogen from Stationary Sources in the South Coast Air Basin," Prepared for California Air Resources Board, NTIS No. PB 237 688/7WP, September 1974.
6. Anon., "Energy Conservation Potential in the Cement Industry," Federal Energy Administration, FEA/D-75/400, June 1975.
7. Baumeister, T., ed., Mechanical Engineer's Handbook, McGraw-Hill Book Co., Inc., 6th ed., 1958.
8. Anon., "Particulate Polycyclic Organic Matter," National Academy of Sciences, 1972.
9. Jacko, R. B. and Neuendorf, D. W., "Trace Metal Particulate Emission Test Results From a Number of Industrial and Municipal Point Sources," Journal of the Air Pollution Control Association, Vol. 27, No. 10, Page 989, October 1977.
10. Cleland, J. G. and Kingsburg, G. L., "Multimedia Environmental Goals for Environmental Assessment," Vol. I & II, EPA-600/7-77-136a and b, November 1977.

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\*See additional references, Appendices A-G.

## SECTION 7.0

CONVERSION FACTORS

SI Units to Metric or English Units

<u>To Obtain</u>	<u>From</u>	<u>Multiply By</u>	<u>To Obtain ppm at 3% O<sub>2</sub> of</u>	<u>Multiply* Concentration in ng/J by</u>
g/Mcal	ng/J	0.004186	<u>Natural Gas Fuel</u>	
10 <sup>6</sup> Btu	GJ	0.948	CO	3.23
Btu	gm cal	3.9685x10 <sup>-3</sup>	HC	5.65
lb/10 <sup>6</sup> Btu	ng/J	0.00233	NO or NO <sub>x</sub>	1.96
ft	m	3.281	SO <sub>2</sub> or SO <sub>x</sub>	1.41
in.	cm	0.3937		
ft <sup>2</sup>	m <sup>2</sup>	10.764	<u>Oil Fuel</u>	
ft <sup>3</sup>	m <sup>3</sup>	35.314	CO	2.93
lb	kg	2.205	HC	5.13
Fahrenheit	Celsius	$t_F = 9/5(t_C) + 32$	NO or NO <sub>x</sub>	1.78
Fahrenheit	Kelvin	$t_F = 1.8t_K - 460$	SO <sub>2</sub> or SO <sub>x</sub>	1.28
psig	Pa	$P_{psig} = (P_{pa}) (1.450 \times 10^{-4}) - 14.7$		
psia	Pa	$P_{psia} = (P_{pa}) (1.450 \times 10^{-4})$	<u>Coal Fuel</u>	
iwg (39.2 °F)	Pa	$P_{iwg} = (P_{pa}) (4.014 \times 10^{-3})$	CO	2.69
10 <sup>6</sup> Btu/hr	MW	3.413	HC	4.69
GJ/hr	MW	3.60	NO or NO <sub>x</sub>	1.64
			SO <sub>2</sub> or SO <sub>x</sub>	1.18

\*These conversions depend on fuel composition.  
The values given are for typical fuels.

English and Metric Units to SI Units

<u>To Obtain</u>	<u>From</u>	<u>Multiply By</u>	<u>To Obtain</u> <u>ng/J of</u>	<u>Multiply*</u> <u>Concentration</u> <u>in ppm @ 3% O<sub>2</sub> by</u>
ng/J	lb/10 <sup>6</sup> Btu	430	<u>Natural Gas Fuel</u>	
ng/J	g/Mcal	239	CO	0.310
GJ	10 <sup>6</sup> Btu	1.055	HC	0.177
m	ft	0.3048	NO or NO <sub>x</sub> (as NO <sub>2</sub> )	0.510
cm	in.	2.54	SO <sub>2</sub> or SO <sub>x</sub>	0.709
m <sup>2</sup>	ft <sup>2</sup>	0.0929	<u>Oil Fuel</u>	
m <sup>3</sup>	ft <sup>3</sup>	0.02832	CO	0.341
kg	lb	0.4536	HC	0.195
Celsius	Fahrenheit	$t_c = 5/9 (t_f - 32)$	NO or NO <sub>x</sub> (as NO <sub>2</sub> )	0.561
Kelvin	Fahrenheit	$t_K = 5/9 (t_f - 32) + 273$	SO <sub>2</sub> or SO <sub>x</sub>	0.780
Pa	psig	$P_{pa} = (P_{psig} + 14.7) (6.895 \times 10^{-3})$	<u>Coal Fuel</u>	
Pa	psia	$P_{pa} = (P_{psia}) (6.895 \times 10^{-3})$	CO	0.372
Pa	iwg (39.2 °F)	$P_{pa} = (P_{iwg}) (249.1)$	HC	0.213
MW	10 <sup>6</sup> Btu/hr	0.293	NO or NO <sub>x</sub> (as NO <sub>2</sub> )	0.611
MW	GJ/hr	0.278	SO <sub>2</sub> or SO <sub>x</sub>	0.850

\*These conversions depend on fuel composition.  
The values given are for typical fuels.

APPENDIX A

EQUIPMENT SURVEY

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## ABSTRACT

This appendix presents the results of a literature survey of industrial combustion devices. The objective of this survey was to recommend a set of devices for subsequent field testing wherein combustion control techniques would be developed to reduce air pollutant emissions and, hopefully, simultaneously increase device operating efficiency.

The survey was accomplished primarily through personal contacts with device manufacturers and device users. Additional useful information was obtained from the national associations representing manufacturers and users.

This appendix presents the approach used in identifying the set of combustion devices and, in essence, first-ranked industries in terms of air pollutant emissions and energy usage and then identified the significant combustion devices within the high ranking industries. The recommended combustion devices were then described in some detail in order to assist in characterizing a representative unit(s). The second task of the overall program involved physically locating these units for the field testing activity.

## CONTENTS

<u>Section</u>	<u>Page</u>
ABSTRACT	229
FIGURES	231
TABLES	232
A-1.0 INTRODUCTION AND SUMMARY	233
A-2.0 APPROACH	235
A-3.0 INDUSTRY EMISSION RANKING	238
A-4.0 ENERGY CONSIDERATIONS	241
A-5.0 COMPARISON BETWEEN EMISSION AND ENERGY RANKINGS	243
A-6.0 INDUSTRY RECOMMENDATIONS	243
A-7.0 COMPARISON WITH OTHER INDUSTRY RECOMMENDATIONS	244
A-8.0 COMBUSTION DEVICE RANKING	247
A-9.0 COMBUSTION DEVICE RECOMMENDATIONS FOR FIELD TEST	249
A-10.0 INDUSTRIAL COMBUSTION DEVICE CHARACTERISTICS	251
A-10.1 Quantity And Geographic Distribution of Fuels Used	251
A-10.2 Cement Kilns	256
A-10.3 Glass Container Furnaces	266
A-10.4 Black Liquor Recovery Boilers	274
A-10.5 Wood Waste Boilers	281
A-10.6 Coke Ovens	286
A-10.7 Blast Furnaces	291
A-10.8 Open Hearth Furnaces	296
A-10.9 Soaking-Pit, Reheating, And Heat-Treating Furnaces	302
A-10.10 Stationary Reciprocating Engines	309
A-10.11 Stationary Gas Turbines	322
A-10.12 Petroleum Refinery Process Heaters	333
A-11.0 POTENTIAL FUEL SAVINGS IN PULP, PAPER, AND PAPERBOARD INDUSTRY	347
REFERENCES	349

## FIGURES

<u>No.</u>		<u>Page</u>
A-10.2-1.	Grate Type Preheater Kiln System (Portland Cement Association)	257
A-10.3-1.	Regenerative Side-Port Glass Container Furnace (Battelle Columbus Laboratories)	267
A-10.3-2.	Burner Configurations For Glass Furnaces (North American Mfg. Co.)	268
A-10.3-3.	Regional Distribution of Glass Container Manufacturers in the United States	271
A-10.4-1.	Process Flow Diagram of a Typical Kraft Pulp and Paper Mill (Babcock & Wilcox)	275
A-10.4-2.	Black Liquor Recovery Boiler (Babcock & Wilcox)	276
A-10.5-1.	Wood Waste Boiler (Babcock & Wilcox)	283
A-10.6-1.	General Cut-Away of Coke Oven	288
A-10.7-1.	Cross-Section of Typical Blast Furnace and Hot Blast Stove (U.S. Steel Corp.)	293
A-10.8-1.	Principal Parts of an Open-Hearth Furnace (U.S. Steel Corp.)	297
A-10.9-1.	Soaking-Pit Furnaces (U.S. Steel Corp.)	304
A-10.10-1.	Internal Combustion Engine With Integral Gas Compressor (Cooper Energy Services)	314
A-10.11-1.	2.8 Mw Gas Turbine (Solar Div. International Harvester)	326
A-10.11-2.	Trends in Size of Turbines Sold For Gas Compression Service	329
A-10.12-1.	Total Emissions of Nitrogen Oxide for Refinery Heaters and Boilers Operating on Refinery Gas	344
A-10.12-2.	Emission Factor for Heaters and Boilers with Refinery Gas Fuel	345

TABLES

<u>No.</u>		<u>Page</u>
A-1-1	Industries and Devices Recommended for Testing	234
A-2-1	National Associations And Other Organizations Contacted	237
A-3-1	Industry NO <sub>x</sub> Ranking	240
A-4-1	Purchased Energy For 1971	242
A-8-1	Combustion Device Emissions	248
A-9-1	Devices Recommended For Field Test And Number Of Tests	250
A-10.1-1	Fossil Fuels Purchased By Two-Digit SIC Industries (1971)	252
A-10.2-1	Trend In Average Cement Kiln Capacity	262
A-10.2-2	Cement Kiln Population By Capacity And Process	263
A-10.2-3	Cement Capacity And Kiln Distributions By State	264
A-10.3-1	Energy Utilization In Glass Container Industry	269
A-10.3-2	Characteristics Of Representative Glass Container Furnaces	272
A-10.4-1	Trends In Babcock And Wilcox Black Liquor Recovery Boilers	278
A-10.4-2	Distribution Of Numbers And Relative Capacities Of Kraft Recovery Boilers By State	279
A-10.5-1	Distribution Of Bark Boilers And Relative Capacities By State	284
A-10.6-1	Coke Oven Distribution By State	289
A-10.7-1	Annual United States Pig Iron Production	292
A-10.7-2	Blast Furnace And Relative Capacity Distributions By State	294
A-10.8-1	Distributions Of Open Hearth Furnaces And Approximate Capacity By State	299
A-10.8-2	Open Hearth Furnace Air Pollution Emissions	301
A-10.9-1	Distributions Of Soaking-Pits, Reheating, And Heat-Treating Furnaces	307
A-10.10-1	IC Engine Manufacturers	310
A-10.10-2	Stationary IC Engine Applications	317
A-10.11-1	Major United States Gas Turbine Manufacturers	323
A-10.11-2	Net Electrical Energy Produced By Gas Turbines	327
A-10.11-3	Gas Turbines Installed In Electrical Generating	330
A-10.11-4	NO <sub>x</sub> Emissions From Gas Turbines	332
A-10.12-1	Typical Refinery Fuel Gas Composition	337
A-10.12-2	Geographic Distribution Of Petroleum Refineries In The United States	339
A-10.12-3	Distribution By Capacity Of Petroleum Refineries In The United States	340
A-10.12-4	Fuel Use in Petroleum Refineries	342

## SECTION A-1.0

### INTRODUCTION AND SUMMARY

A study was conducted to establish a set of significant industrial combustion devices for subsequent field testing during this program. Major inputs to the effort were a literature survey and personal contacts with device manufacturers and users. Contacts were also made with national associations representing the users.

The approach selected for the recommendation process involved consideration of both air pollutant emissions and energy usage within major industries and then searching these industries for the significant combustion devices involved. As will be explained, this approach was deemed more direct than first considering the devices emissions and energy usage and then determining those industries which employed the devices.

The industries and significant combustion devices thus established are shown in Table A-1-1.

Combustion devices of the "dryer" type were not recommended since their air pollutant emissions, as found in the literature, were minor compared to the above devices.

It is further noted that open hearth and heat-treating furnaces are common to both the steel foundry and iron and steel activities. This commonality of usage will allow a carryover of testing results from one industry to the other.

Data necessary to identify representative units in each of the above categories were found to be very limited or nonexistent. As opposed to conventional boilers that are fairly well defined as to type, size, etc., many industrial combustion devices are one-of-a-kind fabricated to specific proprietary specifications. However, it was possible to define certain characteristics as representative in the various categories to a degree sufficient to select units suitable for testing.

TABLE A-1-1. INDUSTRIES AND DEVICES RECOMMENDED FOR TESTING

Industry	Combustion Device
Petroleum refining	process heaters
Cement	kilns
Chemical manufacturing	charcoal retorts ammonia reformers
Steel foundry	open hearth furnaces heat-treating furnaces
Iron and steel*	coke ovens blast furnaces open hearth furnaces soaking-pits reheating furnaces heat-treating furnaces
Wood pulp and pulpboard (kraft process)	wood waste boilers black liquor recovery boilers
Glass container	melting furnaces
†	reciprocating engines gas turbines

\*All these devices can be found in an integrated steel mill, i.e., at one geographical location.

† Not associated with a specific industry.

## SECTION A-2.0

### APPROACH

The primary objective of the survey effort was the preparation of a list of industrial combustion devices recommended for field testing. The following steps were followed to secure this objective:

1. Identify those industries which are major sources of air pollutant emissions.
2. Identify those industries which are major purchasers of fossil fuel energy.
3. Rank those industries which are both major sources of air pollutant emissions and purchasers of fossil fuel energy.
4. Prepare a list of significant combustion devices involved in the top ranked industries from step 3. These devices will be those which are the major emission sources and energy consumers within their respective industries. Comprehensive listings of stationary combustion devices, such as reported in Reference A-2-1, were employed as a guide in establishing, at least on a generic basis, a checklist of potentially significant devices.
5. Modify this list (step 4) by deleting those combustion devices whose emissions are due to the material being processed and not a result of the combustion process.
6. Again modify the step 4 list by including those devices which by reason of an anticipated high level of commonality offer a widespread usage of emission control techniques obtained on a limited number of tests.
7. Prepare the final listing of devices recommended for field testing.

This approach was adopted since air pollutant emissions contained in the EPA NEDS listing (Ref. A-2-2) are grouped by industry and then by device type within the industry. Furthermore, the energy usages contained in Reference A-2-3 are structured by industry groupings only and not by device type within the industry. Thus, it was impractical to undertake an approach which concentrated at the device level and then associated the devices with specific industrial applications.

Simultaneously, contacts were made with national user's associations, device manufacturers, and the users themselves in order to obtain more specific information about those devices recommended for field testing. (Table A-2-1 is a listing of those organizations contacted.) Information requested from these sources consisted of:

- . Device and burner operational characteristics
- . Number distribution vs. device rating and geographical location
- . Current fuel usage and trends
- . Trends in equipment type, rating and age
- . Limitations in equipment use.

This, and other information, was required to establish the groundwork for selecting representative units for field test. (The selection process is performed during Task 2.) The selection of a truly representative unit is of prime importance when the schedule permits testing of only a single unit, i.e., the selection must be very carefully made to allow the widest applicability of combustion control techniques.

In this survey, conventional boilers burning only natural gas, fuel oil, or coal were excluded since previous EPA programs have been directed to those devices. However, boilers burning unusual fuels such as black liquor, wood bark, carbon monoxide, or process gases were considered.

TABLE A-2-1. NATIONAL ASSOCIATIONS AND OTHER ORGANIZATIONS CONTACTED

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Aluminum Association  
International Lead Zinc Organization  
American Paper Institute  
Glass Container Manufacturing Institute  
American Gas Association  
Portland Cement Association  
American Petroleum Institute  
American Bureau of Metal Statistics  
American Iron and Steel Institute  
Copper Development Association  
Institute of Gas Technology  
Federal Energy Administration  
Battelle Columbus Laboratories  
Bureau of Mines - Office of Oil and Gas  
Environmental Protection Agency  
Toledo Engineering  
St. Regis Paper  
Institute of Paper Chemistry  
Technical Association of the Pulp and Paper Industry  
Major glass container manufacturer  
National Council For Air And Stream Improvement (paper industry)  
Combustion Engineering  
Babcock and Wilcox  
Koppers Co., Inc.  
Kaiser Steel  
Surface Combustion Div., Midland-Ross Corp.  
MacMillan-Bloedel Ltd.  
Society of Automotive Engineers  
Engine Manufacturers Association  
Aerotherm Div. Acurex  
Southwest Research Institute  
American Society of Mechanical Engineers  
Solar Div. International Harvester  
McGraw-Hill Inc. (publishers of Electrical World)  
Federal Power Commission  
Petro-chem Development Co., Inc.  
American Boiler Manufacturers Association

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## SECTION A-3.0

### INDUSTRY EMISSION RANKING

The industry ranking by yearly  $\text{NO}_x$  emission rates was accomplished with the NEDS information (Ref. A-2-2).  $\text{NO}_x$  emissions are those produced primarily by the combustion process (nitrogen fixation) and, therefore, can be reduced by modifications in the combustion process. Reduced air pre-heat, delayed combustion, off-stoichiometric operation, etc., can be employed to reduce  $\text{NO}_x$  production in the flame.  $\text{NO}_x$  can also be formed from nitrogen organically bound in the fuel. This source of  $\text{NO}_x$  is more difficult to control.  $\text{SO}_x$  production directly reflects the amount of sulfur present in the fuel and cannot be controlled by combustion modifications. While it is true that the combustion process can affect the production of incompletely reacted species (hydrocarbons, HC, and carbon monoxide, CO) to some extent, the ranking system focused on  $\text{NO}_x$  as the indicator. Each of the industry listings was evaluated and retained if it involved a combustion device. Even then, some listings were deleted if the majority of the  $\text{NO}_x$  emissions could be attributable to the process or process material and not to the combustion device. For example, the production of nitric acid involves a combustion device but the majority of the  $\text{NO}_x$  emissions originate in the process material. In this instance the NEDS information on nitric acid production was not included in the chemical manufacturing industry total.

A problem arises if the NEDS format is strictly followed in that such devices as wood boilers, reciprocating engines and gas turbines are not associated with any specific industry grouping. Rather, they are contained under the general headings of External Combustion - Industrial Boiler and Internal Combustion - Industrial, respectively. These devices are noted to be large emitters, especially of  $\text{NO}_x$ , and they are included in the combustion device ranking discussed in Section A-8. For the purposes of ranking industrial emissions, the NEDS listing for wood/bark boilers was assigned to the wood pulp and pulpboard industry grouping.

The results of this ranking are presented in Table A-3-1 and indicate, for example, that the petroleum refining industry ranks first with  $9.69 \times 10^8$  kg/year (1,065,526 tons/year) of  $\text{NO}_x$ , about a factor of 10 higher than the other categories. In addition, process heaters account for 91% of the petroleum refining industry  $\text{NO}_x$  production.

Also of note from Table A-3-1 is that the  $\text{NO}_x$  emissions from the petroleum refining, wood pulp and pulpboard, and cement industries amount to over 95% of the total for the seven industries listed and that process heaters, wood/bark boilers, and kilns are three important combustion devices involved. The glass industry, although ranking last in  $\text{NO}_x$  emissions, is represented by a single type of combustion device. Thus, there exists a strong potential for industry-wide application of emission reduction techniques evaluated on a limited number of glass furnaces.

No attempt was made to critically assess the NEDS data summaries to determine whether they truly represent total national emissions. Possible data entry errors and the fact that the file may not include all sources requires that the data be viewed with caution.

TABLE A-3-1. INDUSTRY NO<sub>x</sub> RANKING

Kg/Year (Tons/Year)

Rank	Industry	NO <sub>x</sub> Emissions	Device (s)	Device Emission % of Industry Emissions
1	Petroleum Refining	969x10 <sup>6</sup> (1,065,526)	Process Heater	91
2	Wood Pulp and Pulpboard	151x10 <sup>6</sup> (166,327)	Recovery Boiler Wood/Bark Boiler	9 91
3	Cement	132x10 <sup>6</sup> (145,101)	Kiln	99
4	Chemical Mfg.	27x10 <sup>6</sup> (29,209)	Charcoal Retort Ammonia Reformer	49 15
5	Steel foundry	19x10 <sup>6</sup> (20,797)	Heat-Treating Furnace Open Hearth Furnace	*
6	Iron and Steel	16x10 <sup>6</sup> (17,045)	Coke Oven Steel Furnace (blast and open hearth)	34 27
7	Glass Container	5x10 <sup>6</sup> (5,385)	Furnace	~ 100

\*The NEDS listing indicates that heat-treating furnaces and open hearth furnaces are large NO<sub>x</sub> sources. However, the listing contains a large "miscellaneous" entry and it is not possible at this time to assign this entry to specific combustion devices.

## SECTION A-4.0

### ENERGY CONSIDERATIONS

In addition to emission rates, consideration was also given to energy utilization on an industry basis. Information obtained by the Bureau of the Census during 1971 and published in Reference A-2-3 was used in this assessment. It is noted that these data apply only to industry groupings and not to the device within the industry consuming the energy.

As presented, the data in Reference A-2-3 specifically addresses quantities of fossil and electric energy purchased for heat and power by the industry groupings and, therefore, does not necessarily imply an equivalence to energy consumed. The difference between energy purchased and consumed can be the result of such things as combustion of feedstock waste material. The pulp and paper industry, in addition to purchasing energy, produces a significant amount of its energy requirements from waste product boilers. This energy source is not tabulated in Reference A-2-3 but is very important when considering the industry's total energy requirements.

Petroleum refineries consume energy equivalent to approximately 8% of the energy contained in the crude feedstock. This amounts to approximately  $2911 \times 10^{15}$  joules/year\* while the purchased energy quoted in Reference A-2-3 for SIC 29 was  $1600 \times 10^{15}$  joules/year for 1971. Thus, purchased energy in a petroleum refinery amounts to 55.0% of the total consumed with the balance being obtained principally from by-product refinery gas. Similarly, the pulp, paper and paperboard industry for 1975 consumed  $1950 \times 10^{15}$  joules/year and purchased  $1111 \times 10^{15}$  joules/year, or 57.1% (Ref. A-4-1). Black liquor recovery boilers and wood-bark boilers are the main sources of the internally generated energy in this industry.

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\*  $10^{15}$  J =  $0.948 \times 10^{12}$  Btu

In other industries, e.g., glass, there is essentially no difference between energy consumed and energy purchased since there are no waste or by-product combustion sources available to supplement fossil fuel and electricity.

A major objective of this program is to achieve greater efficiency in industrial combustion devices. This increased efficiency can be equated to a decrease in purchased energy requirements since those devices operating on waste or by-product sources will still be using all of these sources available regardless of device efficiency improvements. Thus, ranking of the industries was accomplished on the basis of purchased energy, with the results presented in Table A-4-1.

TABLE A-4-1. PURCHASED ENERGY FOR 1971 (Ref. A-2-3)

Fossil Fuel and Electricity

Total of All Industries Surveyed =  $13,860 \times 10^{15}$  J

Rank	Industry	SIC*	$10^{15}$ J	% of Total
1	Industrial Chemicals	281	2086	15.1
2	Blast Furnace and Basic Steel Products	331	1604	11.6
3	Petroleum Refining	291	1602	11.6
4	Paper and Allied Products	26	1388	10.0
5	Cement, Hydraulic	324	484	3.5
6	Plastic Materials and Synthetics	282	477	3.4
7	Glass and Glassware, Pressed or Blown	322	222	1.6
8	Iron and Steel Foundries	332	167	1.2
9	Flat Glass	321	62	0.5
	Total		8092	58.4

\*Standard Industrial Classification

## SECTION A-5.0

### COMPARISON BETWEEN EMISSION AND ENERGY RANKINGS

A comparison between Tables A-3-1 and A-4-1 indicates that, in general, those industries which are large NO<sub>x</sub> emission sources are also large consumers of purchased energy. For example, the petroleum refining, wood pulp and pulpboard, and cement industries which rank 1, 2, and 3 as NO<sub>x</sub> emitters rank 3, 4, and 5 as energy purchasers. Thus, device efficiency improvement techniques in these three industries could also have a significant impact on national emission rates if both program objectives could be simultaneously satisfied.

## SECTION A-6.0

### INDUSTRY RECOMMENDATIONS

Based on an assessment of both NO<sub>x</sub> emissions and energy usage, the following industries should be studied to determine the important combustion devices involved:

- . Petroleum refining
- . Wood pulp and pulpboard
- . Cement
- . Steel foundry
- . Iron and steel
- . Chemical manufacturing
- . Glass container

The glass container industry is recommended on the basis of an anticipated commonality between furnaces, i.e., this industry utilizes a single major type of combustion device with the device consuming a large majority (approximately 70%) of the entire glass container industry energy requirement. Further, it is noted from Reference A-2-2 that glass container industries (SIC 3221) purchased 50% of the total energy attributable to: flat glass (SIC 3211); glass containers (SIC 3221); pressed and blown glass (SIC 3229); and products of purchased glass (SIC 3231). For these reasons the above recommendations include only the glass container aspect of the glass industry.

## SECTION A-7.0

### COMPARISON WITH OTHER INDUSTRY RECOMMENDATIONS

A previous study performed under contract for the EPA (Ref. A-7-1) developed a list of industries based on the following criteria:

- . Use large amounts of process heat directly from fossil fuel combustion
- . Relatively large emitters of combustion-related air pollutants
- . High potential for reducing energy consumption and air pollutant emission.

Based on these criteria the following industries were selected for further analysis in that study:

- . Iron and steel (all energy-using processes)
- . Cement (primarily kiln operation)
- . Glass (melting, foreheater operation, annealing)
- . Aluminum (primary, melting, reheating, secondary production)
- . Petroleum refining.

The paper and paperboard manufacturing industry, although a large consumer of energy, was not selected in the previous study because 95% of its energy is consumed in boilers for production of steam; this operation is already highly efficient. Thus, it was concluded that there is a low potential for reduction in energy consumption.

The present study does not concur in this observation for two reasons:

1. This industry ranks second in NO<sub>x</sub> emissions, only exceeded by petroleum refining. Thus, any NO<sub>x</sub> reduction would have significant national implications even if the device efficiency could not be increased by any amount.

2. This industry ranks fourth in energy consumption, of which 57.1% is purchased energy (the balance being produced by liquor recovery and wood/bark boilers). As shown in Section A-11, a device efficiency improvement from 80% to 81% will result in a 2.26% reduction in purchased energy requirements which can be translated into a yearly savings of  $3.4 \times 10^6$  barrels of residual oil --not an insignificant amount. This savings represents approximately 5% of this industry's yearly purchase of residual oil.

An examination of the NEDS listing (Ref. A-2-2) for both primary and secondary aluminum operations indicates that combustion generated emissions are minor compared to those contained in Table A-3-1. Indeed, the values of  $\text{NO}_x$  were  $2.11 \times 10^5$  kg/year (232 tons/year) which places the aluminum industry (both primary and secondary operations) far below the last ranked glass container industry in Table A-3-1.

On a purchased fossil fuel energy basis Reference A-2-3 indicates that for 1971 primary aluminum (SIC 3334), aluminum rolling and drawing (SIC 3352), aluminum castings (SIC 3361) and nonferrous forging (SIC 3392), purchased a total of  $260 \times 10^{15}$  J of fossil fuel. This places the aluminum activities higher than glass container (SIC 3221 with  $140 \times 10^{15}$  J) but lower than cement (SIC 3241 with  $450 \times 10^{15}$  J).

In view of the low  $\text{NO}_x$  emissions, moderate fossil fuel consumption, and multiple combustion device types, the aluminum industry was not recommended for field testing.

The previous EPA study did not recommend the chemical manufacturing industry because of the large number of processes and devices involved. That is, although the industry as a whole is a large energy consumer the per unit consumption is small.

The present study, while not addressing a per device energy consideration, identified two combustion devices within the chemical manufacturing industry which are large emission sources. One of these devices, the ammonia reformer, is estimated to have a specific energy consumption (energy/unit weight of product) that is greater than that required in the cement industry.

The "Chemical Manufacturing" industry is too broad to be considered as a single entity. However, this is no reason to ignore it since some aspects of this industry (specific processes) are identifiable by energy consumption and emissions.

The present study and that contained in the previous (Ref. A-7-1) study agree on the remaining industries--iron and steel, cement, petroleum refining and glass--as those industries that would benefit most from research on emissions and energy consumption reductions.

## SECTION A-8.0

### COMBUSTION DEVICE RANKING

An examination of each industry yielded a set of important combustion devices employed in that industry. These devices are ranked in Table A-8-1 by NO<sub>x</sub> emissions and emissions of other criteria pollutants obtained from the NEDS listing are shown. In several instances this set was composed of one member which accounted for nearly all the NO<sub>x</sub> emissions for the entire industry. In these instances there was no question as to the type of device which would be selected for field testing.

In essence, the combustion device ranking involves identifying major equipment items in those industries which have already been ranked as high emission sources and energy users.

The process heater descriptor in the petroleum refining industry is a general title for a family of devices which vary significantly in configuration and operation depending on the type of process involved. A more detailed examination of the process heater family was necessary before specific unit types could be identified for field testing.

The steel furnace device is used in the iron and steel, and steel foundry industries. There may exist some degree of commonality between the two functions which will allow a more widespread use of emission reduction techniques.

As previously discussed, the glass container furnaces should be included in the field testing schedule even though this industry ranks low on a NO<sub>x</sub> emission basis.

An emission source, to be contained in the NEDS listing, must meet certain requirements which consist of either the quantity of emissions (on a weight per year basis) or be used within a specified industrial activity. This latter requirement is rather extensive in length and should preclude "overlooking" an important (high emission) industry. It then follows that there is a low probability of also overlooking a high ranking combustion device. However, there is no way of determining the degree to which all existing industrial devices are actually entered in the NEDS data base system.

TABLE A-8-1. COMBUSTION DEVICE EMISSIONS

kg/year (tons/year)

Device	No. of Records*	NO <sub>x</sub>	SO <sub>x</sub>	HC	CO	Particulates
Process heaters	2,818	8.8x10 <sup>8</sup> (9.7x10 <sup>5</sup> )	1.5x10 <sup>9</sup> (1.7x10 <sup>6</sup> )	6.1x10 <sup>7</sup> (6.7x10 <sup>4</sup> )	2.5x10 <sup>7</sup> (2.8x10 <sup>4</sup> )	1.0x10 <sup>8</sup> (1.1x10 <sup>5</sup> )
Recip. engines - nat. gas	1,549	2.2x10 <sup>8</sup> (2.4x10 <sup>5</sup> )	7.0x10 <sup>6</sup> (7.7x10 <sup>3</sup> )	3.9x10 <sup>7</sup> (4.3x10 <sup>4</sup> )	2.5x10 <sup>7</sup> (2.7x10 <sup>4</sup> )	1.4x10 <sup>6</sup> (1.5x10 <sup>3</sup> )
Wood boilers	1,259	1.4x10 <sup>8</sup> (1.5x10 <sup>5</sup> )	2.2x10 <sup>7</sup> (2.4x10 <sup>4</sup> )	3.5x10 <sup>7</sup> (3.8x10 <sup>4</sup> )	1.7x10 <sup>8</sup> (1.9x10 <sup>5</sup> )	2.4x10 <sup>8</sup> (2.6x10 <sup>5</sup> )
Cement kilns	411	1.3x10 <sup>8</sup> (1.4x10 <sup>5</sup> )	6.8x10 <sup>8</sup> (7.5x10 <sup>5</sup> )	4.1x10 <sup>4</sup> (4.5x10 <sup>1</sup> )	1.3x10 <sup>5</sup> (1.4x10 <sup>2</sup> )	6.9x10 <sup>8</sup> (7.6x10 <sup>5</sup> )
Gas turbines - natural gas	144	2.0x10 <sup>7</sup> (2.2x10 <sup>4</sup> )	1.8x10 <sup>6</sup> (2.0x10 <sup>3</sup> )	1.5x10 <sup>6</sup> (1.6x10 <sup>3</sup> )	1.4x10 <sup>6</sup> (1.5x10 <sup>3</sup> )	2.6x10 <sup>5</sup> (2.9x10 <sup>2</sup> )
Steel foundry furnaces <sup>†</sup>	349	1.6x10 <sup>7</sup> (1.8x10 <sup>4</sup> )	5.1x10 <sup>6</sup> (5.6x10 <sup>3</sup> )	4.3x10 <sup>5</sup> (4.7x10 <sup>2</sup> )	6.3x10 <sup>6</sup> (6.9x10 <sup>3</sup> )	8.5x10 <sup>6</sup> (9.4x10 <sup>3</sup> )
Recip. engines - diesel	35	1.9x10 <sup>7</sup> (2.1x10 <sup>4</sup> )	2.5x10 <sup>6</sup> (2.8x10 <sup>3</sup> )	2.3x10 <sup>6</sup> (2.5x10 <sup>3</sup> )	4.1x10 <sup>6</sup> (4.5x10 <sup>3</sup> )	1.4x10 <sup>6</sup> (1.5x10 <sup>3</sup> )
Waste gas flares	213	1.4x10 <sup>7</sup> (1.5x10 <sup>4</sup> )	1.6x10 <sup>8</sup> (1.8x10 <sup>5</sup> )	1.3x10 <sup>7</sup> (1.4x10 <sup>4</sup> )	1.8x10 <sup>6</sup> (2.0x10 <sup>3</sup> )	2.8x10 <sup>5</sup> (3.1x10 <sup>2</sup> )
Charcoal retorts	110	1.3x10 <sup>7</sup> (1.4x10 <sup>4</sup> )	8.0x10 <sup>6</sup> (8.8x10 <sup>3</sup> )	3.3x10 <sup>7</sup> (3.6x10 <sup>4</sup> )	6.0x10 <sup>7</sup> (6.6x10 <sup>4</sup> )	8.0x10 <sup>7</sup> (8.8x10 <sup>4</sup> )
Recovery boilers	219	1.1x10 <sup>7</sup> (1.2x10 <sup>4</sup> )	7.5x10 <sup>7</sup> (8.2x10 <sup>4</sup> )	3.8x10 <sup>6</sup> (4.2x10 <sup>3</sup> )	6.8x10 <sup>8</sup> (7.5x10 <sup>5</sup> )	2.4x10 <sup>8</sup> (2.6x10 <sup>5</sup> )
Iron and steel furnaces	414	6.1x10 <sup>6</sup> (6.7x10 <sup>3</sup> )	1.0x10 <sup>8</sup> (1.1x10 <sup>5</sup> )	4.3x10 <sup>5</sup> (4.7x10 <sup>2</sup> )	8.5x10 <sup>9</sup> (9.3x10 <sup>6</sup> )	4.4x10 <sup>8</sup> (4.8x10 <sup>5</sup> )
Coke ovens (by-product)	375	5.3x10 <sup>6</sup> (5.8x10 <sup>3</sup> )	1.5x10 <sup>8</sup> (1.6x10 <sup>5</sup> )	8.3x10 <sup>7</sup> (9.1x10 <sup>4</sup> )	3.0x10 <sup>7</sup> (3.3x10 <sup>4</sup> )	8.2x10 <sup>7</sup> (9.0x10 <sup>4</sup> )
Glass furnaces	244	4.9x10 <sup>6</sup> (5.4x10 <sup>3</sup> )	2.1x10 <sup>6</sup> (2.3x10 <sup>3</sup> )	1.7x10 <sup>5</sup> (1.9x10 <sup>2</sup> )	1.9x10 <sup>4</sup> (2.1x10 <sup>1</sup> )	1.3x10 <sup>7</sup> (1.4x10 <sup>4</sup> )
Ammonia reformers	55	3.9x10 <sup>6</sup> (4.3x10 <sup>3</sup> )	5.5x10 <sup>3</sup> (6.0x10 <sup>0</sup> )	1.1x10 <sup>8</sup> (1.2x10 <sup>5</sup> )	6.9x10 <sup>6</sup> (7.6x10 <sup>3</sup> )	1.8x10 <sup>5</sup> (2.0x10 <sup>2</sup> )
Plywood dryers	510	1.5x10 <sup>6</sup> (1.6x10 <sup>3</sup> )	3.4x10 <sup>4</sup> (3.7x10 <sup>1</sup> )	7.3x10 <sup>7</sup> (8.0x10 <sup>4</sup> )	4.4x10 <sup>5</sup> (4.8x10 <sup>2</sup> )	1.9x10 <sup>7</sup> (2.1x10 <sup>4</sup> )
Cement dryers	229	1.4x10 <sup>6</sup> (1.5x10 <sup>3</sup> )	1.2x10 <sup>7</sup> (1.3x10 <sup>4</sup> )	0 (0)	0 (0)	1.4x10 <sup>8</sup> (1.5x10 <sup>5</sup> )

\*Interpreted as being the number of identifiable devices in the EPA National Emissions Data System

<sup>†</sup>Includes open hearth and heat-treating furnace

## SECTION A-9.0

### COMBUSTION DEVICE RECOMMENDATIONS FOR FIELD TEST

Selection of devices for testing involved first searching for industries which were large emitters, especially of NO<sub>x</sub>, and large consumers of energy. Then, each industry was examined to determine the type(s) of combustion device(s) representing a significant fraction of the industry's emission. Other considerations, such as device commonality, also entered into the recommendation process.

The program requires approximately 25 field tests and these were allocated based on the relative NO<sub>x</sub> emissions of the devices but with a minimum of one test per device. This proportioning procedure resulted in the number of tests for each device (Table A-9-1).

Table A-9-1 ranks devices by emissions and energy consumption. In the actual selection, suitability for combustion modifications must also be considered.

TABLE A-9-1. DEVICES RECOMMENDED FOR FIELD TEST AND NUMBER OF UNITS

Device	No. of Units
Process heater, Petroleum	9
Reciprocating engine - natural gas fuel	2
Woodwaste boiler	2
Cement kiln	2
Gas turbine - natural gas fuel	1
Reciprocating engine - diesel fuel	1
Open hearth furnace, steel	1
Soaking pit/reheat furnace	1
Blast furnace	1
Charcoal retort	1
Recovery boiler	1
Coke oven	1
Glass furnace	1
Ammonia reformer	1

## SECTION A-10.0

### INDUSTRIAL COMBUSTION DEVICE CHARACTERISTICS

The following sections present characteristic information of those combustion devices recommended for field testing. The discussions will follow the format of:

1. Major manufacturers
2. Associations
3. Basic equipment and combustor design
4. Current fuel use, trends and properties
5. Trends in equipment type, age, size and use
6. Total number and geographic distribution
7. Limitations in equipment uses and fuels
8. Quantity and geographic distribution of fuels used
9. Air pollutant emissions.

The amount of information presented directly reflects the amount of information obtained from national associations, equipment manufacturers, and device users.

#### A-10.1 QUANTITY AND GEOGRAPHIC DISTRIBUTION OF FUELS USED

Reference A-2-3 presents the quantities of fossil fuels purchased by the two-digit SIC industries in each of the 50 states for 1971. These data were used to prepare Table A-10.1-1 which presents the fossil fuel usage in the following important industries identified by the present study:

- . Paper and allied products - SIC 26
- . Chemicals and allied products - SIC 28
- . Petroleum and coal products - SIC 29
- . Stone, clay, and glass products - SIC 32
- . Primary metal industries - SIC 33
- . Fabricated metal products - SIC 34

The fuels tabulated in Table A-10.1-1 are:

- . Distillate fuel oil
- . Residual fuel oil
- . Coal, coke and breeze
- . Natural gas

TABLE A-10.1-1. FOSSIL FUEL PURCHASED BY TWO-DIGIT SIC INDUSTRIES (1971)  
(gigajoules per year)

	Paper and Allied Products SIC 26		Chemicals and Allied Products SIC 28		Petroleum and Coal Products SIC 29		Stone, Clay and Glass Products SIC 32		Primary Metal Industries SIC 33		Fabricated Metal Products SIC 34	
Alabama	3.3 <sup>6</sup> 2.4 <sup>7</sup>	4.2 <sup>6</sup> 3.9 <sup>7</sup>	9.2 <sup>5</sup> 1.7 <sup>7</sup>	7.2 <sup>5</sup> 3.6 <sup>7</sup>	6.7 <sup>4</sup> -	4.2 <sup>4</sup> 2.6 <sup>6</sup>	1.6 <sup>6</sup> 6.4 <sup>6</sup>	2.9 <sup>4</sup> 2.3 <sup>7</sup>	7.7 <sup>5</sup> 2.7 <sup>7</sup>	4.7 <sup>6</sup> 4.8 <sup>7</sup>	9.1 <sup>4</sup> 1.4 <sup>5</sup>	- 2.6 <sup>6</sup>
Alaska	-	-	-	-	-	-	-	-	-	-	-	-
Arizona	-	-	1.8 <sup>4</sup> -	- 7.6 <sup>5</sup>	-	-	4.4 <sup>4</sup> -	3.3 <sup>5</sup> 6.4 <sup>6</sup>	5.7 <sup>5</sup> -	2.7 <sup>4</sup> 2.4 <sup>7</sup>	-	- 7.6 <sup>5</sup>
Arkansas	8.3 <sup>5</sup> -	3.0 <sup>6</sup> 3.4 <sup>7</sup>	1.8 <sup>3</sup> -	2.8 <sup>6</sup> 4.1 <sup>7</sup>	-	1.1 <sup>7</sup>	5.5 <sup>5</sup> -	4.5 <sup>6</sup> 1.2 <sup>7</sup>	1.4 <sup>5</sup> -	4.6 <sup>4</sup> 6.8 <sup>6</sup>	-	- 8.7 <sup>5</sup>
California	1.2 <sup>6</sup> 1.3 <sup>5</sup>	1.8 <sup>6</sup> 2.5 <sup>7</sup>	1.2 <sup>6</sup> -	2.4 <sup>5</sup> 5.5 <sup>7</sup>	5.1 <sup>5</sup> -	6.8 <sup>5</sup> 1.5 <sup>8</sup>	2.4 <sup>6</sup> 2.2 <sup>4</sup>	2.5 <sup>6</sup> 9.7 <sup>7</sup>	5.6 <sup>6</sup> 3.7 <sup>6</sup>	6.7 <sup>5</sup> 3.8 <sup>7</sup>	2.6 <sup>5</sup> -	1.7 <sup>5</sup> 1.5 <sup>7</sup>
Colorado	6.1 <sup>2</sup> -	1.1 <sup>4</sup> 2.2 <sup>5</sup>	4.9 <sup>3</sup> 2.4 <sup>5</sup>	3.8 <sup>5</sup> 2.1 <sup>6</sup>	7.9 <sup>4</sup> -	1.2 <sup>5</sup> 2.3 <sup>6</sup>	-	-	-	-	1.9 <sup>4</sup> -	- 1.2 <sup>6</sup>
Connecticut	-	-	7.4 <sup>5</sup> 4.1 <sup>4</sup>	1.0 <sup>7</sup> 9.8 <sup>5</sup>	-	-	7.4 <sup>5</sup> -	2.2 <sup>6</sup> 1.1 <sup>6</sup>	2.1 <sup>6</sup> -	5.9 <sup>6</sup> 5.1 <sup>6</sup>	1.1 <sup>6</sup> -	2.2 <sup>6</sup> 1.6 <sup>6</sup>
Delaware	-	-	-	-	-	-	-	-	1.3 <sup>5</sup> 5.5 <sup>3</sup>	1.4 <sup>6</sup> 1.3 <sup>6</sup>	6.8 <sup>3</sup> -	3.4 <sup>4</sup> -
Florida	8.1 <sup>6</sup> -	3.5 <sup>7</sup> 1.5 <sup>7</sup>	3.7 <sup>6</sup> 1.0 <sup>6</sup>	5.2 <sup>6</sup> 3.9 <sup>7</sup>	3.1 <sup>5</sup> -	3.6 <sup>5</sup> 3.3 <sup>5</sup>	6.9 <sup>6</sup> -	1.1 <sup>5</sup> 1.0 <sup>7</sup>	2.3 <sup>4</sup> -	- 1.4 <sup>6</sup>	9.8 <sup>4</sup> -	- 1.3 <sup>6</sup>
Georgia	1.4 <sup>7</sup> 7.7 <sup>6</sup>	2.2 <sup>7</sup> 2.0 <sup>7</sup>	1.5 <sup>6</sup> 2.9 <sup>6</sup>	2.0 <sup>6</sup> 1.5 <sup>7</sup>	-	-	1.7 <sup>6</sup> 1.7 <sup>6</sup>	1.1 <sup>4</sup> 2.2 <sup>7</sup>	3.1 <sup>5</sup> -	- 4.4 <sup>6</sup>	3.2 <sup>4</sup> -	5.3 <sup>3</sup> 1.4 <sup>6</sup>
Hawaii	-	-	-	-	-	-	3.2 <sup>5</sup> -	1.3 <sup>6</sup> -	-	-	-	-
Idaho	-	-	1.4 <sup>4</sup> -	- 3.5 <sup>6</sup>	-	-	-	-	-	-	-	-
Illinois	1.3 <sup>6</sup> 1.1 <sup>7</sup>	1.1 <sup>6</sup> 1.1 <sup>7</sup>	3.5 <sup>6</sup> 2.2 <sup>7</sup>	3.2 <sup>6</sup> 3.4 <sup>7</sup>	5.9 <sup>5</sup> 6.4 <sup>4</sup>	1.8 <sup>6</sup> 2.0 <sup>7</sup>	9.7 <sup>5</sup> 1.8 <sup>7</sup>	1.1 <sup>6</sup> 4.1 <sup>7</sup>	1.1 <sup>7</sup> 5.6 <sup>7</sup>	7.9 <sup>6</sup> 1.1 <sup>8</sup>	1.7 <sup>6</sup> 1.9 <sup>6</sup>	1.2 <sup>6</sup> 2.1 <sup>7</sup>
Indiana	6.6 <sup>5</sup> 5.5 <sup>6</sup>	7.3 <sup>4</sup> 2.4 <sup>6</sup>	7.5 <sup>5</sup> 1.4 <sup>7</sup>	7.2 <sup>5</sup> 2.0 <sup>7</sup>	3.9 <sup>5</sup> -	1.3 <sup>7</sup> 9.4 <sup>6</sup>	1.3 <sup>6</sup> 1.6 <sup>7</sup>	3.6 <sup>5</sup> 2.9 <sup>7</sup>	1.3 <sup>7</sup> 2.7 <sup>7</sup>	1.9 <sup>7</sup> 1.3 <sup>8</sup>	5.6 <sup>5</sup> 1.4 <sup>6</sup>	3.6 <sup>5</sup> 8.2 <sup>6</sup>
Iowa	7.9 <sup>4</sup> 4.2 <sup>5</sup>	1.3 <sup>5</sup> 2.2 <sup>6</sup>	-	-	-	-	-	-	1.5 <sup>5</sup> -	1.7 <sup>4</sup> 5.2 <sup>6</sup>	1.3 <sup>5</sup> -	4.6 <sup>4</sup> 1.9 <sup>6</sup>
Kansas	2.0 <sup>4</sup> -	5.0 <sup>4</sup> 2.0 <sup>6</sup>	4.6 <sup>5</sup> 4.4 <sup>5</sup>	3.5 <sup>5</sup> 3.5 <sup>7</sup>	-	-	1.1 <sup>5</sup> 2.8 <sup>5</sup>	2.0 <sup>5</sup> 1.8 <sup>7</sup>	-	-	3.3 <sup>4</sup> -	- 1.2 <sup>6</sup>

9.1<sup>8</sup> = 9.1x10<sup>9</sup> equivalent gigajoules (GJ)  
1 GJ = 10<sup>9</sup> J = 0.948x10<sup>6</sup> Btu = 277 kW-hr

State	SIC	
	Distillate Coal, Coke	Residual Natural Gas

TABLE A-10.1-1. Continued

	Paper and Allied Products SIC 26		Chemicals and Allied Products SIC 28		Petroleum and Coal Products SIC 29		Stone, Clay, and Glass Products SIC 32		Primary Metal Industries SIC 33		Fabricated Metal Products SIC 34	
Kentucky	3.3 <sup>4</sup>	6.9 <sup>4</sup>	5.8 <sup>5</sup>	3.0 <sup>5</sup>	-	-	3.1 <sup>5</sup>	4.8 <sup>5</sup>	4.1 <sup>5</sup>	3.9 <sup>5</sup>	6.2 <sup>4</sup>	-
	-	6.8 <sup>6</sup>	1.8 <sup>7</sup>	1.1 <sup>7</sup>	-	-	3.1 <sup>6</sup>	4.8 <sup>6</sup>	2.9 <sup>7</sup>	2.1 <sup>7</sup>	1.1 <sup>6</sup>	4.3 <sup>6</sup>
Louisiana	2.0 <sup>6</sup>	5.3 <sup>6</sup>	3.0 <sup>4</sup>	-	6.3 <sup>6</sup>	-	3.7 <sup>4</sup>	-	-	-	3.3 <sup>4</sup>	-
	-	6.4 <sup>7</sup>	-	2.5 <sup>8</sup>	-	2.3 <sup>8</sup>	-	1.7 <sup>7</sup>	-	-	-	3.7 <sup>5</sup>
Maine	4.8 <sup>6</sup>	5.2 <sup>7</sup>	1.3 <sup>4</sup>	1.2 <sup>6</sup>	-	-	1.8 <sup>5</sup>	2.0 <sup>6</sup>	2.6 <sup>4</sup>	7.6 <sup>4</sup>	-	-
	4.5 <sup>5</sup>	-	-	-	-	-	-	-	-	1.1 <sup>5</sup>	-	-
Maryland	9.6 <sup>5</sup>	1.8 <sup>6</sup>	1.3 <sup>6</sup>	5.8 <sup>6</sup>	-	-	2.7 <sup>6</sup>	6.3 <sup>6</sup>	3.2 <sup>6</sup>	2.2 <sup>7</sup>	3.6 <sup>5</sup>	1.4 <sup>5</sup>
	1.1 <sup>7</sup>	2.3 <sup>6</sup>	6.8 <sup>6</sup>	6.6 <sup>6</sup>	-	-	6.1 <sup>6</sup>	6.4 <sup>6</sup>	1.0 <sup>6</sup>	1.3 <sup>7</sup>	-	2.4 <sup>5</sup>
Massachusetts	5.5 <sup>6</sup>	1.1 <sup>7</sup>	2.3 <sup>6</sup>	4.8 <sup>6</sup>	-	-	2.4 <sup>6</sup>	3.2 <sup>6</sup>	1.8 <sup>6</sup>	1.8 <sup>6</sup>	3.5 <sup>6</sup>	1.3 <sup>6</sup>
	3.0 <sup>5</sup>	2.7 <sup>6</sup>	-	3.1 <sup>6</sup>	-	-	-	1.1 <sup>6</sup>	1.1 <sup>5</sup>	3.1 <sup>6</sup>	1.5 <sup>5</sup>	2.8 <sup>6</sup>
Michigan	1.3 <sup>6</sup>	3.2 <sup>6</sup>	5.2 <sup>5</sup>	3.7 <sup>6</sup>	-	-	6.6 <sup>5</sup>	7.3 <sup>5</sup>	4.4 <sup>6</sup>	9.5 <sup>5</sup>	6.2 <sup>5</sup>	4.5 <sup>5</sup>
	1.9 <sup>7</sup>	3.1 <sup>7</sup>	4.2 <sup>7</sup>	2.6 <sup>7</sup>	-	-	3.7 <sup>7</sup>	1.4 <sup>7</sup>	2.3 <sup>7</sup>	6.3 <sup>7</sup>	3.7 <sup>6</sup>	1.6 <sup>7</sup>
Minnesota	3.7 <sup>5</sup>	2.7 <sup>6</sup>	1.7 <sup>5</sup>	1.5 <sup>5</sup>	-	-	6.3 <sup>5</sup>	1.7 <sup>6</sup>	3.6 <sup>4</sup>	3.9 <sup>6</sup>	3.7 <sup>5</sup>	8.4 <sup>4</sup>
	4.4 <sup>6</sup>	2.1 <sup>7</sup>	1.1 <sup>6</sup>	7.6 <sup>5</sup>	-	-	1.1 <sup>6</sup>	5.7 <sup>6</sup>	2.9 <sup>5</sup>	2.7 <sup>6</sup>	2.2 <sup>4</sup>	2.3 <sup>6</sup>
Mississippi	2.0 <sup>6</sup>	1.0 <sup>6</sup>	1.3 <sup>5</sup>	2.7 <sup>5</sup>	-	-	1.0 <sup>5</sup>	7.4 <sup>4</sup>	-	-	2.5 <sup>3</sup>	-
	-	2.8 <sup>7</sup>	-	2.7 <sup>7</sup>	-	-	-	1.1 <sup>7</sup>	-	1.4 <sup>6</sup>	-	5.5 <sup>5</sup>
Missouri	-	-	1.1 <sup>6</sup>	8.0 <sup>4</sup>	6.2 <sup>5</sup>	7.2 <sup>4</sup>	2.9 <sup>5</sup>	6.8 <sup>4</sup>	6.2 <sup>5</sup>	1.6 <sup>5</sup>	8.3 <sup>4</sup>	1.3 <sup>4</sup>
	-	-	7.2 <sup>6</sup>	1.4 <sup>7</sup>	-	5.1 <sup>6</sup>	2.8 <sup>7</sup>	2.7 <sup>7</sup>	2.2 <sup>6</sup>	1.0 <sup>7</sup>	-	4.5 <sup>6</sup>
Montana	-	-	-	-	-	-	9.8 <sup>3</sup>	-	-	-	-	-
	-	-	-	-	-	4.9 <sup>6</sup>	-	4.0 <sup>6</sup>	-	-	-	-
Nebraska	-	-	5.8 <sup>5</sup>	-	-	-	-	3.3 <sup>3</sup>	1.6 <sup>5</sup>	-	2.3 <sup>4</sup>	4.3 <sup>4</sup>
	-	-	-	8.6 <sup>6</sup>	-	-	1.9 <sup>6</sup>	4.6 <sup>6</sup>	-	1.1 <sup>6</sup>	-	9.8 <sup>5</sup>
Nevada	-	-	5.0 <sup>4</sup>	9.9 <sup>4</sup>	-	-	3.5 <sup>5</sup>	3.3 <sup>4</sup>	-	-	-	-
	-	-	-	3.4 <sup>6</sup>	-	-	-	7.9 <sup>6</sup>	-	-	-	-
New Hampshire	4.3 <sup>5</sup>	1.3 <sup>7</sup>	1.7 <sup>5</sup>	1.4 <sup>5</sup>	-	-	2.5 <sup>5</sup>	3.4 <sup>5</sup>	2.2 <sup>5</sup>	-	1.3 <sup>5</sup>	4.5 <sup>4</sup>
	-	8.7 <sup>5</sup>	-	1.1 <sup>5</sup>	-	-	-	2.2 <sup>5</sup>	-	-	-	1.1 <sup>5</sup>
New Jersey	9.8 <sup>6</sup>	1.6 <sup>7</sup>	3.3 <sup>7</sup>	2.2 <sup>7</sup>	3.6 <sup>5</sup>	1.8 <sup>7</sup>	-	-	3.4 <sup>6</sup>	9.5 <sup>6</sup>	2.3 <sup>6</sup>	1.8 <sup>6</sup>
	-	2.9 <sup>6</sup>	7.8 <sup>6</sup>	1.7 <sup>7</sup>	-	7.8 <sup>6</sup>	-	-	7.2 <sup>6</sup>	6.1 <sup>6</sup>	-	5.1 <sup>6</sup>
New Mexico	-	-	-	-	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-
New York	1.2 <sup>7</sup>	1.9 <sup>7</sup>	6.5 <sup>6</sup>	9.2 <sup>6</sup>	1.1 <sup>6</sup>	1.6 <sup>5</sup>	6.6 <sup>6</sup>	8.0 <sup>6</sup>	6.4 <sup>6</sup>	9.3 <sup>6</sup>	1.5 <sup>6</sup>	1.8 <sup>6</sup>
	8.0 <sup>6</sup>	4.9 <sup>6</sup>	2.5 <sup>7</sup>	9.8 <sup>6</sup>	5.8 <sup>4</sup>	2.2 <sup>5</sup>	8.0 <sup>6</sup>	1.3 <sup>7</sup>	1.6 <sup>7</sup>	2.9 <sup>7</sup>	2.2 <sup>5</sup>	6.0 <sup>6</sup>
N. Carolina	8.3 <sup>5</sup>	2.9 <sup>7</sup>	5.8 <sup>6</sup>	5.9 <sup>6</sup>	-	-	1.1 <sup>6</sup>	5.5 <sup>6</sup>	8.5 <sup>4</sup>	2.2 <sup>4</sup>	1.4 <sup>5</sup>	1.1 <sup>4</sup>
	1.9 <sup>7</sup>	2.5 <sup>6</sup>	6.0 <sup>6</sup>	1.8 <sup>7</sup>	-	-	7.5 <sup>4</sup>	9.2 <sup>6</sup>	-	2.1 <sup>6</sup>	-	1.3 <sup>6</sup>
N. Dakota	-	-	-	-	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-
Ohio	1.6 <sup>6</sup>	2.4 <sup>5</sup>	2.5 <sup>6</sup>	2.1 <sup>6</sup>	8.9 <sup>5</sup>	1.1 <sup>6</sup>	2.0 <sup>6</sup>	1.0 <sup>6</sup>	1.5 <sup>7</sup>	4.9 <sup>6</sup>	4.2 <sup>5</sup>	1.8 <sup>5</sup>
	3.9 <sup>7</sup>	1.1 <sup>7</sup>	6.5 <sup>7</sup>	3.1 <sup>7</sup>	9.7 <sup>5</sup>	2.6 <sup>7</sup>	4.0 <sup>7</sup>	7.2 <sup>7</sup>	1.7 <sup>8</sup>	1.7 <sup>8</sup>	7.2 <sup>6</sup>	2.3 <sup>7</sup>
Oklahoma	2.5 <sup>3</sup>	1.1 <sup>5</sup>	-	-	1.1 <sup>5</sup>	-	-	-	-	-	-	-
	-	1.5 <sup>6</sup>	-	1.7 <sup>6</sup>	-	5.7 <sup>7</sup>	-	1.7 <sup>7</sup>	1.0 <sup>6</sup>	8.3 <sup>6</sup>	-	1.6 <sup>6</sup>

TABLE A-10.1-1. Continued

	Paper and Allied Products SIC 26		Chemicals and Allied Products SIC 28		Petroleum and Coal Products SIC 29		Stone, Clay, and Glass Products SIC 32		Primary Metal Industries SIC 33		Fabricated Metal Products SIC 34	
Oregon	1.0 <sup>6</sup>	9.1 <sup>6</sup>	3.7 <sup>5</sup>	1.6 <sup>6</sup>	5.3 <sup>4</sup>	2.7 <sup>5</sup>	-	-	-	-	-	-
	-	2.0 <sup>7</sup>	-	1.2 <sup>6</sup>	-	6.6 <sup>5</sup>	-	-	-	-	-	-
Pennsylvania	9.3 <sup>6</sup>	1.4 <sup>7</sup>	4.0 <sup>6</sup>	1.5 <sup>7</sup>	2.3 <sup>6</sup>	1.4 <sup>7</sup>	4.1 <sup>6</sup>	3.3 <sup>6</sup>	1.7 <sup>7</sup>	3.4 <sup>7</sup>	3.1 <sup>6</sup>	2.0 <sup>6</sup>
	2.6 <sup>7</sup>	2.1 <sup>7</sup>	3.4 <sup>7</sup>	1.4 <sup>7</sup>	5.8 <sup>6</sup>	2.0 <sup>8</sup>	5.5 <sup>7</sup>	5.2 <sup>7</sup>	1.3 <sup>8</sup>	2.4 <sup>8</sup>	1.1 <sup>6</sup>	1.5 <sup>7</sup>
Rhode Island	7.5 <sup>4</sup>	1.3 <sup>6</sup>	3.1 <sup>4</sup>	8.6 <sup>5</sup>	-	-	9.0 <sup>5</sup>	3.1 <sup>5</sup>	7.3 <sup>5</sup>	7.9 <sup>5</sup>	-	-
	-	2.2 <sup>5</sup>	-	3.3 <sup>5</sup>	-	-	-	2.0 <sup>6</sup>	-	1.5 <sup>6</sup>	-	-
S. Carolina	1.4 <sup>7</sup>	1.2 <sup>7</sup>	1.5 <sup>6</sup>	1.7 <sup>6</sup>	-	-	5.3 <sup>5</sup>	8.9 <sup>5</sup>	5.1 <sup>5</sup>	2.9 <sup>5</sup>	-	-
	2.1 <sup>6</sup>	7.4 <sup>6</sup>	2.9 <sup>7</sup>	1.4 <sup>9</sup>	-	-	-	1.4 <sup>7</sup>	-	9.8 <sup>5</sup>	-	-
S. Dakota	-	-	-	-	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-
Tennessee	1.7 <sup>6</sup>	5.8 <sup>6</sup>	8.6 <sup>5</sup>	5.8 <sup>5</sup>	-	9.0 <sup>4</sup>	4.4 <sup>5</sup>	3.3 <sup>5</sup>	3.4 <sup>5</sup>	-	1.4 <sup>5</sup>	9.0 <sup>4</sup>
	6.1 <sup>6</sup>	8.0 <sup>6</sup>	6.6 <sup>7</sup>	4.5 <sup>7</sup>	-	1.7 <sup>6</sup>	1.1 <sup>7</sup>	2.1 <sup>7</sup>	1.7 <sup>6</sup>	1.1 <sup>7</sup>	1.9 <sup>4</sup>	3.6 <sup>6</sup>
Texas	6.8 <sup>4</sup>	5.7 <sup>5</sup>	1.8 <sup>3</sup>	6.4 <sup>5</sup>	1.4 <sup>5</sup>	9.6 <sup>6</sup>	1.8 <sup>6</sup>	1.0 <sup>5</sup>	1.5 <sup>6</sup>	7.2 <sup>5</sup>	1.4 <sup>4</sup>	-
	-	3.4 <sup>7</sup>	-	6.1 <sup>8</sup>	-	8.0 <sup>8</sup>	-	8.7 <sup>7</sup>	4.1 <sup>7</sup>	1.0 <sup>8</sup>	-	1.3 <sup>7</sup>
Utah	-	-	2.8 <sup>5</sup>	1.2 <sup>4</sup>	-	-	9.0 <sup>4</sup>	3.2 <sup>5</sup>	-	-	-	-
	-	-	-	7.6 <sup>5</sup>	-	3.8 <sup>6</sup>	1.4 <sup>6</sup>	4.8 <sup>6</sup>	-	-	-	-
Vermont	-	-	1.2 <sup>5</sup>	-	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-
Virginia	3.4 <sup>6</sup>	1.1 <sup>7</sup>	1.2 <sup>7</sup>	1.3 <sup>7</sup>	-	-	3.2 <sup>6</sup>	1.5 <sup>5</sup>	7.3 <sup>5</sup>	-	7.1 <sup>4</sup>	2.4 <sup>4</sup>
	2.2 <sup>7</sup>	5.8 <sup>6</sup>	4.3 <sup>7</sup>	4.1 <sup>6</sup>	-	-	1.3 <sup>7</sup>	1.1 <sup>7</sup>	1.2 <sup>6</sup>	4.0 <sup>6</sup>	1.1 <sup>4</sup>	7.6 <sup>5</sup>
Washington	4.9 <sup>6</sup>	1.9 <sup>7</sup>	5.6 <sup>5</sup>	6.8 <sup>5</sup>	-	-	-	-	7.0 <sup>5</sup>	1.6 <sup>6</sup>	2.8 <sup>4</sup>	1.6 <sup>5</sup>
	-	3.6 <sup>7</sup>	8.5 <sup>5</sup>	1.1 <sup>7</sup>	-	-	-	-	5.5 <sup>3</sup>	1.3 <sup>7</sup>	-	7.6 <sup>5</sup>
W. Virginia	-	-	4.6 <sup>5</sup>	2.4 <sup>5</sup>	3.6 <sup>4</sup>	8.2 <sup>4</sup>	1.3 <sup>5</sup>	1.0 <sup>5</sup>	2.4 <sup>6</sup>	3.3 <sup>3</sup>	1.1 <sup>5</sup>	1.6 <sup>4</sup>
	-	-	9.2 <sup>7</sup>	2.1 <sup>7</sup>	6.3 <sup>5</sup>	1.1 <sup>6</sup>	6.0 <sup>6</sup>	2.7 <sup>7</sup>	2.9 <sup>7</sup>	1.7 <sup>7</sup>	3.6 <sup>4</sup>	1.6 <sup>6</sup>
Wisconsin	1.9 <sup>6</sup>	2.7 <sup>6</sup>	4.8 <sup>5</sup>	2.2 <sup>5</sup>	-	-	4.6 <sup>5</sup>	-	6.1 <sup>5</sup>	8.6 <sup>5</sup>	3.6 <sup>5</sup>	2.2 <sup>5</sup>
	5.4 <sup>7</sup>	3.5 <sup>7</sup>	4.8 <sup>6</sup>	3.1 <sup>6</sup>	-	-	2.2 <sup>6</sup>	2.8 <sup>6</sup>	4.9 <sup>6</sup>	1.5 <sup>7</sup>	7.3 <sup>5</sup>	6.8 <sup>6</sup>
Wyoming	-	-	-	-	-	5.3 <sup>4</sup>	-	-	-	-	-	-
	-	-	-	-	-	1.1 <sup>7</sup>	-	-	-	-	-	-
U.S. Totals	1.1 <sup>8</sup>	3.1 <sup>8</sup>	9.1 <sup>7</sup>	1.3 <sup>8</sup>	2.0 <sup>7</sup>	7.1 <sup>7</sup>	6.8 <sup>7</sup>	5.6 <sup>7</sup>	9.8 <sup>7</sup>	1.4 <sup>8</sup>	1.8 <sup>7</sup>	1.3 <sup>7</sup>
	2.6 <sup>8</sup>	5.2 <sup>8</sup>	5.1 <sup>8</sup>	1.6 <sup>9</sup>	9.9 <sup>6</sup>	1.4 <sup>9</sup>	2.8 <sup>8</sup>	7.7 <sup>8</sup>	6.0 <sup>8</sup>	1.2 <sup>9</sup>	1.8 <sup>7</sup>	1.7 <sup>8</sup>

State	SIC	
	Distillate Coal, Coke	Residual Natural Gas

The use of Table A-10.1-1 is illustrated by the following example:

In the state of Alabama, paper and allied products (SIC 26) purchased the equivalent of:

- $9.1 \times 10^8$  kw-hr of distillate fuel oil
- $1.2 \times 10^6$  kw-hr of residual fuel oil
- $6.6 \times 10^9$  kw-hr of coal, coke and breeze
- $1.1 \times 10^{10}$  kw-hr of natural gas

during 1971.

As presented in Reference A-2-3 these purchased fossil fuel usages cover only the two-digit SIC activities. Thus, it was not possible to extract similar information on, for example, the four-digit cement activity (SIC 3241).

Table A-10.1-1 is intended to supply the bulk of the geographic fuel usage data in one central location within the report instead of breaking the information down when discussing specific industrial combustion devices.

## A-10.2 CEMENT KILNS

### Major Manufacturers

There are four major manufacturers of cement kilns:

Allis-Chalmers (Wisconsin)  
Fuller (Pennsylvania)  
Polysius (Georgia)  
F. L. Schmidt (Pennsylvania)

These manufacturers can perform a "turn-key" operation; they will design and construct an entire plant to the user's specifications. In some instances an engineering firm will do the design work.

### Associations

There are no known associations of cement kiln manufacturers. However, the Portland Cement Association (Skokie, Illinois) represents the cement manufacturers.

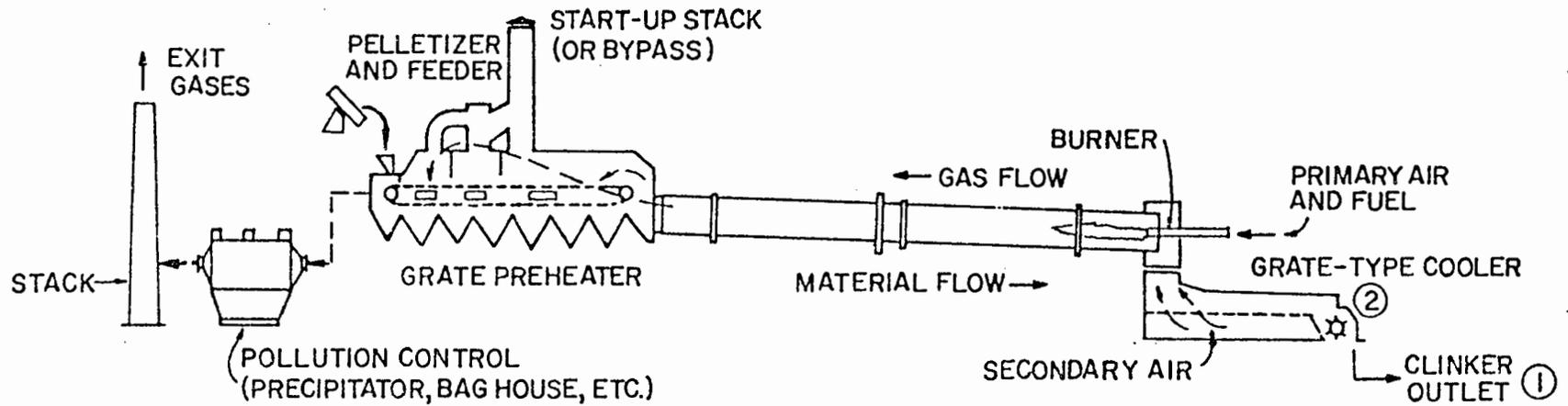
### Basic Equipment and Combustor Design (Ref. A-10.2-1)

Cement kilns are typically of the rotary type and in dimension can be up to 183 m (600 ft) long and 7.6 m (25 ft) in diameter constructed of a refractory lined metal shell. The axis of rotation is tipped so that the feed end is higher than the discharge end. Typically a single burner is fitted at the discharge end with the exhaust gases passing countercurrent to the material motion.

Waste heat is extensively utilized, e.g.:

- . Secondary combustion air is preheated in the process of cooling the clinker (kiln finished product)
- . Waste gas is used to preheat the incoming raw materials - a substantial amount of calcining can be performed in this manner
- . Waste gas can also be used in a steam boiler.

Figure A-10.2-1 is a sketch of a grate preheater kiln system.



- ① SECONDARY CLINKER COOLING MAY OCCUR HERE
- ② EXCESS COOLER AIR MAY BE VENTED TO ATMOSPHERE THROUGH POLLUTION CONTROL DEVICES OR RECYCLED TO GRATE PREHEATER

Figure A-10.2-1. Grate type preheater kiln system (Portland Cement Association).

Wet or dry processes are used to produce most of United States' cement production with the wet process accepting raw feed material which contains 20% or more water. The choice of a process for a cement kiln is dictated by the water content of the raw materials available at the plant location.

Shortly after entering the kiln, the feed material encounters a chain system (a series of long strands, garlands, or curtains of steel chains fastened to the kiln shell). The chains are alternately exposed to hot exhaust gases and the feed slurry as the kiln rotates. This action causes an increased heat transfer rate to the slurry and also assists in conveying the material down the length of the kiln. A kiln operating on the dry process may also contain a chain system for an increased heat transfer rate. Kiln speed affects the heat transfer rate.

As water evaporates, the material gradually is converted to plastic modules, which the chains convey further. Slightly beyond the end of the feed end chain system, the water is gone, and the dry raw feed progresses through preheating, calcining, and burning zones. The preheating zone raises the temperature from 373 to 1173 K (212 to 1652 F); it also drives off combined water in the raw materials. The calcining zone decarbonates the calcium and magnesium carbonates, and the burning zone (at 1533 K [2300 F] to 1866 K [2900 F] material temperature) causes the clinker-forming chemical reactions to occur. The fresh clinker then travels through the cooling zone of the rotary kiln and drops into a clinker cooler in which ambient air is forced through the hot clinker. A substantial portion of this heated air is then used for combustion of the fuel in the burning zone, while the cool clinker is eventually removed from the cooler ready for finish grinding or intermediate storage.

Material preheaters are stationary devices located upstream from the kiln feed entrance. The function of this device is to initiate the calcining process using waste gas energy. The preheater may consist of a series of from one to five cyclones within which the powder feed is flowing countercurrent to the exhaust gas. The highly turbulent motion is sufficient to induce 40-50% calcination of the raw feed by the time it enters the rotary kiln. In another preheater configuration the feed is first processed into pellets which are placed on a traveling grate which conveys the pellets toward the kiln inlet. At the same time, the kiln exhaust gases are passed through the bed once, or more often twice, to dry, preheat, and partially calcine the feed.

Burners for cement kilns are produced in a variety of configurations primarily depending on the type of fuel being used. The burner is located at the discharge end of the kiln on a non-rotating structure and may be positioned above the kiln axis of rotation and directed toward the charge. This positioning is necessary to avoid direct flame impingement on the refractory lining.

For operation on natural gas the burner may consist of a single pipe which introduces the fuel coaxially within the primary airstream. The burner is designed to produce complete combustion within the minimum distance ("short, hot flame"), or is adjustable to achieve a wide range of flame shapes. The latter is a result of injecting a central core of natural gas (which will yield a long, narrow flame) and another stream through radial holes (provides a very short, bushy flame). By varying the percentage of flow between these two streams, any desired resultant flame shape is obtained.

For fuel oil, the mechanism is much the same. One controlled oil stream flows to oil tips that provide a very long, narrow flame; the other oil stream flows to the tips that are wider in spray angle. A typical adjustable oil burner will use six tips.

Combination gas and oil adjustable kiln burners are designed so that both gas and oil may be fired simultaneously. This permits changeover from one fuel to the other without shutdown.

Burners are presently in service which permit the simultaneous use of coke and either natural gas or fuel oil. These same burners are capable of using any of these fuels alone or substituting pulverized coal for the coke.

Development is proceeding on burners capable of using a coal-oil slurry and a combination of refuse and natural gas.

Approximately 90% of the cement kilns in the United States are presently capable of using more than one fuel. (However, in 1975 only 77% of the kilns actually used more than one fuel type.) The remaining kilns lack the storage or handling facilities (e.g., coal pulverizers, oil storage tanks) which would allow multiple fuel usage, i.e., a facility problem rather than a kiln burner inadequacy.

#### Current Fuel Use, Trends and Properties

Between 1960 and 1973, according to Reference A-10.2-1, there was a gradual shifting away from the use of coal in the U.S. cement industry. During the same time period there were increases by factors of 3.3 and 1.3 in the use of petroleum products and natural gas, respectively. However, in 1973 coal still supplied 39% of the industry energy usage with petroleum products accounting for 15.6% and natural gas for 45.4%. Energy utilization information recently released for 1975 (Ref. A-10.2-2) indicates that the fuel usage trend has reversed to the extent that coal now supplies 48% of the energy requirements with petroleum products and natural gas accounting for 9.4% and 42.6%, respectively. Thus, between 1973 and 1975 the use of coal has increased by 23% while the use of petroleum products and natural gas has decreased by 40% and 6%, respectively, in supplying the energy needs of the cement industry.

Again between 1960 and 1973 kiln energy consumed per unit weight of cement produced decreased by 12%; this decrease is partly attributable to the proportionately greater use of the less energy intensive dry process.

#### Trends In Equipment Type, Age, Size, and Use

Since 1965, according to Reference A-10.2-1, there has been a small shifting toward the use of the less energy intensive dry process. In 1975 (Ref. A-10.2-2) the dry process accounted for 42% of the industry production, an increase from the 1965 level of 39.6%.

Table A-10.2-1, from information contained in Reference A-10.2-1, shows the present kiln capacity broken down by year built. It is concluded from these data that the newer kilns are being built in larger capacities. Table A-10.2-2 is the present kiln population by capacity and process with the size ranges between  $46 \times 10^6$  kg/year and  $320 \times 10^6$  kg/year containing the greatest number.

There are no data available giving the trend in kiln age; however, the arithmetically average kiln was built in 1955, i.e., 20-21 years old.

#### Total Number and Geographical Distribution

As of December 31, 1975 there were 412 cement kilns in the United States producing  $85.0 \times 10^9$  kg/year ( $93.5 \times 10^6$  short tons/year) of cement. Reference A-10.2-3 details the distribution of the kilns by company and geography, and Table A-10.2-3 herein lists the number of kilns and total capacity (wet and dry) by state.

#### Limitations In Equipment Uses and Fuels

There are no limitations on the type of fuel used. Indeed, as previously mentioned approximately 90% of the cement kilns are capable of operating with more than one fuel type.

TABLE A-10.2-1. TREND IN AVERAGE CEMENT KILN CAPACITY

Time Period Built	No. Built	Average Kiln Clinker Capacity	
		10 <sup>3</sup> kg/Year	(10 <sup>3</sup> Short Tons/Year)
1975	9	370 000	(407)
1965 - 1974	69	367 000	(404)
1955 - 1964	152	219 000	(241)
1945 - 1954	79	136 000	(149)
1935 - 1944	17	155 000	(170)
Before 1935	88	96 000	(106)

TABLE A-10.2-2. CEMENT KILN POPULATION BY CAPACITY AND PROCESS

Capacity		Number by Process	
10 <sup>6</sup> kg/YR	10 <sup>3</sup> Tons/YR	Wet	Dry
0 - 45.9	0 - 50	2	14
45.9 - 91.7	50 - 100	27	44
91.7 - 137.6	100 - 150	48	20
137.6 - 183.5	150 - 200	38	23
183.5 - 229.4	200 - 250	36	32
229.4 - 275.2	250 - 300	27	15
275.2 - 321.1	300 - 350	15	11
321.1 - 367.0	350 - 400	6	5
367.0 - 412.8	400 - 450	3	6
412.8 - 458.7	450 - 500	6	4
458.7 - 504.6	500 - 550	3	4
504.6 - 550.5	550 - 600	3	8
550.5 - 596.3	600 - 650	0	2
596.3 - 642.2	650 - 700	1	0
642.2 - 688.1	700 - 750	3	0
688.1 - 733.9	750 - 800	3	1
1055.1 - 1100.9	1150 - 1200	<u>1</u>	<u>0</u>
		222	189

TABLE A-10.2-3. CEMENT CAPACITY AND KILN DISTRIBUTIONS BY STATE

State	Capacity, 10 <sup>6</sup> kg/Year	No. Kilns
Alabama	2043	18
Arizona	1564	10
Arkansas	1132	2
California	9404	41
Colorado	1568	6
Florida	3407	11
Georgia	1433	5
Hawaii	509	3
Illinois	2535	8
Indiana	3152	13
Iowa	2395	17
Kansas	2043	14
Kentucky	600	1
Louisiana	991	6
Maine	427	1
Maryland	1645	7
Michigan	5828	22
Mississippi	878	4
Missouri	4352	12
Montana	600	2
Nebraska	959	6
Nevada	364	2
New Mexico	382	2
New York	5121	18
North Carolina	555	2
Ohio	2627	12
Oklahoma	1491	6
Oregon	573	5
Pennsylvania	8752	63
South Carolina	2308	7
South Dakota	518	3
Tennessee	2172	13
Texas	8125	48
Utah	636	6
Virginia	900	4
Washington	1487	7
West Virginia	820	3
Wisconsin	401	1
Wyoming	172	1

According to Reference A-10.2-1, most of the cement industry is potentially an ideal consumer of higher-sulfur fuels, particularly bituminous coal, a commodity which, for environmental reasons, is not acceptable for power generating plants or other applications. Because of the nature of the process, cement manufacturers can use higher-sulfur fuels without the SO<sub>x</sub> emission problems experienced by power plants, and such use is in progress at some plants. During formation of cement clinker, lime-rich materials are present throughout the kiln. These reactive materials are capable of combining with sulfur oxides formed by combustion of the fuel. In effect, the sulfur from the fuel becomes part of the cement clinker rather than being emitted into the atmosphere.

#### Air Pollutant Emissions

The air pollution emissions from cement kilns, as contained in the NEDS listing (Ref. A-2-2), were shown in Table A-8-1. Cement kilns are ranked fourth in NO<sub>x</sub> emissions. Particulate emissions are highest of all the classes indicated. HC and CO emissions are relatively low because of the long residence time in the kiln. SO<sub>x</sub> emissions shown are high in spite of the expected natural scrubbing. Some cement feed materials may provide the scrubbing action.

### A-10.3 GLASS CONTAINER FURNACES

#### Major Manufactures

There are two major manufacturers of glass container furnaces:

Toledo Engineering (Toledo, Ohio)

Anderson Construction (Pico Rivera, California).

Each of these organizations will design and build the furnace to the user's specifications or the user may do the design work. In either event, the burners are furnished by another supplier (of which there are 75) or will be built directly for the user by a local shop.

#### Associations

There are no known associations representing the furnace manufacturers. However, the Glass Packaging Institute (Washington, D.C.) represents the users.

#### Basic Equipment and Combustor Design

The furnaces are divided into two parts. The first part melts the raw materials at high temperature and the second part refines the molten glass at a lower temperature. Two burners are fitted in the end-port configuration (wherein the flame is directed the length of the furnace) and multiple burners are used in the side-port arrangement (the flame being directed across the width of the furnace). Natural gas is the primary fuel with No. 2 oil or propane as a standby fuel. Regenerative air preheaters are employed and consist of refractory brick checker work located at one end of an end port furnace and on each side of a side-port furnace. Figure A-10.3-1 is a sketch of a side-port glass container furnace showing these major components, while Figure A-10.3-2 shows two types of burner configurations.

Electric boosting can be used to increase the production of a furnace. Thus, the production of a fossil fueled furnace, which is designed to meet a certain market demand, can be increased to meet an increased market demand.

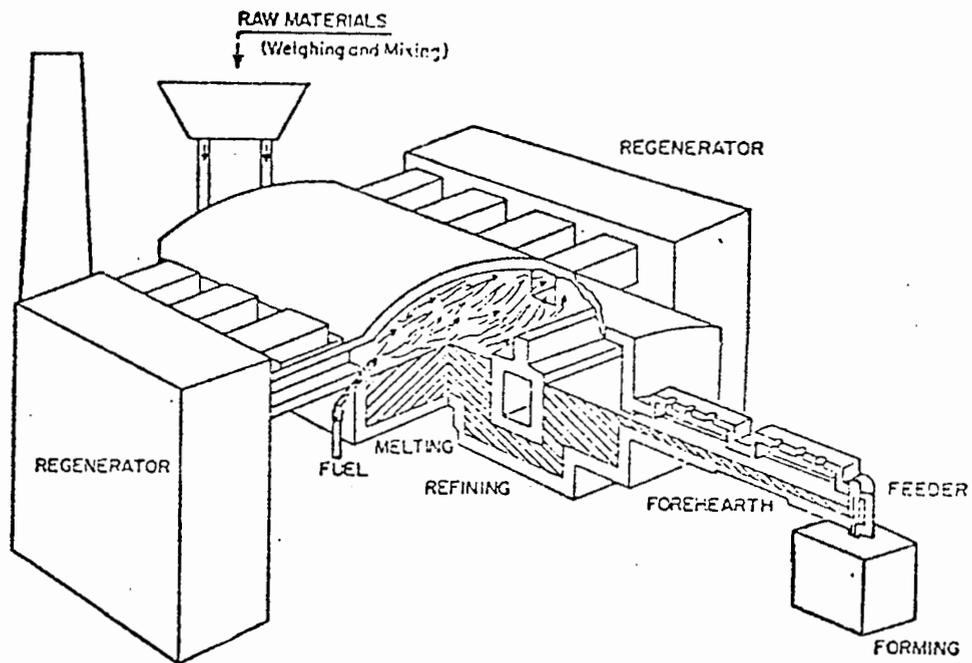
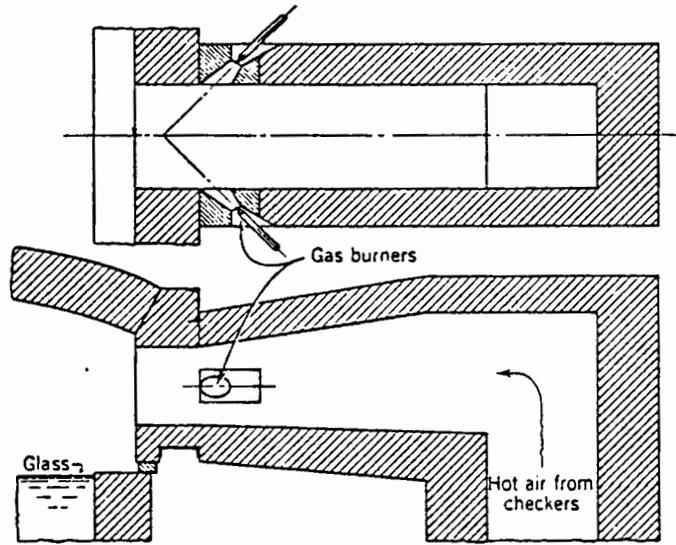
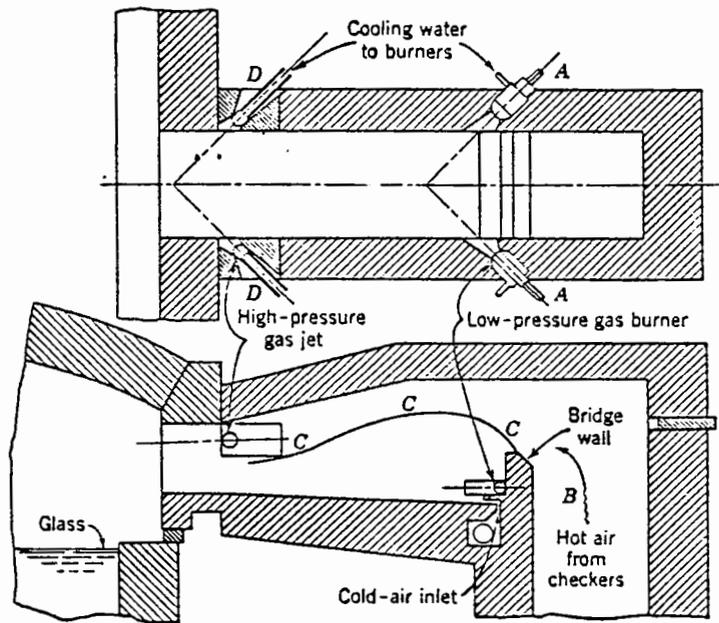


Figure A-10.3-1. Regenerative side-port glass container furnace (Battelle Columbus Laboratories).



Standard inside-mixing burners for glass tanks.



Cracking and mixing burners for glass tanks.

Figure A-10.3-2. Burner configurations for glass furnaces (North American Mfg. Co.).

Natural gas fired annealing kilns are the next largest energy consumers in the glass container industries and are used to stress relieve the finished glass products.

Current Fuel Use, Trends and Properties

Table A-10.3-1, reproduced from Reference A-10.3-1, presents the energy utilization in the glass container industry for the years 1971, 1973, and 1974. During this time period the percentage use of natural gas has decreased while that of both distillate and residual fuel oils has increased; this reflects the limited supply of natural gas. The total energy consumption has been estimated to have increased by 17.6% for the 1971-1974 time period (Ref. A-10.3-1).

TABLE A-10.3-1. ENERGY UTILIZATION IN GLASS CONTAINER INDUSTRY (PERCENT)

	1971	1973	1974
Natural Gas	77.2	70.5	64.9
Electricity*	17.1	17.4	19.6
Distillate Fuel Oil	3.9	7.8	9.0
Residual Fuel Oil	1.7	3.8	6.1
Propane	--	0.5	0.4
	100.0	100.0	100.0

\* Represents energy used to produce the electricity, i.e., a factor of 3.1 times larger than electricity actually consumed.

Trends In Equipment Type, Age, Size and Use

No trends in equipment type were found since each furnace is designed and built to meet the needs of a particular manufacturer. Extensive research has been, and is being, carried out to affect energy conservation in the glass container industry. These areas include:

- . using exhaust gas to batch preheat the incoming load
- . pelletizing the incoming load to more effectively allow preheating

- . proper burner positioning to eliminate flame impingement
- . use of oxygen enhancement to maintain flame temperature while reducing fuel requirements
- . placing the burners at the bottom of the furnace under the molten glass instead of having them above the molten glass.

It is not apparent that any of these research activities have been widely incorporated into the furnaces.

There is essentially little flexibility in glass container furnaces since the choices in configuration are limited, e.g., end port vs. side port, with/without electric boost, separately heated refining section or combustion gas heating from melting section.

The furnace is rebuilt periodically since the sidewall insulation wears thin with time and the regenerators become plugged with material carried over from the furnace. The time between rebuilds ("campaign") varies from 4 to 8 years with the shorter time period corresponding to furnaces which are "pulled" harder (higher production rate). After a campaign the furnace could be rebuilt so as to satisfy a new market demand for glass containers. Thus, the average age of a furnace is 2-4 years old. . .

A leading glass container manufacturer has supplied representative characteristics on their furnaces. These data are presented in Table A-10.3-2.

#### Total Number and Geographical Distribution

According to Reference A-10.3-2 there are 334 continuous glass container furnaces in the continental United States. Figure A-10.3-3 taken from Reference A-10.3-1 shows the regional distribution of the 117 glass container manufacturing plants.

No detailed information was found on furnace capacities, since these data are closely held in this competitive industry.

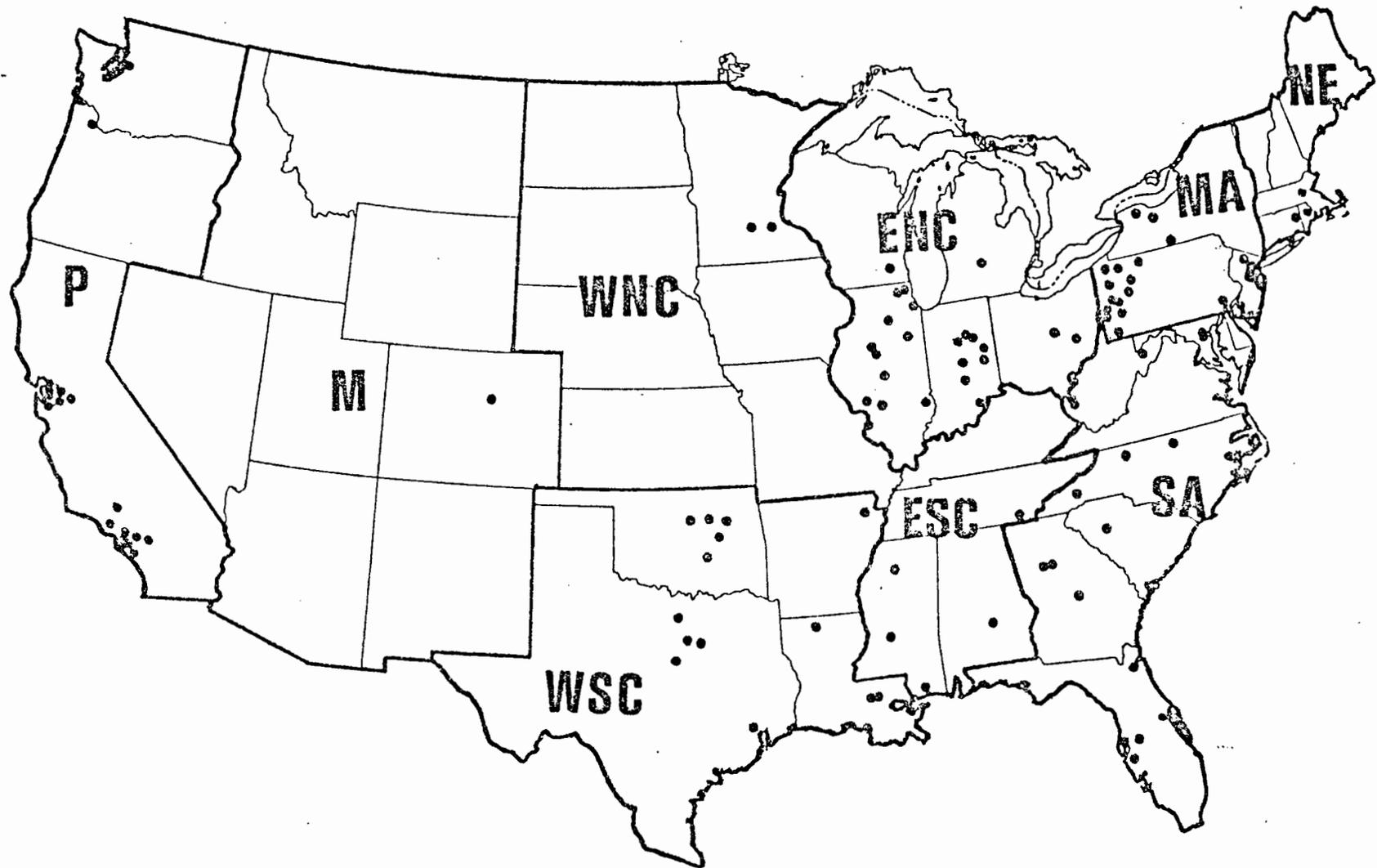


Figure A-10.3-3. Regional distribution of glass container manufacturers in the United States.  
(Ref. 10.3-1)

TABLE A-10.3-2. CHARACTERISTICS OF REPRESENTATIVE GLASS CONTAINER FURNACES

	Side-Port	End-Port
Melter Area, m <sup>2</sup> (ft <sup>2</sup> )	83.7 (900)	60.0 (645)
Production Rate, kg/day (short tons/day)	141 000 (155)	120 000 (132)
Furnace Rating, m <sup>2</sup> /kg/day (ft <sup>2</sup> /short ton/day)	0.00059 (5.8)	0.0005 (4.9)
Energy Requirement, kJ/kg (10 <sup>6</sup> Btu/short ton)	6012 (5.7)	5591 (5.3)
Age, years	4.6	2.0
Glass Color	Flint or green	Flint or green
Melter Bridgewall Temperature, K (°F)	1767 (2722)	1783 (2750)
Waste Gas Temperature, K (°F)	783 (950)	723 (842)
Number of Ports	10	2
Primary Fuel	Natural Gas	Natural Gas
Standby Fuel	No. 2 Oil	No. 2 Oil

#### Limitations In Equipment Uses and Fuels

Present equipment limitations require that natural gas be used in the refining section (if separately heated), forehearth, and annealing ovens. Distillate oils can be substituted for natural gas in the melting area of the furnace.

Greater use of distillate oils is possible but only with equipment specifically designed for oil operation.

The use of electricity exclusively in the melter section is possible once the charge has been brought to a molten state by a fossil fuel source. However, the total energy requirements are greater for electricity than fossil fuels if the energy required to produce the electricity is considered.

Most likely coal will not be directly used in the furnace since the fly ash would adversely affect glass quality.

#### Air Pollutant Emissions

The yearly air pollution emissions from glass furnaces was shown in Table A-8-1. The high level of particulate emissions is mostly due to entrainment of glass batch particles by the exhaust gas stream. The NEDS information (Ref. A-2-2) does not differentiate the emissions by the type of glass (flat, container, pressed or blown) being produced.

#### A-10.4 BLACK LIQUOR RECOVERY BOILERS

##### Major Manufacturers

There are two major manufacturers of black liquor recovery boilers used in the sulfate (kraft) process for wood pulp:

Babcock and Wilcox (Wilmington, North Carolina)

Combustion Engineering (Chattanooga, Tennessee)

##### Associations

There are no known associations of black liquor recovery boiler manufacturers. However, both of the above manufacturers are members of the American Boiler Manufacturers Association. The Black Liquor Recovery Boiler Advisory Committee serves the users in a safety advisory capacity.

The American Paper Institute (New York, NY), Technical Association Of The Pulp and Paper Industry (Atlanta, Georgia) and the National Council For Air And Stream Improvement (New York, NY) represent the pulp and paper manufacturers.

##### Basic Equipment and Combustor Design (Ref. A-10.4-1)

These devices are used in the recovery (refining) of the caustic chemicals from the wood pulp digesters. The boilers require careful attention to air distribution within the furnace to avoid excessive loss of the chemical by oxidation. Figure A-10.4-1 is a flow diagram of the kraft process and Figure A-10.4-2 is a cross-sectional view of a recovery boiler.

The black liquor, containing up to 60% by weight of organic material, is sprayed onto the furnace walls by an oscillating nozzle where it is dehydrated to form a char which drops to the furnace bottom. The organic material is carried upward through the furnace where it is burned with air from secondary and tertiary ports. Ash (inorganic material) from the char bed is exposed to a reducing atmosphere to convert its sodium sulfate to sodium sulfide which is then collected in the furnace bottom as a molten smelt. The smelt is carefully kept from contact with a proportion of water which would cause a violent reaction.

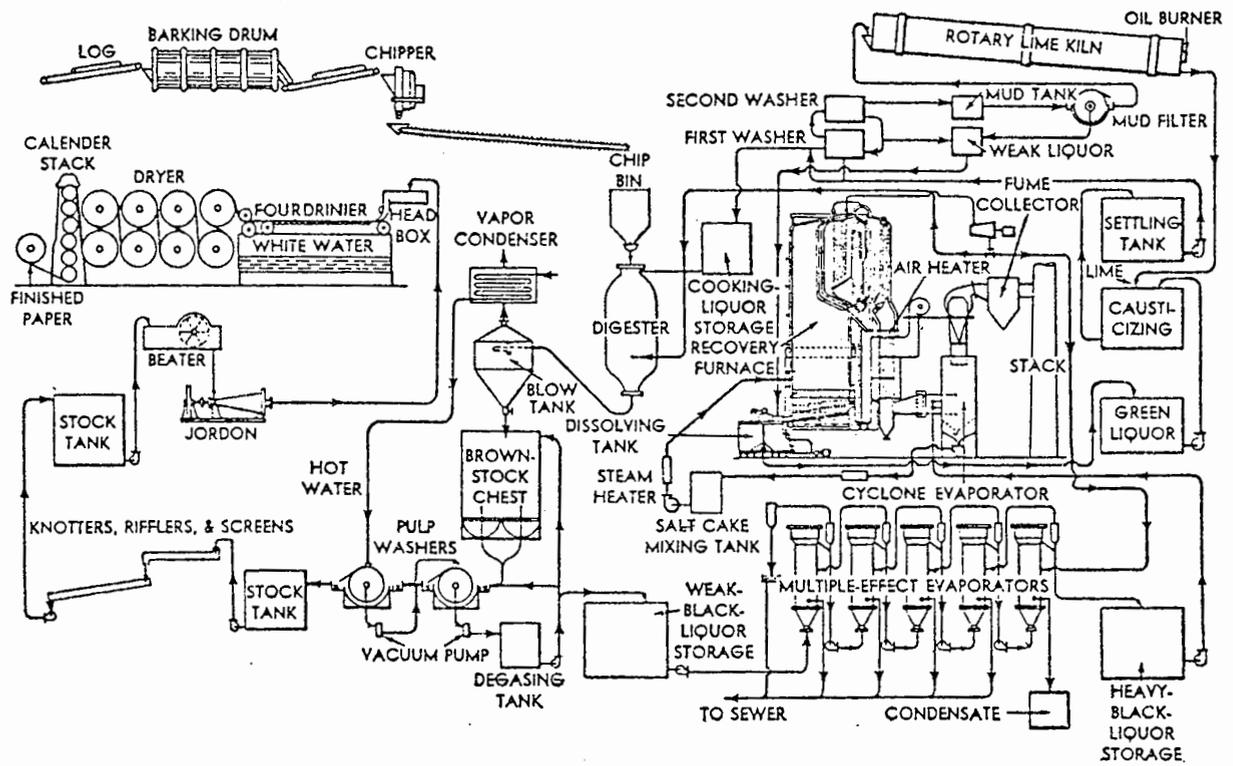


Figure A-10.4-1. Process flow diagram of a typical kraft pulp and paper mill (Babcock & Wilcox).

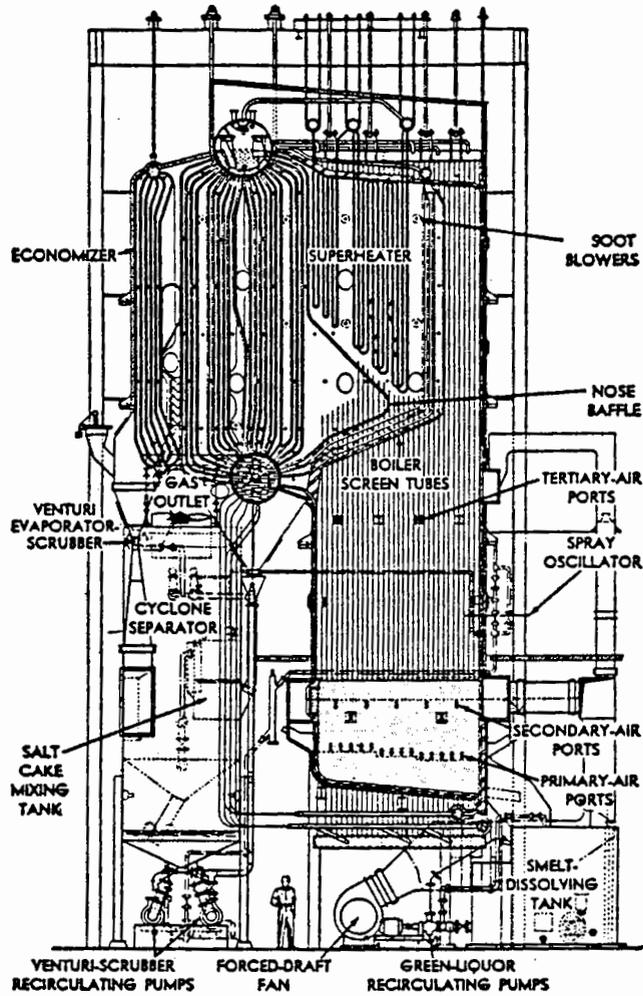


Figure A-10.4-2. Black liquor recovery boiler (Babcock & Wilcox).

The use of supplemental fuels is limited to the boiler start and warm-up cycle but may also be used for load sustaining.

#### Current Fuel Use, Trends and Properties

Aside from boiler start and warm-up only black liquor fuel is used. Therefore, there was no data on fuel use, trends and properties.

#### Trends In Equipment Type, Age, Size and Use

Information supplied by Babcock and Wilcox (Ref. A-10.4-2) was used to determine trends in recovery boiler rating (size) between 1954 and 1975 for units installed in the United States. These data are summarized in Table A-10.4-1 with the number built and average B&W rating as a function of time. (The non-dimensional B&W recovery boiler rating involves the: weight of solids in the liquor per weight of pulp; heating value of the solids; daily pulp output; and a constant. The trend in this rating factor, and not its magnitude, is of interest for this discussion. A unit measure of the B&W rating corresponds to 5,714 kW-hr/day ( $19.5 \times 10^6$  Btu/day) gross heat input to the furnace.)

It is seen from Table A-10.4-1 that there has been a general increase in the size (rating) of the recovery boilers. The "average" boiler was built in 1964.

#### Total Number and Geographic Distribution

Information supplied by Babcock and Wilcox and Combustion Engineering (Refs. A-10.4-2 and A-10.4-3) was used to determine the geographical distribution of recovery boilers by state. Table A-10.4-2 presents the state-wide distribution of the 274 units reported by both manufacturers. Also shown in Table A-10.4-2 is the distribution of recovery boiler relative capacity which is directly proportional to the furnace gross heat input. In essence, the relative capacity data presented in Table A-10.4-2 is an indicator of the amount of wood pulp processed by each state. The arithmetically average recovery boiler has a gross furnace heat input of  $2.80 \times 10^6$  kw-hr/day ( $9.56 \times 10^9$  Btu/day, 117 MW).

TABLE A-10.4-1. TRENDS IN BABCOCK AND WILCOX BLACK LIQUOR RECOVERY BOILERS

Year Built	No. Built	Aver. B&W Rating *
1954	5	213.4
1955	13	331.4
1956	9	356.7
1957	3	255.0
1958	-	-
1959	7	390.0
1960	4	253.0
1961	1	666.0
1962	5	340.0
1963	9	600.0
1964	4	650.0
1965	15	494.5
1966	7	754.9
1967	2	700.0
1968	5	565.0
1969	6	640.0
1970	7	798.0
1971	2	475.0
1972	8	712.4
1973	7	482.1
1974	4	725.0
1975	5	582.0
	<u>128</u>	

\*This rating is dimensionless

(The non-dimensional B&W recovery boiler rating involves the: weight of solids in the liquor per weight of pulp; heating value of the solids; daily pulp output; and a constant. The trend in this rating factor, and not its magnitude, is of interest for this discussion. A unit measure of the B&W rating corresponds to 5,714 kW-hr/day ( $19.6 \times 10^6$  Btu/day) gross heat input to the furnace.)

TABLE A-10.4-2. DISTRIBUTIONS OF NUMBER AND RELATIVE CAPACITY  
OF KRAFT RECOVERY BOILERS

State	No.	Rel. Cap., %
Alabama	26	9.76
Arizona	2	0.60
Arkansas	14	5.47
California	6	1.55
Florida	19	8.01
Georgia	30	10.99
Idaho	4	0.80
Kentucky	3	1.00
Louisiana	24	10.03
Maine	13	4.01
Maryland	2	1.16
Michigan	5	1.17
Minnesota	4	1.03
Mississippi	9	4.24
Montana	4	1.55
New Hampshire	2	0.51
New York	2	0.48
North Carolina	18	6.56
Ohio	2	0.37
Oklahoma	1	1.12
Oregon	17	5.43
Pennsylvania	4	0.61
South Carolina	7	3.51
Tennessee	3	0.99
Texas	14	5.67
Virginia	13	4.39
Washington	19	7.44
Wisconsin	7	1.57
	<u>274</u>	

### Limitations In Equipment Uses And Fuels

There are no known limitations in either equipment or fuel used. However, operation of these devices, especially air distribution, is quite important where chemical recovery efficiency and safety are concerned.

### Quantity And Geographic Distributions Of Fuel Used

There was no specific information found concerning this subject. Aside from device start and warm-up there is no other requirement for fossil fuels.

### Air Pollutant Emissions

Total yearly emissions from recovery boilers are shown in Table A-8-1. Ranked tenth in order of  $\text{NO}_x$  emissions, recovery boilers are sixth in magnitude of  $\text{SO}_x$  emissions. The high sulfur content of the black liquor is the source of  $\text{SO}_x$  as well as potential  $\text{H}_2\text{S}$  and other reduced sulfur compounds. Particulate emission levels are third highest in the tabulation. CO emission levels are ranked second following iron and steel furnaces.

## A-10.5 WOOD WASTE BOILERS

### Major Manufacturers

The major manufacturers of wood waste (wood and bark) boilers are:

- . Babcock and Wilcox (Wilmington, North Carolina)
- . Combustion Engineering (Chattanooga, Tennessee)
- . Foster Wheeler (Livingston, New Jersey)
- . Riley Stoker (Worcester, Massachusetts)

### Associations

There is no known national association specifically for wood waste boiler manufacturers. However, all the above organizations are members of the American Boiler Manufacturers Association.

### Basic Equipment And Combustor Design (Refs. A-10.4-1 and A-10.5-1)

The material burned in these boilers consists of slabs, logs, bark strips, sawdust and shavings originating in sawmills, plywood facilities and pulp and paper mills. These materials will have a highly variable moisture content reflecting the tree species, time of year when cut, part of the tree, and its exposure to moisture during transit and storage. In addition, salt content in the bark resulting from transportation by sea creates other problems which must be considered during boiler design. Due to seasonal variations in wood waste supply, all boilers are equipped to burn a secondary fuel(s). All material, except sawdust, is first reduced to chip size (hogged) in order to facilitate both charging into the furnace and subsequent combustion.

Burning of the wood waste occurs in three steps: drying of the material; distillation and combustion of the volatile matter; and, combustion of the fixed carbon. Furnace designs for accomplishing these steps include pile burning where the waste is deposited in a pile on a grate; combustion air enters from beneath the grate and flows around the burning pile. This method of firing requires between

30 and 40% excess air at the boiler outlet. The wood waste may also be burned in a furnace equipped with a traveling grate and a spreader stoker similar to that used with coal. The smaller particles will dry out and burn during flight with the balance of the burning occurring on the grate.

Figure A-10.5-1 is a cross-sectional view of a wood waste boiler designed to burn hogged wood with either oil, gas, or pulverized coal.

#### Current Fuel Use, Trends and Properties

Information supplied by Babcock and Wilcox and Combustion Engineering (Refs. A-10.4-2 and A-10.4-3) tabulates characteristics of wood bark boilers installed by these firms. In each instance a supplementary fuel (or fuels) was indicated and steam capacity on wood waste alone ranged from 28-92% of the total steam capacity, with the supplemental fuel(s) accounting for the balance. (The use of a supplemental fuel can lead to the formation of an ash of lower melting temperature than that of either ash taken separately and may become a problem.) In several instances the furnace has been designed so that another supplemental fuel, usually pulverized coal, can be used in the future.

The limited amount of information obtained precluded establishing specific trends in fuel usage.

#### Total Number And Geographic Distribution

The total number of bark boilers reported in References A-10.4-2 and A-10.4-3 (107) was not sufficient to establish a definitive distribution by state of these devices. Rather, the number reported for each state was expressed as a percentage of all the units reported. This assumes that the distributions of bark boilers installed by these manufacturers are representative of units installed by all manufacturers. These results are shown in Table A-10.5-1.

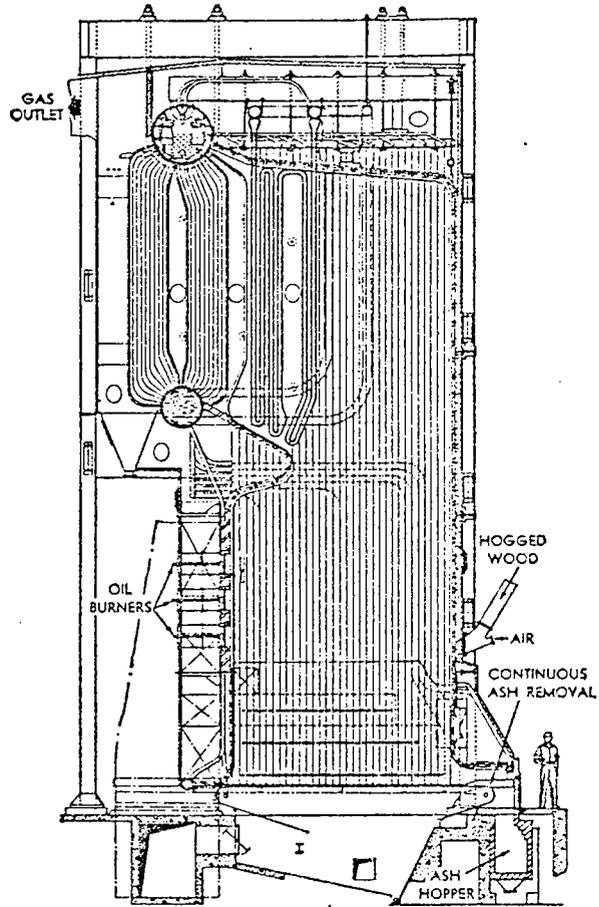


Figure A-10.5-1. Wood waste boiler (Babcock & Wilcox).

TABLE A-10.5-1. DISTRIBUTIONS OF BARK BOILERS AND RELATIVE CAPACITIES

State	Rel. No., %	Rel. Cap., %
Alabama	14.0	11.9
Arkansas	3.7	4.5
California	1.9	1.9
Florida	9.4	7.3
Georgia	8.4	11.9
Idaho	0.9	0.7
Louisiana	3.7	6.5
Maine	5.6	8.0
Maryland	0.9	0.1
Michigan	0.9	0.5
Minnesota	0.9	0.8
Mississippi	3.7	6.7
North Carolina	3.7	1.8
Oklahoma	0.9	1.7
Oregon	7.5	4.9
South Carolina	1.9	1.0
Tennessee	1.9	1.2
Texas	7.5	10.5
Virginia	1.9	1.8
Washington	14.0	7.8
Wisconsin	6.5	8.8

$$\text{Relative Capacity, \%} = \frac{\text{Boiler Steam Rate}}{\text{All Boilers Steam Rate}} \times 100$$

Total sample number = 107

Total steam rate =  $12.16 \times 10^6$  kg steam/hr

#### Limitations In Equipment Uses And Fuels (Refs. A-10.4-1 and A-10.5-1)

Wood waste boilers are limited by wood supply and wood moisture; wood supply fluctuates with mill production. The net heating value of the wood waste decreases as the moisture content increases and with moisture contents above 65%, a large part of the energy in the wood is required to evaporate the moisture, and little remains for steam generation. Burning of this wet waste becomes a means of disposal rather than a source of energy.

Combustion temperatures resulting from burning dry waste may be high enough for impurities to cause fluxing of furnace refractories and fouling of heating surfaces. In addition, a furnace designed to burn wet fuel will operate poorly with dry fuel, and a dry fuel furnace may be unable to carry its normal load when supplied with wet fuel. In some cases, extremely dry fuel is sprayed with water so that its moisture content is closer to design moisture.

#### Quantity And Geographic Distribution Of Fuels Used

No information was obtained for this subject in regard to either wood waste or supplementary fossil fuels used. As noted in Reference A-4-1, energy produced by hogged fuel and bark (at 50% moisture content for each) amounted to 6.8% of the total energy consumption in the pulp, paper and paperboard industry during the first six months of 1975.

#### Air Pollutant Emissions

The NEDS listing for air pollution emissions from wood and/or bark boilers was shown in Table A-8-1. The boilers rank third in magnitude of  $\text{NO}_x$ , CO, and particulates emissions but are sixth in terms of HC and seventh in  $\text{SO}_x$  emissions.

## A-10.6 COKE OVENS

### Major Manufacturers

The major manufacturers of coke ovens are:

- . Koppers Co. (Pittsburgh, Pennsylvania)
- . Wilputte Coke Oven Div., Salem Corp. (Morriston, New Jersey)
- . Otto-McKee (Independence, Ohio)
- . Dravo-Still (Pittsburgh, Pennsylvania)
- . Kaiser-Didier (Oakland, California)

The last two named are recent entries into the field and as of December 1976 had not produced any ovens.

Each manufacturer will perform a turn-key operation in that they will design, procure components, and construct the ovens as well as the by-product plants which extract chemicals from the coke oven gas.

### Associations

There are no known coke oven manufacturer's trade associations.

### Basic Equipment And Combustor Design

Modern by-product coke ovens are tall, thin, long devices which will heat metallurgical grade coal in the absence of air to produce coke. The older beehive configurations are not common and will not be discussed. The fuel for heating the coal is mostly coke oven gas, i.e., the gaseous products of coal distillation, or blast furnace gas with a small usage of both coke oven and blast furnace gas. All coke oven gas is first routed through a by-product recovery plant and then approximately 60% of the gas is used within the oven with the balance routed to the steel mill. A grouping of coke ovens is termed a battery and there may be anywhere from 5 to 106 ovens in a battery. Typically, there is a minimum of 15 ovens in a battery. Reference

A-10.6-1 presents details showing differences between the several types of coke ovens. Basically, these differences involve the specific arrangement of the hot gas flues within the ovens. Figure A-10.6-1, taken from Reference A-10.6-1, is a cut-away view of a coke oven.

#### Current Fuel Use, Trends And Properties

Approximately 85% of the devices use coke oven gas, 12% use blast furnace gas, and 3% use a combination of these two fuels (Ref. A-10.6-2). No other fuel types are used.

No information was obtained regarding trends in fuel usage. Such trends might be approximately proportional to yearly coke production.

#### Trends In Equipment Type, Age, Size And Use

The trend in equipment type has been to the by-product method; as a result only one location in the United States uses the older beehive method.

The life of a by-product oven battery is from 20 to 30 years (Ref. A-10.6-1) but no information was found on representative oven age nor the trend in age.

There has been an upward trend in oven height and length, i.e., greater coke capacity per oven. The width of the oven is fairly well fixed to allow for coking of the coal within approximately 17 hours, i.e., if the width (minimum oven dimension) were increased the coking time would also be increased. At the present state-of-the-art a representative oven is 6.1 m (20 ft) high, 15.2 m (50 ft) long, and 0.5 m (18 in.) wide.

#### Total Number And Geographical Distribution

As of 1974, according to Reference A-10.6-3, there were 11,694 coke ovens in the United States at 50 plant locations. The majority of ovens (59%) were located in Pennsylvania, Indiana, and Ohio.

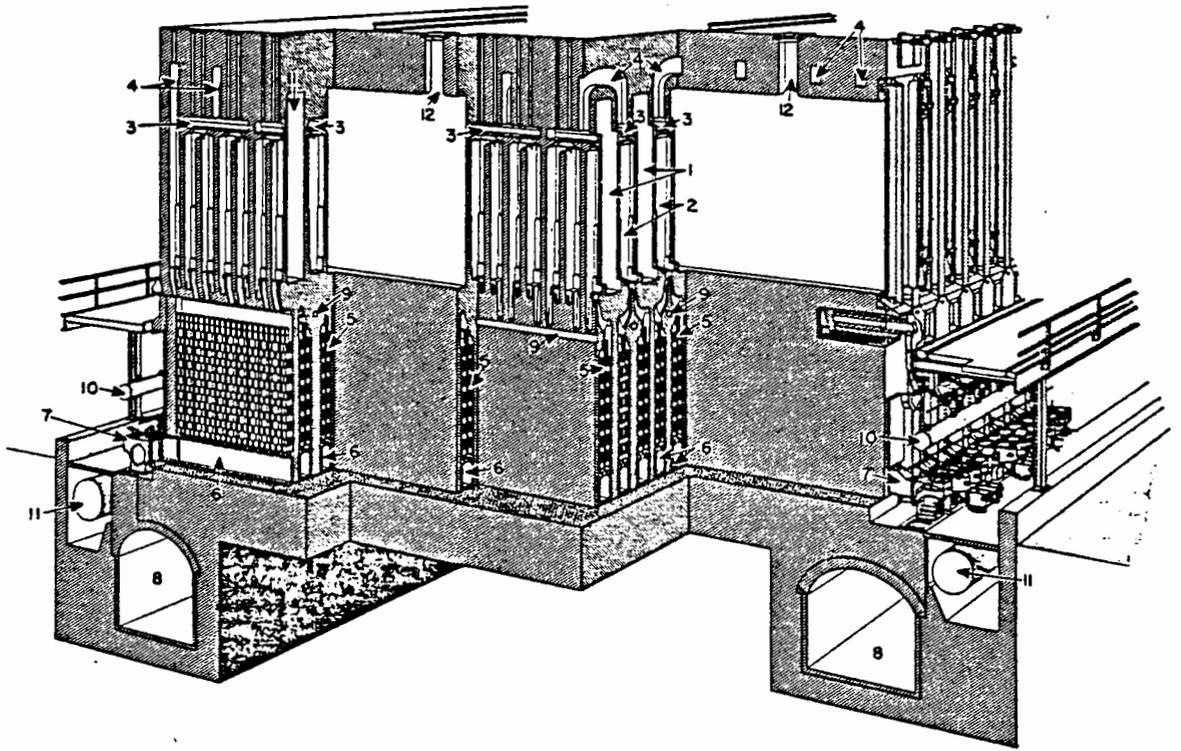


Figure A-10.6-1. General cut-away of coke oven. 1. Oven chamber. 2. Vertical combustion flues. 3. Horizontal flues. 4. Cross-over flues. 5. Regenerators. 6. Oven sole flues. 7. Gas and air connections to waste-gas flue. 8. Waste-gas flues. 9. Gas ducts for coke-oven gas. 10. Oven gas main. 11. Blast-furnace gas main. 12. Charging holes. (Koppers Company, Inc.)

Additionally, 97.7% are the by-product type and the balance (2.3%) are the beehive type. Table A-10.6-1 presents the coke oven distribution by state.

TABLE A-10.6-1. COKE OVEN DISTRIBUTION BY STATE

State	No. of Ovens
Alabama	691
California	315
Colorado	216
Illinois	424
Indiana	1669
Maryland	757
Michigan	438
Minnesota	115
New York	645
Ohio	1665
Pennsylvania*	3568
Tennessee	44
Texas	140
Utah	252
West Virginia	755
	<u>11,694</u>

\* State total includes 266 beehive ovens

Limitations In Equipment Uses And Fuels

A coke oven battery can use either coke oven or blast furnace gas if it were originally designed to accommodate both fuels. A substantial capital investment would be required to substitute blast furnace gas for coke oven gas in that piping from the blast furnace to the battery would be required. In addition, the marked differences in heating value between the gases: coke oven gas 18.6 MJ/m<sup>3</sup> (500 Btu/cf); blast furnace gas 3.3 - 3.7 MJ/m<sup>3</sup> (90 - 100 Btu/cf)-- would probably require extensive revisions in the flue ductwork within

the oven since a greater volume of gas would be needed. In view of the latter consideration it does not appear economically feasible to substitute blast furnace gas in those batteries which were not originally designed for this fuel.

#### Quantity And Geographic Distribution Of Fuels Used

In a coke oven, the coal charge (feedstock) itself is the primary source of fuel via the generated coke oven gas. According to Reference A-10.6-4 for the year 1972,  $77.9 \times 10^9$  kg ( $85.7 \times 10^6$  short tons) of coal were used in the production of coke;  $62.3 \times 10^9$  kg ( $68.5 \times 10^6$  short tons) of coke, screening and breeze were produced. Also produced were  $4.59 \times 10^{10}$  m<sup>3</sup> ( $1.62 \times 10^{12}$  ft<sup>3</sup>) of coke oven gas. However, the amount of coke oven gas used as fuel within the oven is less than this amount for two reasons:

1. The extraction of by-product chemicals
2. Routing of approximately 40% of the remaining gas to the steel mill.

Thus, it is not possible at this time to determine the total quantity and geographic distribution of fuels (coke oven and blast furnace gas) used in coke ovens.

#### Air Pollutant Emissions

The yearly air pollution emissions from by-product coke ovens are contained in Table A-8-1. In this instance the "Number of Records" obtained from the NEDS listing (Ref. A-2-2) is assumed to refer to the number of coke oven batteries where each battery may contain a large number of individual ovens. HC emissions are high (second) relative to other devices tabulated. Emission levels of other pollutants listed are much lower in the ranking order.

## A-10.7 BLAST FURNACES

### Major Manufacturers

The major manufacturers of blast furnaces are:

- . Koppers Co., Inc. (Pittsburgh, Pennsylvania)
- . Arthur G. McKee (Cleveland, Ohio)
- . Dravo (Pittsburgh, Pennsylvania)

Each of these manufacturers will perform a complete operation from design, to component procurement, and construction.

### Associations

There are no known associations of blast furnace manufacturers. The American Iron and Steel Association (AISI) represents the equipment users.

### Basic Equipment And Combustor Design (Ref. A-10.6-1)

A blast furnace is a device which produces essentially pure metallic iron (pig iron) from iron containing materials. It is a refractory lined, circular, conical structure with a hearth (lower) diameter ranging from 6.1 m to 9.2 m (20 - 30 ft) and total height between 27.4 - 33.5 m (90 - 110 ft). The top end (smaller diameter) of the furnace is fitted with a removable seal arrangement to allow charging of materials which consist of:

- . Iron-bearing material (ore, sinter, pellets, scale, slag, scrap)
- . Fuel (coke)
- . Flux (limestone and/or dolomite).

The hearth region is fitted with tuyeres for admitting preheated (blast) air and, in most instances, a secondary fuel (gas, oil or pulverized coal). The preheated blast air burns with part of the fuel (coke) to produce heat for the chemical reactions involved and for melting the iron. The balance of the fuel and part of the gas produced reduces (i.e., removes oxygen from) the metal. The blast furnace exhaust gas, a low energy content gas, is cleaned and burned in the air preheaters.

Each furnace is furnished with from 3 to 8 (3 or 4 are typical) hot blast stoves. These stoves are brick-lined regenerators whose function is to preheat the blast air before entry into the furnace. These devices are fueled with cleaned blast-furnace gas (with some usage of coke oven gas) and contain brick checkerwork for countercurrent air heating. For a 3 stove arrangement one is supplying heated air to the blast furnace while the other two stoves are being heated by burning blast-furnace gas. Figure A-10.7-1 is a general arrangement of a blast furnace and hot blast stove.

Blast furnaces are rated in terms of their internal (stack) volume while hot blast stoves are rated by their internal heat transfer area.

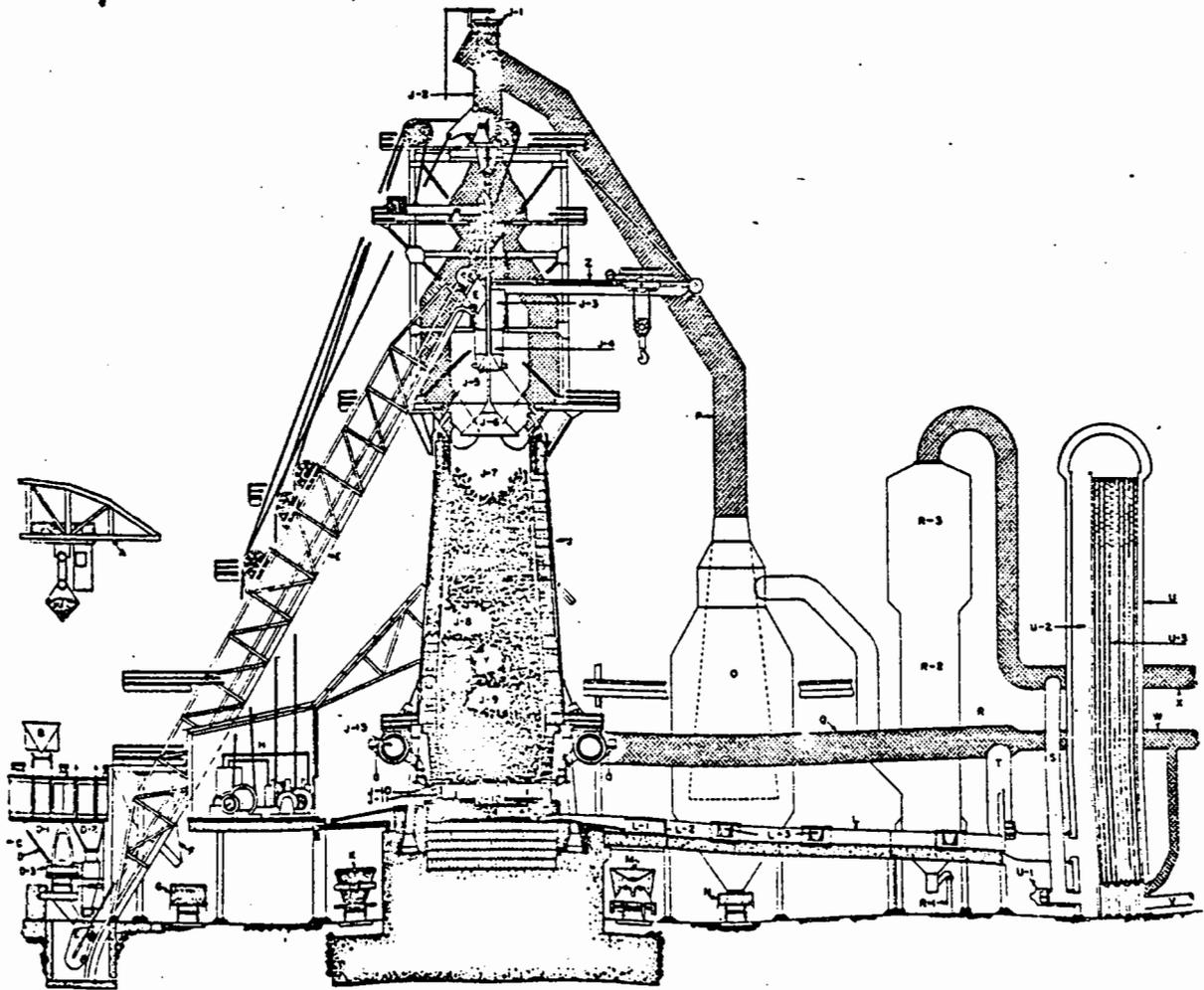
#### Current Fuel Use, Trends And Properties

Currently, coke is the main fuel used in the blast furnace proper. Some oil, natural gas and pulverized coal are used as secondary fuels (the coal is used at only one mill in the U.S.).

No information was found concerning fuel use trends as a result of device efficiency improvements. Therefore, it was assumed that fuel usage trends would follow the annual production of pig iron. Information was obtained on pig iron production from the American Iron and Steel Institute, and is presented in Table A-10.7-1, for the years 1966-1975. These data reflect the general national economic climate in the United States, i.e., pig iron production is high during periods of relative prosperity and low during recessional phases.

TABLE A-10.7-1. ANNUAL UNITED STATES PIG IRON PRODUCTION  
10<sup>3</sup> Metric Tons (10<sup>3</sup> Short Tons)

Year	Production	
1966	83,182	(91,500)
1967	79,076	(86,984)
1968	80,709	(88,780)
1969	86,379	(95,017)
1970	83,123	(91,435)
1971	73,908	(81,299)
1972	80,856	(88,942)
1973	91,670	(100,837)
1974	87,190	(95,909)
1975	72,657	(79,923)



- Legend**
- |                             |                    |                                    |
|-----------------------------|--------------------|------------------------------------|
| A. Ore bridge               | J-5 Small bell     | P. Downcomer                       |
| B. Ore transfer car         | J-6 Large bell     | Q. Hot blast line to furnace       |
| C. Ore storage yard         | J-7 Stock line     | R. Gas washer                      |
| D. Stockhouse               | J-8 Stack          | R-1 Sludge line to thickener       |
| D-1 Ore and limestone bins  | J-9 Bosh           | R-2 Spray washer                   |
| D-2 Coke bin                | J-10 Tuyeres       | R-3 Electrical precipitator        |
| D-3 Scale car               | J-11 Slag notch    | S. Gas offtake to stove burner     |
| E. Skip                     | J-12 Hearth        | T. Hot blast connection from stove |
| F. Coke dust recovery chute | J-13 Bustle pipe   | U. Stove                           |
| G. Freight car              | J-14 Iron notch    | U-1 Gas burner                     |
| H. Skip and bell hoist      | K. Slag ladle      | U-2 Combustion chamber             |
| I. Skip bridge              | L. Cast house      | U-3 Checker chamber                |
| J. Blast furnace            | L-1 Iron trough    | V. Exhaust gas line to stack       |
| J-1 Bleeder valve           | L-2 Slag skimmer   | W. Cold blast line from blower     |
| J-2 Gas uptake              | L-3 Iron runner    | X. Surplus gas line                |
| J-3 Receiving hopper        | M. Hot-metal ladle | Y. Stock—Iron ore, coke, limestone |
| J-4 Distributor             | N. Flue dust car   | Z. Jib boom crane                  |
|                             | O. Dust catcher    |                                    |

Figure A-10.7-1. Cross-section of typical blast furnace and hot blast stove (U.S. Steel Corp.).

### Trends In Equipment Type, Age, Size And Use

No quantitative information was found concerning these aspects of blast furnaces. In general, the furnace is rebuilt (refractories changed) every five years and it is during these rebuilds that provision is made for incorporating supplemental fuels.

New blast furnaces are being made larger ususally to replace several smaller units. However, no specific information was obtained regarding size as a function of time.

### Total Number And Geographic Distribution

Table A-10.7-2, prepared from data in Reference A-10.6-3, presents the blast furnace number distribution by state. Of the total number (189), 63.0% are concentrated in Pennsylvania, Ohio, and Indiana.

The blast furnace internal volume (stack volume) is the unit of measure of capacity. Using data from Reference A-10.6-3 a tabulation was made of stack volumes to arrive at a relative pig iron capacity (i.e., pig iron capacity was taken as proportional to stack volume) by state. The results are also shown in Table A-10.7-2. Pennsylvania, Ohio, and Indiana account for 59.5% of the relative capacity.

TABLE A-10.7-2. BLAST FURNACE AND RELATIVE CAPACITY DISTRIBUTIONS BY STATE

State	No. of Blast Furnaces	Rel. Cap., %
Alabama	9	4.48
California	4	2.28
Colorado	4	1.54
Illinois	16	8.39
Indiana	27	15.79
Kentucky	2	1.64
Maryland	10	5.59
Michigan	9	5.77
New York	8	5.16
Ohio	36	18.72
Pennsylvania	56	25.00
Texas	1	1.31
Utah	3	1.73
West Virginia	4	2.61

### Limitations In Equipment Uses And Fuels

The only fuel limitation noted was in secondary fuels. These can be used only when the furnace was originally designed, or retrofitted, to burn secondary fuels.

### Quantity And Geographic Distribution Of Fuels Used

Table A-10.1-1 contains fossil fuels purchased by SIC 33, Primary Metal Industries, by state. It is assumed that nearly all the coal and coke entries for this industry are used in blast furnaces.

### Air Pollutant Emissions

Air pollution emissions for the general heading of iron and steel furnaces are shown in Table A-8-1. Emissions specific to blast furnaces were not found. NO<sub>x</sub> emissions are expected to be low based on limited data (Ref. A-10.12-2) because of the low heat content of blast furnace gas.

## A-10.8 OPEN HEARTH FURNACES

### Major Manufacturers

Open hearth furnaces are no longer being made for the Iron and Steel Industry but the major manufacturer was Koppers Co., Inc. (Pittsburgh, Pennsylvania).

### Associations

No information was obtained on associations of open hearth manufacturers.

### Basic Equipment And Combustor Design (Ref. A-10.6-1)

The open hearth furnace consists of a refractory lined vessel which is shallow compared to its length. A refractory lined arched roof completes the basic reverberatory furnace structure. Regenerative checkerwork is used for air preheating, and a wide variety of fuels are used. Figure A-10.8-1 is a view of the principal parts of an open hearth furnace.

A carefully controlled charging sequence is followed. First, limestone (flux), scrap and iron ore is charged into the furnace and then melted--mainly by radiation from the flame and roof. Then, molten pig iron is charged and the heat is refined and ready for tapping in about 8-10 hours from the initial charging. (The shorter time period corresponds to those furnaces equipped with roof mounted oxygen lances.)

A complex series of chemical reactions occurs within the molten metal to remove the impurities by oxidation. The carbon content is also carefully controlled. Oxygen is obtained partly from the iron ore and partly from the furnace atmosphere.

At the correct time the furnace is tapped and deoxidizing agents and alloying elements are added as the molten metal flows into the ladle.

No specific details were obtained on burner characteristics.

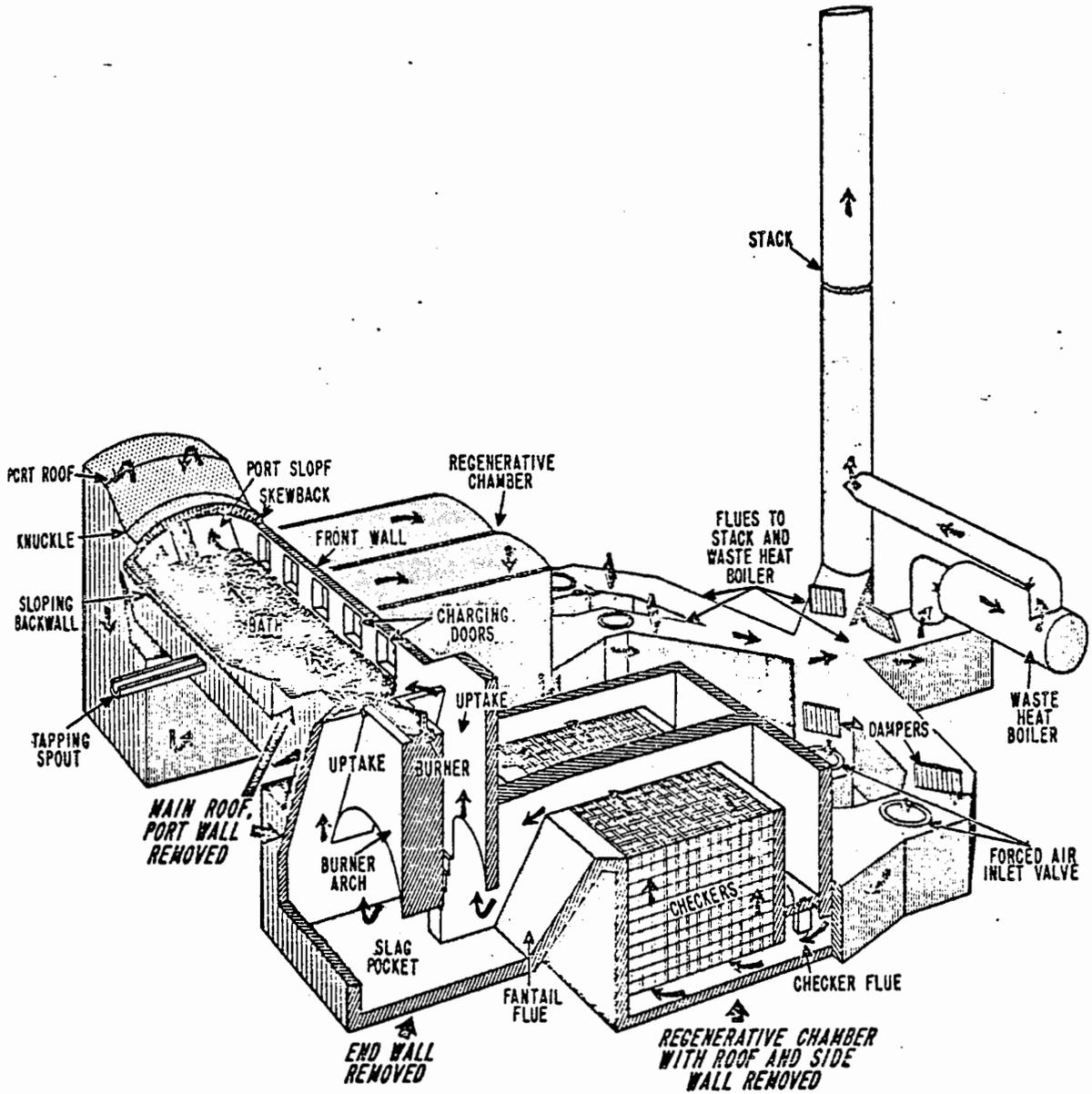


Figure A-10.8-1. Principal parts of an open-hearth furnace (U.S. Steel Corp.).

Open hearth furnaces are being gradually replaced by basic oxygen furnaces (BOF) and electric arc furnaces. Between the years 1964 and 1974 production by the open hearth has dropped from 77.2% to 24.5% of total steel output. During the same time period the use of BOF has increased from 11.8% to 56.2% of the total steel production. However, the open hearth furnace will probably survive for another 20 years before being completely replaced. Additionally, BOF's are not combustion devices as no fuel source is required directly in the BOF unit.

The capacity of open hearth furnaces is expressed by the amount of charge loaded per heating cycle. Furnaces currently operating range from 45 Mg (50 tons) to 381 Mg (420 tons) per heat with the average size about 227 Mg (250 tons) per heat.

#### Current Fuel Use, Trends And Properties

Current practice is to use the following fuels, (usually in combinations of two or more) (Ref. A-10.6-3):

- . coke oven gas
- . pitch
- . tar
- . oil (grade not specified)
- . natural gas.

Only natural gas is definitely a purchased fuel while the others are normal products of by-product coke ovens.

No information was obtained on the relative proportions of these fuels when used in combinations. Further, no specific information was obtained on fuel usage trends; however, overall usage should approximate the overall open hearth steel production previously quoted.

#### Trends In Equipment Type, Age, Size And Use

No information was obtained other than that no new units are being constructed and existing units are being phased out.

Total Number And Geographical Distribution

Table A-10.8-1, prepared from data contained in Reference A-10.6-3, gives the distribution of the 189 open hearth furnaces by state. Open hearth furnaces are rated on the amount of steel produced per cycle (heat) since the furnace is a batch processor. (A heat may vary in duration from 8 to 10 hours.) This rating factor was used to determine the approximate open hearth steel production by state; the results are also shown in Table A-10.8-1. Ohio, Pennsylvania, and Indiana comprise 71.4% of all the furnaces and 70.4% of the approximate capacity.

TABLE A-10.8-1. DISTRIBUTIONS OF OPEN HEARTH FURNACES AND APPROXIMATE CAPACITY BY STATE

State	No. of Furnaces	Approx. Cap., %
Alabama	9	3.66
California	16	5.82
Illinois	4	2.19
Indiana	27	16.20
Maryland	7	6.45
New York	3	1.25
Ohio	57	27.72
Pennsylvania	51	26.50
Texas	5	2.74
Utah	10	7.46

Limitations In Equipment Uses And Fuels

In a steel mill which contains coke ovens, blast furnaces and open hearth furnaces, equipment fuel usage is established during the initial mill design phase. Extensive hardware changes would be required to substitute fuels in the devices, e.g., substituting coke oven gas for fuel oil or natural gas necessitates long runs of large diameter ductwork and burner changes. Thus, the economics of the situation would probably preclude using fuels other than called for in the original design.

### Quantity And Geographic Distribution Of Fuels Used

It is assumed that the distribution of fuels used in open hearth furnaces is proportional to the amount of coal and coke purchased by SIC 33, Primary Metal Industries, as shown in Table A-10.1-1. The rationale for this assumption is that in a steel mill with on-site by-product coke ovens, the major source of fuel for the open hearth furnaces would be coke oven gas and that the amount of this gas is proportional to the amount of coal and coke purchased. (In this context, "purchasing" may amount to a "paper" transfer of a material within the same company from one activity to another.)

### Air Pollutant Emissions

Open hearth air pollution emissions are included in Table A-8-1 as part of the "Iron and steel furnace" category. Table A-10.8-2 breaks them out as a separate entry. Open hearth furnaces contribute 67% of the iron and steel furnace category emissions. These furnaces have very high temperatures and long residence times that are conducive to NO<sub>x</sub> formation. Emissions also vary considerably over each cycle (Ref. A-10.12-2).

TABLE A-10.8-2. OPEN HEARTH FURNACE AIR POLLUTION EMISSIONS

kg/Year (Short Tons/Year)

	No. of Records	NO <sub>x</sub>	SO <sub>x</sub>	HC	CO	Particulates
With O <sub>2</sub> Lance	66	2.5x10 <sup>6</sup> (2.8x10 <sup>3</sup> )	3.5x10 <sup>7</sup> (3.8x10 <sup>4</sup> )	2.7x10 <sup>3</sup> (3x10 <sup>0</sup> )	0 (0)	3.8x10 <sup>7</sup> (4.2x10 <sup>4</sup> )
Without O <sub>2</sub> Lance	75	1.6x10 <sup>6</sup> (1.8x10 <sup>3</sup> )	9.0x10 <sup>5</sup> (9.9x10 <sup>2</sup> )	6.8x10 <sup>4</sup> (7.5x10 <sup>1</sup> )	1.1x10 <sup>7</sup> (1.2x10 <sup>4</sup> )	4.9x10 <sup>7</sup> (5.4x10 <sup>4</sup> )
Total	141	4.1x10 <sup>6</sup> (4.6x10 <sup>3</sup> )	3.6x10 <sup>7</sup> (3.9x10 <sup>4</sup> )	7.1x10 <sup>4</sup> (7.8x10 <sup>1</sup> )	1.1x10 <sup>7</sup> (1.2x10 <sup>4</sup> )	8.7x10 <sup>7</sup> (9.6x10 <sup>4</sup> )

301

## A-10.9 SOAKING-PIT, REHEATING, AND HEAT-TREATING FURNACES

### Major Manufacturers

Major manufacturers of soaking-pit and reheating furnaces are:

- . Surface Combustion Div., Midland-Ross Corp. (Toledo, Ohio)
- . Swindell-Dressler Div., Pullman Inc. (Pittsburgh, Pennsylvania)
- . Loftus Engr. Corp., Western Gear Corp. (Pittsburgh, Pennsylvania)

The major manufacturers of heat-treating furnaces are:

- . Surface Combustion
- . Swindell-Dressler

### Associations

There are no known associations of manufacturers of these devices. However, each of the above is a member of the American Iron and Steel Engineers (Pittsburgh, Pennsylvania).

### Basic Equipment And Combustor Design (Ref. A-10.6-1)

The primary functional objective of each of these devices is the same -- to raise the steel temperature to a specified range. In common usage, a soaking-pit furnace is charged with steel ingot from the steel mill and raises its temperature to a normal range between 1450 and 1617 K (2150 - 2450°F) in preparation for the first rolling or forming operations. A reheating furnace raises the temperature of the partially formed steel to the same temperature range for further hot-working.

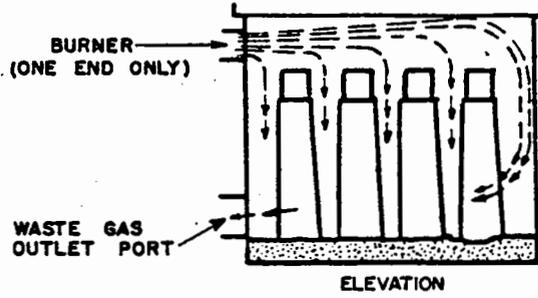
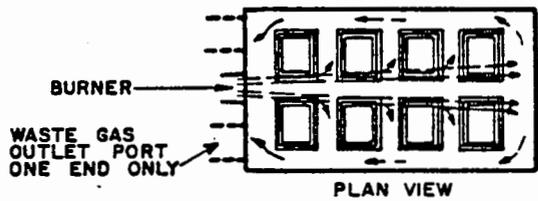
Heat-treating furnaces raise the finished steel product to a temperature between 700 and 1144 K (800 - 1600°F) for the specific purpose of controlling the mechanical properties of the final product. Therefore, the operation of a heat-treating furnace is more critical than that of a soaking-pit or reheating device insofar as the metal is concerned, e.g., heating and cooling rates, as well as temperature levels, must be carefully controlled. Additionally, the chemical composition within the furnace must not adversely affect product surface quality.

Soaking-pit furnaces are usually batch type devices designed to heat steel ingot prior to rolling or forming operations. Several furnaces are usually grouped together so as to share the same ingot handling equipment and interior walls. Each pit, in turn, is designed to accommodate several ingots with the constraint being that the ingots never cover more than 50% of the floor-plan area.

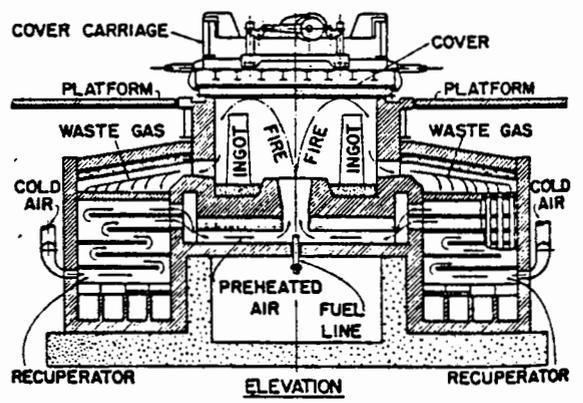
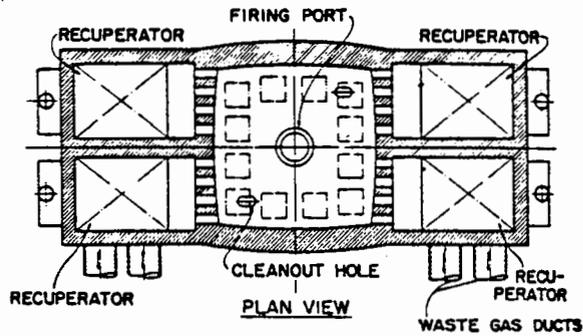
Burner design and placement, as well as exhaust port placement, are chosen to promote strong internal circulation patterns of the combustion gases to provide a uniform heating environment for the ingots. This requirement has led to the development of a family of furnace geometrical designs; each will generate these gas circulation patterns. For example, one design ("vertically-fired") has the combustor centrally located and firing vertically into the furnace with the waste gases being drawn off through the furnace outer walls. Another design has a series of burners firing tangentially into a cylindrical furnace with the exhaust port centrally located in the furnace floor. Figure A-10.9-1 shows two types of soaking-pit furnaces--the one-way and vertically-fired configurations.

Recuperators or regenerators are usually provided to preheat the incoming combustion air. (Current practice is to provide recuperators or regenerators on all furnaces. Such was not the case 20 years ago.)

Reheating furnaces are of both batch and continuous type and are also designed to promote strong internal gas circulation. These devices are used to reheat slabs, billets and blooms prior to further hot-working operations. Burner placement in continuous reheating furnaces vary from a single burner at the steel discharge end (firing countercurrent to the metal travel) to a series of up to five burner zones located along the length of the furnace. The latter arrangement allows the metal to undergo preheating, heating and soaking during its travel through the furnace. This multi-zone furnace permits better control of metal heating rates and the gradual temperature rise enables charging all grades of cold steel without having to cool the furnace.



A. One-way fired



B. Vertically-fired

Figure A-10.9-1. Soaking-pit furnaces (U.S. Steel Corp.).

Heat-treating furnaces are either batch or continuous devices and are further identified as being directly or indirectly heated. They are usually well insulated and built tight to avoid the loss of special atmosphere gas. Special attention is given to achieve a uniform temperature distribution within the working volume. For annealing operations the rate of temperature increase and decrease is very carefully controlled. Quenching tanks are located in close proximity to the furnace to minimize the time between discharge from the furnace to immersion in the quenching tank.

Special atmosphere gases are used to minimize scaling caused by attack of normal atmospheric gases. Continuous furnaces may also include fire curtains at both the charging and discharging ends to prevent atmospheric oxygen from entering the working volume.

There are many configurations of the batch and continuous furnaces. An example of the former is the bell-type in which the steel is loaded on a tracked carrier which is then moved into position under the furnace body. The body is then lowered over the carrier and the heating cycle commences. A single furnace body can be repositioned to service several carriers.

A walking-beam furnace is an example of a continuous device and consists of a series of pivoted beams running the length of the furnace. The steel is moved through the furnace as a set of beams are pivoted causing the charge to move to the next set of beams, etc.

#### Current Fuel Use, Trends And Properties (Ref. A-10.9-1)

Current fuel use includes fuel oil, natural gas, coke-oven and cold blast furnace gas. Trends in fuel usage have been away from natural gas to a combination of blast furnace and coke-oven gas, with Nos. 2 and 6 fuel oils as alternates. Economic considerations preclude furnace operation on blast furnace gas alone as this low energy fuel would require extensive ductwork and burner modifications.

### Trends In Equipment Type, Age, Size And Use

According to Reference A-10.9-1, up until 3-4 years ago 30-40% of their inquiries concerned nonregenerative (no air preheat) devices. Since that time all requests have specified preheated air (either recuperative or regenerative) in the interest of fuel economy.

Devices which had used natural gas exclusively have been retrofitted with new burners to allow operation on other gaseous fuels, e.g., coke-oven and blast furnace gas.

There has been no marked shift toward greater use of continuous type furnaces mainly because these larger capacity devices are already extensively used. However, within the continuous type device category, newer installations have favored the walking-beam configuration to achieve greater capacity. The capacity of a pusher type reheating furnace is limited by the length of the pushing mechanism but such is not the case for the walking-beam type.

No specific information was obtained on device age and size-- except that the trend is for larger capacity units.

### Total Number And Geographic Distribution

According to Reference A-10.6-3, there are 1435 soaking-pit furnaces, 1264 reheating furnaces, and 3836 heat-treating furnaces (for a grand total of 6535) distributed by state as shown in Table A-10.9-1. Whenever possible devices using electricity as the heat source were not included in the tabulation.

### Limitations In Equipment Uses And Fuels

Limitations in this area pertain to fuels used. A device which was originally designed to burn a specific fuel can not burn a substitute fuel unless subsequent burner retrofit has been performed. As previously discussed, there is no economic justification in using low energy blast furnace gas by itself.

TABLE A-10.9-1. DISTRIBUTIONS OF SOAKING-PITS, REHEATING,  
AND HEAT-TREATING FURNACES

State	Soaking-Pits	Reheating Furnaces	Heat-Treating Furnaces
Alabama	29	20	64
Arizona	-	1	-
Arkansas	-	1	-
California	32	34	120
Colorado	59	10	18
Connecticut	4	7	86
Delaware	5	7	2
Florida	-	2	2
Georgia	8	5	5
Hawaii	-	1	-
Illinois	73	92	155
Indiana	212	100	248
Kentucky	60	5	51
Maryland	85	75	127
Michigan	49	33	205
Minnesota	-	-	1
Mississippi	-	1	2
Missouri	12	5	-
New Jersey	2	5	15
New York	135	102	200
North Carolina	-	17	3
Ohio	204	121	806
Oklahoma	-	1	-
Pennsylvania	372	573	1529
Rhode Island	-	-	9
South Carolina	-	1	-
Tennessee	-	2	1
Texas	58	19	39
Utah	10	7	1
Virginia	-	3	-
Washington	12	4	29
West Virginia	14	5	90
Wisconsin	-	5	28
Total	1435	1264	3836

### Quantity And Geographic Distribution Of Fuels Used

A very approximate assessment of this subject is given by the data in Table A-10.1-1 for SIC 33 - Primary Metal Industries and, to a lesser degree, SIC 34 - Fabricated Metal Products. If it is assumed that coke-oven gas consumption in heating furnaces is proportional to coke consumption then Table A-10.1-1 provides at least the relative amounts, on a geographic basis, of fuels used.

Aside from this approach there was no specific information found at this time on distributions of fuel used.

### Air Pollutant Emissions

In this instance, the NEDS listing (Ref. A-2-2) for these devices is completely inadequate. A total of only 134 records (each record assumed to be a separately identifiable device) was found for soaking-pit and heat-treating furnaces in activity headings of: primary metals - steel production (1 record); secondary metals - gray iron (16 records); secondary metals - steel foundry (113 records); and, secondary metals - malleable iron (4 records). As previously mentioned, Reference A-10.6-3 listed a combined total of 6,535 soaking-pits, reheating furnaces, and heat-treating furnaces.

In addition, Reference A-10.9-2 does not contain emissions factors (weight of emission/unit measure of product) for any of these combustion devices. Therefore, it is concluded that no comprehensive air pollution emissions data are available for soaking-pits, reheating furnaces, and heat-treating furnaces in the steel industry.

## A-10.10 STATIONARY RECIPROCATING ENGINES

### Major Manufacturers

The major manufacturers of internal combustion engines, both diesel and spark ignition, are shown in Table A-10.10-1 together with information pertaining to engine characteristics. (These data were secured from an unpublished source.)

### Associations

The following associations represent engine manufacturers:

- . Engine Manufacturers Association (Chicago, Illinois)
- . American Trucking Association (Washington, D.C.)
- . Diesel Engine Manufacturers Association (Cleveland, Ohio)

### Basic Equipment And Combustor Design

Diesel engine (compression ignited, CI) combustion is achieved by injecting fuel into a cylindrical chamber containing compressionally heated air with combustion occurring spontaneously. Spark ignited (SI) engines employ a high energy electrical spark to initiate combustion. Usually these engines induct a premixed fuel-air mixture into the cylinder (the mixing function being performed by the carburetor). However, fuel injection into the cylinder containing compressed air is also utilized. Gaseous fueled SI engines mix the fuel with air at the intake valve.

Diesel engines of the dual-fuel type also operate on gaseous fuels but require a small amount of liquid diesel fuel to initiate the combustion process. Such engines are designed to operate with from 6 to 100 percent liquid fuel.

Both CI and SI engines are produced in two- and four-stroke cycle arrangements. In the CI, a power stroke is generated for every 360 deg of crankshaft rotation (corresponding to two strokes of the piston) while the SI delivers a power stroke for every 720 deg of crankshaft rotation, i.e. one power stroke for every four

TABLE A-10.10-1. IC ENGINE MANUFACTURERS

Manufacturer	Bore, inches	CID/cyl*	Power Range, hp†	Cylinder Power, hp/cyl	Speed Range, rpm
<u>Large Bore Engines</u>					
Alco	9	666	1000 - 4400	175 - 250	400-1200
Colt	8 - 16	1037-3526	850 - 9400	175 - 500	500-900
Cooper-Bessemer	13 - 20	2155-6283	900 - 13500	360 - 675	250-600
ElectroMotive Div (GM)	9	645	800 - 3600	100 - 180	900
Enterprise	13 - 17	1200-4770	1600 - 13500	280 - 680	400-600
Dresser-Clark	17 - 19	3860-5100	1000 - 10000	200 - 500	300-330
Ingersoll-Rand	11 - 17	1350-4993	1000 - 5500	125 - 330	300-550
Worthington‡	14 - 16	2972-4021	2300 - 8600	125 - 330	300-500
White Superior	8 - 14	510-3300	400 - 2400	75 - 150	900-1000
<u>Medium Bore Engines</u>					
Allis-Chalmers	3-1/2 - 6	43-169	29 - 850	10 - 70	1200-2600
Case	3-3/4 - 4-1/8	47-84	50 - 125	12 - 30	1200-2200
Caterpillar	4-1/2 - 6-1/4	79-246	85 - 1000	21 - 63	1200-2400
Chevrolet-Oldsmobile (GM)	3-7/8 - 4-1/4	26-57	50 - 215	13 - 27	3600-4000
Chrysler	3-1/4 - 4-1/4	28-52	43 - 175	12 - 30	1200-4000
Cooper-Penjax§	5 - 15	128-2827	15 - 300	15 - 150	200-900
Cummins	4-1/2 - 6-1/4	63-192	120 - 1200	20 - 100	1200-2100
Detroit Diesel	3-7/8 - 5-3/4	53-149	50 - 1100	20 - 68	1800-2500
Ford	4-1/8 - 4-1/2	26-67	38 - 200	9 - 22	2500-4600
International Harvester	3-7/8 - 5-3/8	39-136	16 - 325	9 - 50	1800-3000
John Deere	4 - 4-3/4	55-89	44 - 180	15 - 30	1500-2500
Minneapolis-Moline	4-1/4 - 5-5/16	71-133	90 - 180	15 - 29	1800
Murphy	5-1/2 - 6-3/8	142-207	110 - 520	30 - 60	1200-1800
Sterling	3 - 5-1/2	16-166	16 - 152	8 - 20	1200-1800
Stewart and Stevenson	3-7/8 - 4-3/4	53-149	30 - 1100	20 - 68	1200-1800
Teledyne Continental	3-7/8	28-41	50 - 80	12 - 14	2000-2400
Waukesha#	3-5/8 - 9-3/8	38-586	52 - 1550	8 - 110	1000-1800
White Engines (Hercules)	3-3/4 - 4-1/2	35-80	34 - 130	12 - 26	2400-2800

\* Cubic inch displacement per cylinder

† Horsepower is for rated conditions (continuous operation) @ 130°F intercooler water temperature for large bore engines and 85°F inlet air temperature for medium bore engines.

‡ Worthington ceased producing engines during the writing of this report.

§ This manufacturer produces high power one- and two-cylinder engines.

# The manufacturer straddles the medium-large bore categories, however, the majority of engine production is in the medium bore category.

Continued

TABLE A-10.10-1 continued

Manufacturer	Bore, inches	CID/cyl*	Power Range, hp†	Cylinder Power, hp/cyl	Speed Range, rpm
<u>Small Engines and Generator Sets</u>					
Kohler	—		3-3/4 - 28	3 - 7	2000-2700
Onan	3-1/4		8 - 30	6 - 8	1800-3900
Teledyne Wisconsin	2-3/4 - 4-1/8		3-1/2 - 80	3-1/2 - 20	2400-3600
Wills Industries	—		11 - 28	11 - 14	3000
Witte	4-1/4 - 5		9 - 27	9 - 14	800-1800
<u>Very Small Engines</u>					
Briggs and Stratton	2-3/8 - 3-9/16		2 - 16	2 - 16	3100-4000
Chrysler	2 - 2-1/4		3-1/4 - 8	3-1/4 - 8	5500-7000
Clinton	2-1/2 - 2-3/8		4 - 7	4 - 7	4600-5800
Homelite	1-7/16 - 2-3/4		2 - 4	2 - 4	—
Jacobsen	2-1/8		3	3	3600
Outboard Marine Corp. (Lawn Boy)	2-3/8		<10	—	—
McCulloch	1-3/8 - 2-1/4		<20	—	—
O&R	1-1/8 - 1-17/32		1 - 2-1/4	1 - 2-1/2	6300-7200
Tecumseh	2-3/8 - 3-1/2		2-1/2 - 16	2-1/2 - 16	2500-3600

\*Cubic inch displacement per cylinder

†Horsepower is for rated conditions (continuous operation) @ 130°F intercooler water temperature for large bore engines and 85°F inlet air temperature for medium bore engines.

piston strokes. The two-stroke arrangement offers the advantages of a simpler mechanical design since it is possible to completely eliminate the valves and valve drive train while also achieving twice as many power strokes per unit of cylinder volume. However, these advantages are achieved at the expense of fuel economy because a portion of the incoming fuel charge may be swept across the cylinder and out the exhaust port before complete combustion has been achieved.

The method of inducting air into the cylinder may also vary. In the naturally aspirated design, the air is drawn into the cylinder by piston pumping action. This is achieved by the slight negative pressure produced in the cylinder of a four-stroke design as the piston starts its downward motion during the intake stroke. In a two-stroke engine, air is either inducted into the crankcase as the piston begins its upward motion during the exhaust portion of the cycle or blown into the cylinder. Thus, the amount of air inducted (and fuel also) in a naturally aspirated engine is limited by geometry, valve timing, and rotational speed.

In order to ease this limitation, engines are fitted with turbochargers which are turbine driven air compressors operating from engine exhaust energy. In this manner a greater mass of air can be charged into the same cylinder volume and, therefore, can burn with a greater mass of fuel. Thus, turbocharged engines can produce a greater power output per unit cylinder volume. Estimates, reported in Reference A-10.10-1, are that 55-60% of the diesels built today are turbocharged and that this ratio will grow to 80% or more in years to come.

Combustion chamber designs may include a precombustion volume into which nearly all the fuel is injected and partially burned in a fuel rich environment. The combustion is completed as these gases expand into the main chamber and react with the balance of the air. These divided chamber designs are incorporated into both CI and SI engine

and may reduce NO<sub>x</sub> emissions via a staged combustion technique. This reduction is achieved, however, at an increase in fuel consumption brought about partly by additional heat transfer losses through the surface area represented by the precombustion chamber walls.

Figure A-10.10-1 shows an internal combustion engine--in this instance a 2-stroke, spark ignited, natural gas fueled, turbocharged unit with an integral gas compressor.

Current Fuel Use, Trends And Properties

Current fuels used in reciprocating IC engines include: distillate oil, residual oil and natural gas (dual fuel engines) for CI engines; gasoline and natural gas for SI engines. Residual oil with a sulfur content of 0.5 percent or less is considered to be acceptable - higher sulfur concentrations are not recommended because of possible excessive engine wear and acid compound contamination of the lubricating oil.

No reference was found concerning the use of coal either directly (pulverized or in a slurry) or indirectly (coal gasification) for these engine types.

Based on unpublished data it was determined that the total energy produced by IC engines amounts to:

. Diesel (distillate and residual oil)	71.6x10 <sup>15</sup> J/yr
. Dual Fuel	22x10 <sup>15</sup> J/yr
. Natural Gas	338x10 <sup>15</sup> J/yr
. Gasoline	<u>48x10<sup>15</sup> J/yr</u>
Total	480x10 <sup>15</sup> J/yr

Natural gas accounts for 70.5% of the total energy produced by these engines. Indeed, the use of natural gas is even greater when dual fuel engines are operating with a high percentage (90-95%) of natural gas on an energy basis. For 90% natural gas usage in dual fuel engines, natural gas supplies 74.6% of all the energy produced by reciprocating internal combustion engines.

314

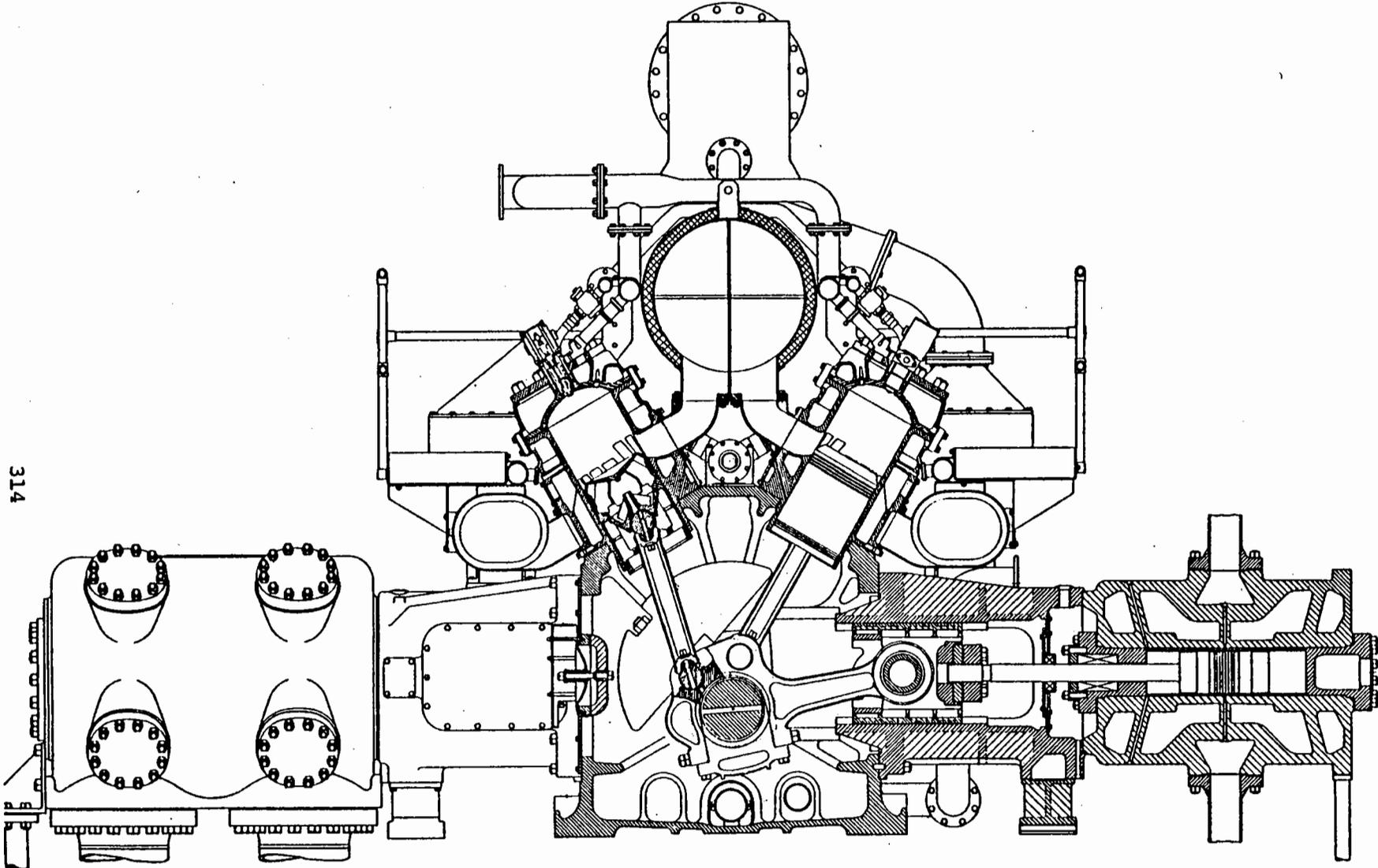


Figure A-10.10-1. Internal combustion engine with integral gas compressor (Cooper Energy Services).

Further, natural gas fueled engines used in the oil and gas production and oil and gas industry categories account for  $275 \times 10^{15}$  J/year or 81.2% of the energy produced by all natural gas fueled devices. This is due to the close physical proximity of the fuel supply to the device, e.g., an engine driving a natural gas pipeline compressor will be a very short distance from a fuel source (the pipeline).

Fuel use trends, while not quantitatively established, are anticipated to result from shortages in both natural gas and low sulfur content fuel oils (especially the former). Thus, in the future dual fuel diesel engines could be operated with a higher percentage of fuel oil.

#### Trends In Equipment Type, Age, Size And Use

Reference A-10.10-2 indicates that there is no discernible trend in IC engines, especially those with outputs between 746 and 1864 kw (1,000 - 2,500 HP). There has been a tendency toward including turbochargers on new engines and retrofitting turbochargers on older naturally aspirated units in the interest of improved fuel economy. There has also been some discussion by engine manufacturers to convert natural gas fueled engines to utilize oil fuels in the event that rising natural gas prices make it economically justifiable.

The matter of engine age, especially for large stationary units, is difficult to establish since major components, e.g., cylinder head, crankshaft, connecting rods, main and rod bearings, will last indefinitely if the engine is properly operated. Minor overhauls are performed after 8,000 to 16,000 hours (0.9 to 1.8 years) and include new piston rings, new or reground valves, and occasionally new or rebuilt pistons. After 20,000 to 80,000 hours (2.3 to 9.1 years) a major overhaul is performed and may include new cylinder liners in addition to those items covered by the minor overhaul.

Usually the old parts are either rebuilt to original specifications or replaced with identical new items. Occasionally the new parts have been altered from original specifications, e.g., different piston crown design, injector timing, etc., to reflect component improvement.

This distinction is quite important since the former component replacement approach probably will not require that the engine be subject to emission regulations if it had not been previously necessary. The latter approach, i.e., substitution of new design components, may require that the engine be subject to emission regulations if these new components result in greater emissions or emission of a new pollutant.

#### Total Number And Geographic Distribution

An unpublished study has produced the total number of stationary internal combustion engines categorized primarily by fuel type (diesel, dual fuel, natural gas and gasoline) and application. For some applications the strict definition of "stationary" is not clear but seems to include those engines which are used in a non-propulsive mode and those propulsive units whose area and/or velocity of movement is "small". For the latter category "small" would refer to the subsequent spatial dispersion of air pollutant emissions as being governed by atmospheric motion and not by the motion of the source. This definition would then include, for example, gasoline powered lawn mowers but would exclude diesel powered refrigeration units used on long distance tractor-trailer rigs. Table A-10.10-2 herein is reproduced from the unpublished study.

No information was contained in the unpublished study or found elsewhere as to the geographic distribution of the devices.

#### Limitations In Equipment Uses And Fuels

Large capacity stationary IC engines are designed to operate for long periods of time at rated power and, as a result, there is little flexibility to change basic operational characteristics in an effort to reduce air pollutant emissions. Such characteristics as spark or injection timing are not varied from the manufacturers specifications. Indeed, such specifications were originally established in older models as corresponding to maximum fuel efficiency. Obviously, engines used in utility and industrial electric generation are not permitted any variation in rotational speed.

TABLE A-10.10-2. STATIONARY IC ENGINE APPLICATIONS

Category	Annual Production, units/yr	Population,* units	Average Power hp	Load Factor	Annual Usage, . . hr/yr	Annual Energy Production - Yearly Sales; hp-hr/yr x 10 <sup>6</sup>	Annual Energy Production - Installed Units, hp-hr/yr x 10 <sup>6</sup>	Constant Load	Variable Load	Constant Speed	Variable Speed	Basis of Estimate
<b>DIESEL</b>												
<u>Oil &amp; Gas Production</u>												
Off shore drilling	} 800 <sup>†</sup>	675	350	0.8	2000		378		X		X	AGA Market Study AGA Market Study
Land drilling		3,050	350	0.8	2000		1,708		X		X	
<u>Oil &amp; Gas Transport</u>	50 <sup>†</sup>	500	2000	0.8	6000		4,800	X			X	McGowin, Gas Facts
<u>Electric Generation</u>	150 <sup>†</sup>	400	2500	0.8	2600		2,160		X	X		FPC, Diesel & Gas Power Costs
<u>General Industrial &amp; Agriculture</u>												
Municipal water supply	200 <sup>†</sup>	2,100	120	0.75	3000		567	X		X		AGA Market Study
Marine nonpropulsive	5,000 <sup>‡</sup>	15,000	100	0.5	3500	62.5	1,875		X		X	Current Industrial Report, Industry contacts
Construction, small	5,000	50,000	50	0.5	500	62.5	625		X		X	
Miscellaneous, large <sup>§</sup>	1,700		750	0.5	100	56.3	1,125					
Construction, large	5,000	50,000	240	0.5	500	300.0	3,000		X		X	
Portable compressors <sup>#</sup>	9,000	90,000	75	0.5	500	168.8	1,688		X		X	
Welders	8,000	80,000	55	0.5	500	110	1,000	X	X		X	
Pumps	5,000	25,000	100	0.5	1000	250	1,250	X		X		
Generator sets(stand by)												
<50 kw	7,000	70,000	75	0.5	500	35.0	350		X	X	X	
50 kw - 400 kw	8,000	160,000	250	0.5	250	250	5,000	X	X	X	X	
400 kw - 1000 kw	1,500	30,000	750	0.5	100	56.3	1,125	X	X	X	X	

Footnotes appear at end

TABLE A-10.10-2 (continued). STATIONARY IC ENGINE APPLICATIONS

Category	Annual Production, units/yr	Population,* units	Average Power hp	Load Factor	Annual Usage, hr/yr	Annual Energy Production - Yearly Sales, hp-hr/yr x 10 <sup>6</sup>	Annual Energy Production - Installed Units, hp-hr/yr x 10 <sup>6</sup>	Constant Load	Variable Load	Constant Speed	Variable Speed	Basis of Estimate
DUAL FUEL												
<u>Oil &amp; Gas Transport</u>	} included in Diesel	} included in Diesel		0.8	6000		2,228	X			X	McGowin, Gas Facts
<u>Electric Generation</u>				0.8			6,000		X	X		FPC, Diesel & Gas Power Costs
NATURAL GAS **												
<u>Agriculture</u>		91,000	100	0.75	2500		17,063	X		X		AGA Market Study
<u>Oil &amp; Gas Production</u>												
Oil & gas well pumps		266,000	15	0.7	3500		9,776	X		X		AGA Market Study
Secondary recovery		5,600	200	0.8	6000		5,376	X		X		AGA Market Study
Well drilling		3,050	350	0.8	2000		1,708	X		X		AGA Market Study
Plant processing		4,000	750	0.8	8000		19,200	X		X		McGowin
<u>Oil &amp; Gas Industry</u>												
Utility compressors††		} 4,500	2000	0.9	6000		51,800	X		X		Southwest Research Institute††
			4,000	750	0.8	6000		14,400	X		X	
<u>Electric Generation</u>												
Private/public utility				0.8			166.5		X	X		FPC, Diesel & Gas Power Costs
Commercial-institutional		450	200	0.45	4000		162		X	X		AGA Market Study
Stand-by		2,000	100	0.9	50		9	X		X		AGA Market Study
Industrial on-site		1,500	300	0.6	4000		1,080		X	X		AGA Market Study

Footnotes appear at end

TABLE A-10.10-2 (continued). STATIONARY IC ENGINE APPLICATIONS

319

Category	Annual Production, units/yr	Population, units	Average Power hp	Load Factor	Annual Usage, hr/yr	Annual Energy Production - Yearly Sales, hp-hr/yr x 10 <sup>6</sup>	Annual Energy Production - Installed Units, hp-hr/yr x 10 <sup>6</sup>	Constant Load	Variable Load	Constant Speed	Variable Speed	Basis of Estimate	
<u>General Industrial</u>													
Industrial shaft power		2,900	200	0.75	5000		2,175		X		X	AGA Market Study	
Plant air		750	100	0.5	4000		150.4		X		X	AGA Market Study	
Air conditioning		3,760	80	0.4	2000		240.6		X		X	AGA Market Study	
Commerical shaft power		600	2000	0.6	1000		720		X		X	AGA Market Study	
Municipal water supply		2,100	120	0.75	3000		567	X		X		AGA Market Study	
waste treatment		1,740	400	0.45	4000		1,566	X		X		AGA Market Study	
<u>GASOLINE</u>													
<u>Agriculture</u>													
Misc. machinery	20,000	400,000	30	0.5	200	60	1,200	X	X	X	X	Current Industrial Reports, Industry contacts	
Irrigation	5,000	10,000	100	0.75	2000	750	1,500	X	X	X	X		
<u>General Industrial</u>													
Generator sets >5 kw	35,000	350,000	55	0.5	400	715	7,150		X	X		Current Industrial Reports	
Compressors	7,000	70,000	55	0.5	400				X				X
Welders	18,000	180,000	55	0.5	400				X	X	X		X
Miscellaneous	5,000	50,000	55	0.5	400				X	X	X		X
Construction	5,000	40,000	150	0.5	500	188	1,500		X	X	X		
Small (<15 hp)	12,600,000	63,000,000	4.2	0.5	50	1100	6,615	X	X	X	X		

See footnotes on following page.

TABLE A-10.10-2 (continued). STATIONARY IC ENGINE APPLICATIONS

Footnotes

- \* Annual production multiplied by life in years (based on estimated service life of 5000 hours for diesel engines, 4000 hours for gasoline engines, or as noted) to complete population.
- † Approximated, based on estimated population and annual usage.
- ‡ 7500-hr service life assumed.
- § Applications include pumps, snow blowers, aircraft turbine starters, etc.
- # Excludes mobile refrigeration units.
- \*\* Population estimates come from the AGA market study. Annual production is not estimated for this category since production has been changing rapidly, decreasing continuously since 1966 and, therefore, an annual estimate of production could be misleading.
- †† Includes transport, distribution, gathering, and storage.
- ‡‡ Pull combines, balers, sprayers, dusters, etc.
- §§ Estimated service life of 5 years.

Aside from dual fuel engines there is a fairly definite limitation in fuel usage. Diesel engines have some flexibility in substituting a lower grade fuel oil especially if the engines include a precombustion (divided) chamber (Ref. A-10.10-3). However, the use of residual oil with a sulfur content greater than 0.5 percent is not recommended.

#### Quantity And Geographic Distribution Of Fuels Used

No information was obtained on this subject.

#### Air Pollutant Emissions

Air pollutant emissions for natural gas fuel reciprocating engines, as found in Reference A-2-2 are shown in Table A-8-1. The emissions for this fuel classification are much greater than for any other fuel.

## A-10.11 STATIONARY GAS TURBINES

### Major United States Manufacturers

Table A-10.11-1, abstracted from Reference A-10.11-1, lists the major U.S. manufacturers of stationary gas turbines along with their applications and fuels used.

### Associations

Gas turbine manufacturers are represented by the American Society of Mechanical Engineers, Gas Turbine Division (New York, N.Y.).

### Basic Equipment And Combustor Design

A stationary gas turbine is composed of three basic components:

1. A compressor which produces high pressure air.
2. A combustion chamber within which fuel and air are burned.
3. A turbine which supplies energy to the compressor and delivers useful shaft energy to the load.

There are several variations on each of these basic components:

#### Compressor

The compressor may consist of a few (one or two) centrifugal stages wherein the air inlet is in the axial direction and the discharge is in the radial direction (with respect to the axis of rotation). Usually, this arrangement is employed on smaller capacity units. On larger units the air flow is mainly in the axial direction with the compressor consisting of a large number of stages (up to 17) with each rotor stage separated by a set of stator blades (which redirect the air flow for the following rotor stage).

#### Combustor

For smaller units there may be only a single combustion chamber arranged in an annular manner around the axis of rotation. Larger units will contain a series of individual combustor chambers (as many as 18)

TABLE A-10.11-1. MAJOR UNITED STATES GAS TURBINE MANUFACTURERS  
(Ref. A-10.11-1)

Manufacturer	Application*	Fuel†
AiResearch	G, SP	JP-4, JP-5, Jet A
AVCO Lycoming	I	NG, No. 2
Cooper-Bessemer	SP	NG, GT1, GT2
Curtiss-Wright	SP, G	NG, GT1, GT2, No. 1, No. 2
Delaval Turbine	CP	NG, GT
Detroit Diesel Allison	G, GC	NG, No. 1, No. 2
Dresser Clark	SP	G, L (gaseous or liquid available)
General Electric	SP, G	(Not specified)
Ingersoll-Rand	SP	NG, Diesel (grade not specified)
Rohr Industries	PG	No. 1, No. 2, JP-5, Jet A
Solar	G, GC	NG, GT1, GT2
Turbodyne	G, SP	NG, BF, No. 1-6, GT1-4
Turbo Power and Marine Systems	I	NG, No. 1, No. 2
Westinghouse	G, PG, PL	NG, GT1 - GT4

\* CP = Compressor drive  
 G = Generator drive  
 GC = Gas compressor drive  
 I = Industrial  
 PG = Packaged power plant  
 PL = Peak load  
 SP = Shaft power

† BF = Blast-furnace gas  
 GT1 - GT4 = Gas turbine fuels per ASTM Spec. D-2880  
 Jet A = Aircraft kerosene  
 JP-4, JP-5 = USAF jet fuels or equivalent  
 NG = Natural gas  
 No. 1 - No. 6 = ASTM D-396 burner fuels or D-975 diesel fuels or equivalent.

with the chambers also arranged in an annular manner. In either situation the combustor's functions are to inject and atomize the fuel (in the case of liquid fuels), mix the fuel vapor and air, initiate combustion, stabilize the flame zone, and, by introducing additional air, reduce the combustion gas temperature to a level consistent with the turbine's capability. This last requirement will necessitate that the device operate, on an overall basis, with a significant amount of excess air.

### Turbine

The turbine may also be of the radial or axial flow design with the former typically having one stage and the latter having anywhere from 1 to 6 stages. In addition, the multi-stage arrangement can have some of the stages mounted on a shaft separate from the compressor shaft. In this instance the "free" turbine stage(s) is delivering useful energy to the load. This configuration allows the free turbine rotational speed to be matched more closely with that required by the load. The compressor and its turbine stage(s) can then rotate at a rate different from the free turbine and the load.

At present, there are three gas turbine cycles in use-- simple, regenerative and compound (Ref. A-10.11-2). In the simple cycle the exhaust gas is discharged without any waste heat recovery. This cycle will show a thermal efficiency on the order of 25 to 30%. The regenerative cycle employs the turbine exhaust gas, at a temperature of 756 to 867 K (900 to 1100°F), in a recuperative air preheater heat exchanger. Typical thermal efficiency is from 35 to 37%. The combined cycle is another manner in which waste heat is recovered from the turbine exhaust. In this case, the exhaust gas is used to produce steam in a steam boiler before being exhausted. The steam boiler output may then be used to drive a steam turbine in which case the gas turbine generates typically 60% of the total power produced with the steam turbine producing 40%. In some cases, additional fuel is burned with the oxygen rich turbine exhaust gas to produce higher capacity/quality steam in the boiler. Thermal efficiency for the compound cycle gas turbine is on the order of 40 to 42%.

Figure A-10.11-1 shows a simple cycle gas turbine unit rated at 2.8 MW and intended for gas compression and shaft power applications.

#### Current Fuel Use, Trends And Properties

According to Reference A-10.11-1, and as shown in Table A-10.11-1, current stationary gas turbine fuel use includes natural gas, residual and distillate oils, and in one instance blast furnace gas. No use of coal is noted because of possible particulate erosion of the turbine blades. Indeed, Reference A-10.11-3, which is a listing of gas turbines on a worldwide basis, does not contain a single listing of a gas turbine using coal as a fuel.

Dual fuel operation is not typical (Ref. A-10.11-4). This manufacturer's gas turbines cannot operate simultaneously on gaseous and liquid fuels--rather a change in the fuel supply system must be made when switching from a gaseous to a liquid fuel and vice versa. This fuel supply system change does not require any change in the combustor.

Information obtained from the Federal Power Commission (Ref. A-10.11-5) listed net electrical energy produced by gas turbines for the years 1970-1975 by fuel type. (This is not to be confused with fuels consumed by gas turbines in electrical generating activities.) The FPC data, shown in Table A-10.11-2, does not differentiate between fuel oil types, e.g., distillate, residual, etc.

These data are of prime interest in establishing trends in fuel usage. As can be seen from Table A-10.11-2 the general trend since 1970 has been toward a greater utilization of fuel oil at the expense of natural gas with the dip in 1973 probably due to the combined effects of the national economic recession and oil embargo imposed by the producing nations.

#### Trends In Equipment Type, Age, Size And Use

As noted in Table A-10.11-1 stationary gas turbines find a widespread application in electrical generation and pipeline activities (oil pumping and gas compression). According to Reference A-10.11-2 installed gas turbine capacity in electrical generating in 1970 was 16,500 MW - approximately 5%

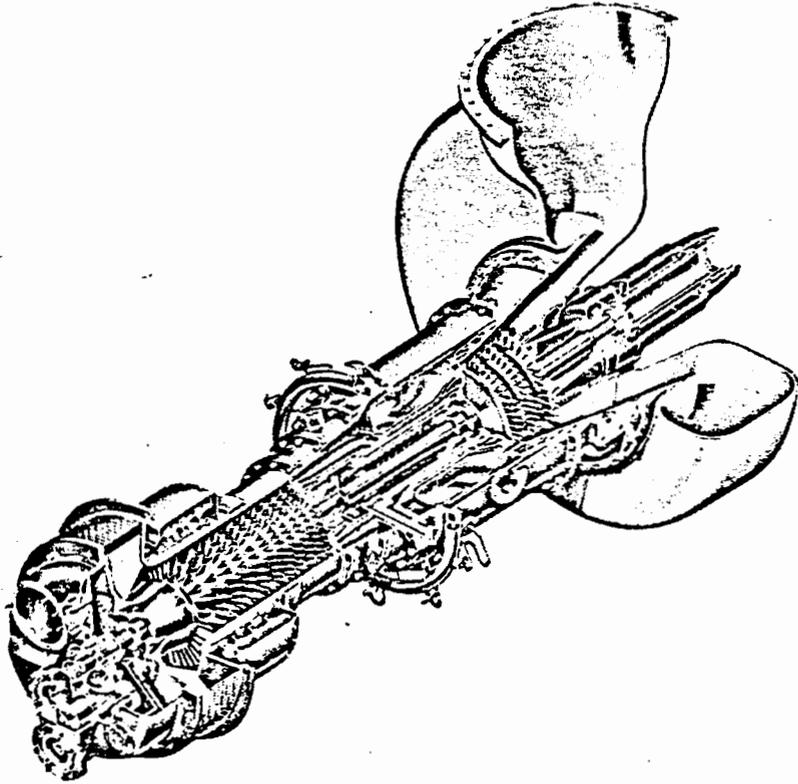


Figure A-10.11-1. 2.8 Mw gas turbine (Solar Div. International Harvester).

TABLE A-10.11-2. NET ELECTRICAL ENERGY PRODUCED BY GAS TURBINES

(10<sup>15</sup> joules)

Year	Nat. Gas	Oil*	Total	Oil, % Of Total
1970	28.3	26.8	55.1	48.7
1971	37.7	41.4	79.1	52.3
1972	39.0	66.7	106.0	63.1
1973	47.4	58.8	106.0	55.4
1974	45.3	70.0	115.0	60.7
1975	30.0	50.2	80.2	62.6

\*type not specified

of the capacity from all sources. As of December 31, 1975 these figures had increased to 43,526 MW and 8.6% (Ref. A-10.11-6). Thus, in 5 years, gas turbine electrical generating capacity had increased by 164%. By 1980 planned additions will increase gas turbine capacity to 55,950 MW - an increase in capacity of 239% between 1970 and 1980.

Current electrical utility plans still envisage the gas turbine in a peaking role with a required life expectancy of 30 years. As a result only 11 combined cycle units have been planned to be added in an electrical generating application (Ref. A-10.11-7). (Peaking usage of a combined cycle unit would require that the steam boiler undergo several on-off cycles per day. This intermittent operation of a steam boiler is not desirable. In addition, the gas turbine portion of the unit can be brought on-line much faster than the boiler, i.e., the steam boiler response time is the controlling factor in the overall unit response time.)

As of 1971, according to Reference A-10.11-7, the largest gas turbine electric generating station in the United States was the Astoria, New York station of Consolidated Edison. This station had 13 units with a combined capacity of 744.5 MW.

The largest single gas turbine produced in the United States has a capacity of approximately 100 MW (Ref. A-10.11-7). It is a very common practice for manufacturers to compound two or more separate units together and sell them as a single unit with a nameplate capacity equal to the sum of the individual, separate units. Thus, the 176.5 MW unit located at Consolidated Edison's plant in Astoria, New York, is actually composed of 4 individual gas turbines packaged together.

Projections (Ref. A-10.11-2) indicate that a 1,000 MW plant will be available in the future and will probably be composed of 5 combined cycle units each generating 200 MW.

Figure A-10.11-2, reproduced from Reference A-10.11-2, reports the sales of gas turbines for gas compression service by power rating for the years 1965 through 1970. These figures indicate the increasing

acquisition of units with ratings of 7457 kW (10,000 hp) and larger. No further information was obtained on trends in gas compression service, however, additional information is probably available.

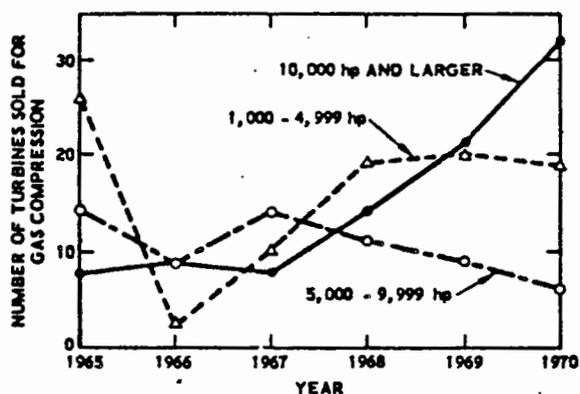


Figure A-10.11-2. Trends in size of turbines sold for gas compression service. (Ref. A-10.11-2)

#### Total Number And Geographic Distribution

As of January 1, 1974, according to Reference A-10.11-1, there were 350 gas turbines in gas transmission line service in the United States with a total power rating of 1,970 MW ( $2.64 \times 10^6$  hp). No information was found on the geographic distribution of gas turbines used in this service.

A survey conducted by the Federal Power Commission in 1975, and reported in Reference A-10.11-5, tabulated the state-wide distribution of gas turbine electrical generating plants and installed capacity. (The survey did not ask for information broken down on a per device basis.) The results of this survey are shown in Table A-10.11-3 and indicate that there were gas turbines at 506 plants in the United States with a combined capacity of 43,526.6 MW.

A similar survey conducted in 1971 (Ref. A-10.11-3) tabulated a total of 761 gas turbines installed in electric generating service. Only 15 units had any form of waste heat recovery, and only 4 of these

TABLE A-10.11-3. GAS TURBINES INSTALLED IN ELECTRICAL GENERATING

State	No. Plants	Capacity, MW	State	No. Plants	Capacity, MW
Alabama	4	604.4	Alaska	6	281.6
Arizona	14	1,719.8	Arkansas	3	308.1
California	20	1,205.4	Colorado	4	200.0
Connecticut	15	454.7	Delaware	7	156.7
Florida	25	4,532.6	Georgia	10	1,255.2
Hawaii	3	131.9	Idaho	1	50.0
Illinois	19	2,227.0	Indiana	10	466.2
Iowa	11	637.5	Kansas	14	756.1
Kentucky	5	190.1	Louisiana	6	90.8
Maine	3	45.1	Maryland*	12	1,419.3
Massachusetts	16	567.7	Michigan	17	993.4
Minnesota	15	953.8	Mississippi	10	223.2
Missouri	15	717.3	Montana	2	47.1
Nebraska	8	460.6	Nevada	4	176.0
N. Hampshire	4	88.0	N. Jersey	25	4,260.5
N. Mexico	3	44.5	N. York	31	4,389.6
N. Carolina	11	894.4	N. Dakota	1	8.0
Ohio	25	1,688.7	Oklahoma	9	467.4
Oregon	3	719.2	Pennsylvania	34	3,067.2
S. Carolina	21	1,512.5	S. Dakota	1	12.5
Tennessee	3	2,034.0	Texas	24	1,610.7
Vermont	5	129.0	Virginia	7	525.7
Washington	3	120.0	W. Virginia	1	18.6
Wisconsin	15	1,048.5	Wyoming	1	16.0

\* Includes District of Columbia

were a combined cycle device. The vast majority of the units (746 out of 761) were simple open cycle gas turbines.

#### Limitations In Equipment Uses And Fuels

A definite limitation in gas turbine operation is the gas temperature at the turbine inlet. Present turbine materials and blade designs require that this temperature not exceed 1255 to 1310 K (1800 - 1900°F). Material and blade design advances are expected to raise this limit to 1590 K (2400°F), with the blades being cooled by circulating air bled from the compressor.

The use of heavy residual oils is limited primarily by metals content as related to turbine blade corrosion.

The direct use of coal, as opposed to gasified coal, is not anticipated for use in a gas turbine. This is because of turbine blade erosion due to the fly ash in the combustor exhaust gases.

#### Quantity And Geographic Distribution Of Fuels Used

No specific information was obtained on this subject. However, the relative amount of natural gas and fuel oil used can be approximated from proportioning the data in Table A-10.11-2 (for 1975) with that in Table A-10.11-3 (also for 1975). Thus, if it is assumed that fuel oil supplied 62.57% of the energy throughout the United States, then this value can be applied to the state-wide capacity distribution. The balance of the fuel used would be natural gas.

#### Air Pollutant Emissions

Air pollutant emissions from natural gas fueled gas turbines are shown in Table A-8-1. A more detailed examination of the NEDS listing (Ref. A-2-2) indicates the NO<sub>x</sub> emissions for gas turbines shown in Table A-10.11-4.

TABLE A-10.11-4. NO<sub>x</sub> EMISSIONS FROM GAS TURBINES

Fuel	No. of Records	kg/Year	NO <sub>x</sub> Short Tons/Year
Distillate	21	1 561 000	1,717
Natural Gas	144	19 627 000	21,590
Residual	2	0	0
Jet Fuel	1	0	0
Process Gas	1	238 000	262
	<u>169</u>	<u>21 426 000</u>	<u>23,569</u>

If the number of records does indeed correspond to the number of gas turbines inventoried, then the NEDS listing is decidedly incomplete since there are at least 1111 units in gas compression and electric generation. Even if the number of records corresponds to the number of locations using gas turbines (with each location having one or more units), the NEDS listing still appears incomplete. Reference A-10.11-5 tabulates 506 locations using gas turbines in the electric generating service alone.

## A-10.12 PETROLEUM REFINERY PROCESS HEATERS

### Major Manufacturers

No published information was found to be available. Contact with refineries, API (American Petroleum Institute), and construction companies provided the following list of major manufacturers:

- . Born, Inc. (Houston, Texas)
- . C-E Lummus (Bloomfield, New Jersey)
- . Foster Wheeler Energy Corporation (Livingston, New Jersey)
- . Heat Research Corp. (New York, NY)
- . Petro-chem Development Co., Inc. (New York, NY)
- . Selas Corp. of America (Dresher, PA)

The major burner manufacturers are:

- . John Zink Company (Tulsa, OK)
- . National Airoil Burner Co. (Philadelphia, PA)
- . Coen Company (Burlingame, CA)

### Associations

The American Petroleum Institute is the major association. Activities related to petroleum refinery heaters are concentrated in the API Manufacturers and Contractors Subcommittee on Fired Heaters and in the API Committee on Stationary Source Emissions.

### Basic Equipment and Combustor Designs

The function of refinery process heaters is to provide heat for three basic functions:

1. temperature increase of liquid oil
2. vaporization
3. promoting chemical reactions.

All heating is indirect in that the flame does not directly contact the material processed. Construction consists of an outer shell, refractory lining, internal tubing to contain the heated process material, burner equipment arranged for proper flame shape, and air inlet and exhaust ducting for proper heat distribution and combustion. Heat is transferred by flame

radiation and by convection. Furnaces are generally divided into two sections: (1) a radiant section in which tubes are exposed to direct flame radiation and (2) a convection section. The process oil being heated is generally introduced in the cold end of the convection section and exits after passing through the radiant section. Some heaters may not have a convection section.

There are two major types of refinery heater construction:

1. Vertical tube cylindrical shell heaters
2. Horizontal tube box heaters.

Manufacturers indicate that construction is about equally divided between these two types so that neither type is prevalent. Variations of these basic types occur based on the specific needs for heat distribution within the heater as discussed in Reference A-10.12-1. The proper division of heat delivery by radiation and convection is the most critical design parameter. Improper design or operation can cause tube overheating resulting in product coking or tube failure. Product output temperature is the primary control parameter.

The heater process function has a major influence on the combustion process. Processes can be ordered by the degree of process sensitivity to combustion changes:

1. Heat medium heaters - heat oil or steam used as heat source in other processes
2. Low temperature reboilers
3. Crude heating
4. Chemical reforming.

There are many other processes performed but the above are the primary ones.

The process sensitivities are indicated by manufacturers to be more important than heater design in influencing limitations on combustion modifications that could be performed for emissions reduction or efficiency improvement.

Combustor (burner) designs can be classified by the following characteristics:

1. Draft
  - . natural
  - . balanced or forced
2. Burner orientation
  - . horizontal or side fired
  - . vertical-upward
  - . vertical-downward
3. Atomization (liquid fuels)
  - . mechanical
  - . air
  - . steam
4. Air register type
  - . straight injection
  - . swirl promoting
5. Flame shape

The majority of refinery heaters have natural draft burners. Horizontal tube box heaters tend to have many more burners than vertical cylindrical heater types. Horizontal tube box heaters can be fired with burners in any orientation. Vertical tube cylindrical heaters normally have burners located at the bottom firing vertically upward. Most natural draft burners employ steam for liquid fuel atomization and tend to have fairly simple straight injection air registers. Natural draft designs generally do not have any windbox around the burners and air preheating cannot be performed. Excess air required tends to be higher than for forced draft burners.

Forced draft designs require a windbox to distribute the pressurized air from a fan. These units are, therefore, more adaptable to air preheat and to the use of flue gas recirculation. Higher air pressures also allow the use of swirl promoting air registers. This improves the fuel-air mixing allowing operation at lower excess air compared to natural draft types.

### Current Fuel Use, Trends And Properties

About 50% of total refinery energy is provided by fuel gas generated in the various refinery processes. This gas varies widely in composition, containing carbon monoxide, hydrogen, various light hydrocarbons and inerts. Natural gas may be mixed in to reduce heat content variation but heat content can still vary from 19 to 74 MJ/m<sup>3</sup> (500 to 2000 Btu/CF). It is not possible to specify a typical refinery gas since properties vary with time in every refinery. Refinery gas composition at various levels of heat content is illustrated in Table A-10.12-1 based on samples collected in refineries by KVB during the study reported in Reference A-10.12-2. The variation in composition can occur very quickly and this makes tests of these devices difficult because stable operating conditions cannot be established. Some heaters are operated at a constant air flow high enough to compensate for fuel variations and therefore excess oxygen varies with fuel composition. Other units may have excess air controls to adjust air as fuel composition changes.

Refinery gas fuel is supplemented with oil or natural gas to provide a total refinery energy input to heaters equivalent to about 3 to 12% of the crude input energy content. Smaller refineries require 3 to 5% and larger refineries require 5-12% heater heat input based on crude heat content. Crude energy content is about 42 GJ/m<sup>3</sup> (6.3 million Btu per barrel). Heating a crude oil from 293 K to 543 K (68°F to 700°F) requires a heat input of about 660 MJ/m<sup>3</sup> (100,000 Btu/barrel) or about 1.5% of the crude heat content. This heating is required for the initial crude distillation process and the crude heaters required are generally the largest in the refinery. A large refinery will have up to 6 separate crude heaters.

Details on refinery fuel use by device type are not published. However, the general trend is to operate heaters on refinery gas and steam boilers on oil or natural gas. Therefore, while overall only 50% of the refinery energy is provided by refinery gas, more than 50% of heater fuel is refinery gas.

TABLE A-10.12-1. TYPICAL REFINERY FUEL GAS COMPOSITION

Component	Composition, mole fraction					
	1	2	3	4	5	6
H <sub>2</sub> hydrogen	0.644	0.535	0.245	0.393	0.259	0.155
N <sub>2</sub> nitrogen	0.010	0.027	0.014	0.014	0.023	0.018
CO <sub>2</sub> carbon dioxide	---	---	0.004	0.001	0.001	---
CH <sub>4</sub> methane	0.245	0.278	0.537	0.240	0.248	0.307
C <sub>2</sub> H <sub>4</sub> ethylene	---	0.008	0.006	0.039	0.026	0.039
C <sub>2</sub> H <sub>6</sub> ethane	0.055	0.071	0.136	0.111	0.088	0.087
C <sub>3</sub> H <sub>6</sub> propene	---	---	0.003	0.030	0.093	0.106
C <sub>3</sub> H <sub>8</sub> propane	0.034	0.078	0.042	0.087	0.143	0.120
i-C <sub>4</sub> H <sub>10</sub> i-butane	0.004	0.002	0.003	0.037	0.043	0.030
n-C <sub>4</sub> H <sub>10</sub> n-butane	0.002	0.001	0.005	0.039	0.069	0.123
C <sub>5</sub> H <sub>12</sub> pentane	0.006	---	0.005	0.010	0.007	0.015
Heating value MJ/m <sup>3</sup>	25.66	30.0	38.8	45.7	57.1	64.2
(Btu/CF)	(690)	(807)	(1041)	(1227)	(1534)	(1724)

337

### Trends In Equipment Type, Age, Size And Use

Information on refinery heater type, age, size and use is not published. The reported reason for this lack of data is the proprietary and competitive nature of the industry.

Contact with manufacturers and refineries indicates that there is a general trend toward increased use of air preheat and forced draft burner designs. These trends are in the direction of improved efficiency through reduced excess air and reduced stack temperatures.

Most older heaters are designed for gas firing only. Newer designs are built for both gas and oil firing and many of the older heaters are being converted to fire oil. No evidence was found for any significant use of solid fuels.

Increased requirements for low sulfur fuel oil as a replacement for natural gas can be expected to cause a shift in refinery processes away from gasoline processes such as cracking and reforming and toward increased hydrogen desulfurization and demetallization.

### Total Number And Geographic Distribution

No published data on petroleum refinery heaters is available. The EPA NEDS file indicates about 2900 such heaters in the U.S. There were 256 petroleum refineries tabulated in the 1976 annual refinery survey (Ref. A-10.12-3). Table A-10.12-2 shows that most (32%) of these refineries are located in Texas and California. Table A-10.12-3 shows the distribution of refineries by crude capacity. The average refinery size is about 8000 m<sup>3</sup>/day (50,000 barrels/day). However, 52% of the refineries are very small, less than 4800 m<sup>3</sup>/SD (30,000 B/SD) and account for only 10% of total capacity. These refineries would be expected to have only a few heaters and subsequently low total emissions. There are 60 refineries in the range of 4900-23900 m<sup>3</sup>/SD (30,000-150,000 B/SD) accounting for 36% of total capacity. The 26 largest refineries account for 43% of total capacity. Excluding the small refineries (under 4800 m<sup>3</sup>/SD), the average refinery size is 17,610 m<sup>3</sup>/SD (111,000 B/SD).

TABLE A-10.12-2. GEOGRAPHIC DISTRIBUTION OF PETROLEUM REFINERIES  
IN THE UNITED STATES

State	Number of Refineries	Crude Capacity	
		Barrels per Stream Day	Cubic Meters per Stream Day
Alabama	3	53,000	8 425
Alaska	4	78,158	12 425
Arizona	1	4,211	669
Arkansas	4	62,425	9 924
California	35	1,993,503	316 908
Colorado	3	65,000	10 300
Delaware	1	150,000	23 845
Florida	1	6,000	954
Georgia	2	19,400	3 084
Hawaii	2	107,105	17 027
Illinois	11	1,232,958	196 000
Indiana	7	527,300	83 825
Kansas	11	468,940	74 548
Kentucky	3	169,500	26 945
Louisiana	19	1,827,031	290 444
Maryland	2	31,211	4 962
Michigan	6	151,395	24 067
Minnesota	3	223,905	35 594
Mississippi	5	346,842	55 138
Missouri	1	108,000	17 169
Montana	7	164,016	26 074
Nebraska	1	5,500	874
New Jersey	4	562,764	89 463
New Mexico	7	106,305	16 900
New York	2	114,500	18 200
North Dakota	3	60,163	9 564
Ohio	7	614,500	97 687
Oklahoma	12	559,719	88 979
Oregon	1	14,737	2 343
Pennsylvania	11	796,415	126 606
Tennessee	1	44,800	7 122
Texas	46	4,144,778	658 897
Utah	7	158,878	25 257
Virginia	1	55,000	8 743
Washington	7	383,105	60 902
West Virginia	3	20,200	3 211
Wisconsin	1	46,800	7 440
Wyoming	<u>11</u>	<u>194,557</u>	<u>30 929</u>
	256	15,687,321	2 493 821

TABLE A-10.12-3. DISTRIBUTION BY CAPACITY OF  
PETROLEUM REFINERIES IN THE UNITED STATES

Refinery Capacity Range		Number of Refineries	Percent of Total Number	Percent of Total Capacity
1000 B/SD*	m <sup>3</sup> /SD			
0 - 10	0 - 1.6	77	30	3
11 - 20	1.7 - 3.2	28	11	3
21 - 30	3.3 - 4.8	27	11	4
31 - 40	4.9 - 6.4	15	6	3
41 - 50	6.5 - 8.0	23	9	7
51 - 100	8.1 - 16.0	40	15	20
101 - 150	16.1 - 23.9	20	8	16
151 - 200	24.0 - 32.0	10	4	11
201 - 300	32.1 - 47.7	8	3	13
301 - 460	47.8 - 73.1	8	3	19
		256	100	100

\*B/SD = Barrels per stream day

Data gathered by KVB for inventory of NO<sub>x</sub> from stationary sources in the Los Angeles area (Ref. A-10.12-2) indicates that small refineries have 4 to 10 heaters but larger ones can have up to 60 heaters per refinery, and the average is about 26 heaters per refinery. Using these averages together with total refinery count data by capacity indicates that there are about 7000 refinery heaters in the United States.

Every refinery has at least one crude heater. This is usually the largest heater since all the refinery input is processed through this unit as the initial step in the refining process.

#### Limitations in Equipment Uses and Fuels

Refinery process heaters are designed to perform a specific refining process and therefore are not readily adapted to other uses. The only changes that may occur relate to the processing of crudes of differing source and properties.

Refinery heaters have been primarily fired with refinery gas but distillate and residual oils are now being used in greater amounts. The main fuel use limitation relates to the heat distribution to the heater tubes. A change from a gas fuel to a heavy oil fuel would increase the fraction of heat transferred by radiation. This could result in problems with internal tube coking or other overheating failures. Heaters designed for oil firing require larger radiant fireboxes, larger tube clearances and greater distances between the burners and tubes.

Convection sections on heaters designed for gas fuel have high density finned tubes that are subject to plugging when oil is used. Conversion to oil may require retubing with wider spaced fins. Sootblowing equipment must also be installed.

Firing of liquid fuels that contain sulfur, vanadium and sodium can present problems with heater tube corrosion in heaters designed for gas fuel. This limits use to light distillate oils or requires retubing with corrosion resistant tubes.

Firing heaters on oil requires about 20% excess air while gas fuel requires only 5-10% excess air. Therefore, natural draft heaters may have a lower heat input capacity on oil because of draft limitations. This can be resolved by conversion to forced draft burners.

Quantity And Geographic Distribution Of Fuels Used

Petroleum refineries generate many petroleum fractions that can be used as fuels in process heaters:

- . Liquified petroleum gas
- . Refinery process off gases
- . Naptha
- . Light Distillate
- . Atmospheric Residue
- . Vacuum Residue
- . Crude
- . Tar
- . Petroleum Coke

Information on the usage by refinery process heaters of each of the above was not found. However, Reference A-10.12-4 indicates the process heaters consume about 65% of refinery fuel input, with steam generation consuming 25% and electricity generation consuming the remaining 10%.

Reference A-10.12-5 indicates the following distribution of fuel use by type in petroleum refineries (Table A-10.12-4):

TABLE A-10.12-4. FUEL USE IN PETROLEUM REFINERIES

	<u>% of Total Fuel Use</u>	<u>Average Rate, TJ/day</u>
Crude Oil	0	0
Distillate Oil	1	78
Residual Oil	11	858
Liquified Petroleum Gas	1	78
Natural Gas	31	2418
Refinery Gas	40	3120
Petroleum Coke	16	1248
Coal	<u>0</u>	<u>0</u>
Total	100	7800

This data is based on a survey of 56 refineries constituting 92.9 of U.S. refinery capacity for July 1 - December 31, 1975. While process heaters consume about 65% of total fuel energy input most of this is believed to be refinery gas but specific use of each fuel type in process heaters alone is not available.

Geographic distribution of fuels consumed in petroleum refineries is given in Table A-10.1-1. The consumption rates are highest in Texas and California, the states with the largest number of refineries.

#### Air Pollutant Emissions

There are only a few published sources of refinery heater emissions. The Los Angeles Air Pollution Control District conducted a study in 1956 (Ref. A-10.12-6).

A study performed for the California Air Resources Board (Ref. A-10.12-2) provides data on  $\text{NO}_x$  emissions as shown in Figure A-10.12-1 for operation on refinery gas. This data was further correlated by heater characteristics as shown in Figure A-10.12-2. Conclusions from this correlation are that natural draft heaters with no air preheat have lowest  $\text{NO}_x$  emissions and emissions per unit heat input are not a function of size. The use of forced draft or air preheat increased  $\text{NO}_x$  and results in a size sensitivity.

The high variation in  $\text{NO}_x$  emissions per unit heat input for the various heater types and the lack of specific information on numbers of heaters by type result in a high uncertainty in any estimate of total  $\text{NO}_x$  emission in the U.S.

Emissions of  $\text{SO}_x$  from refinery heaters are a direct function of fuel sulfur content. Refinery gas sulfur content can vary widely depending on the effectiveness of sulfur removal operations. Data for Los Angeles area refinery gas indicates an average of about 140 mg of

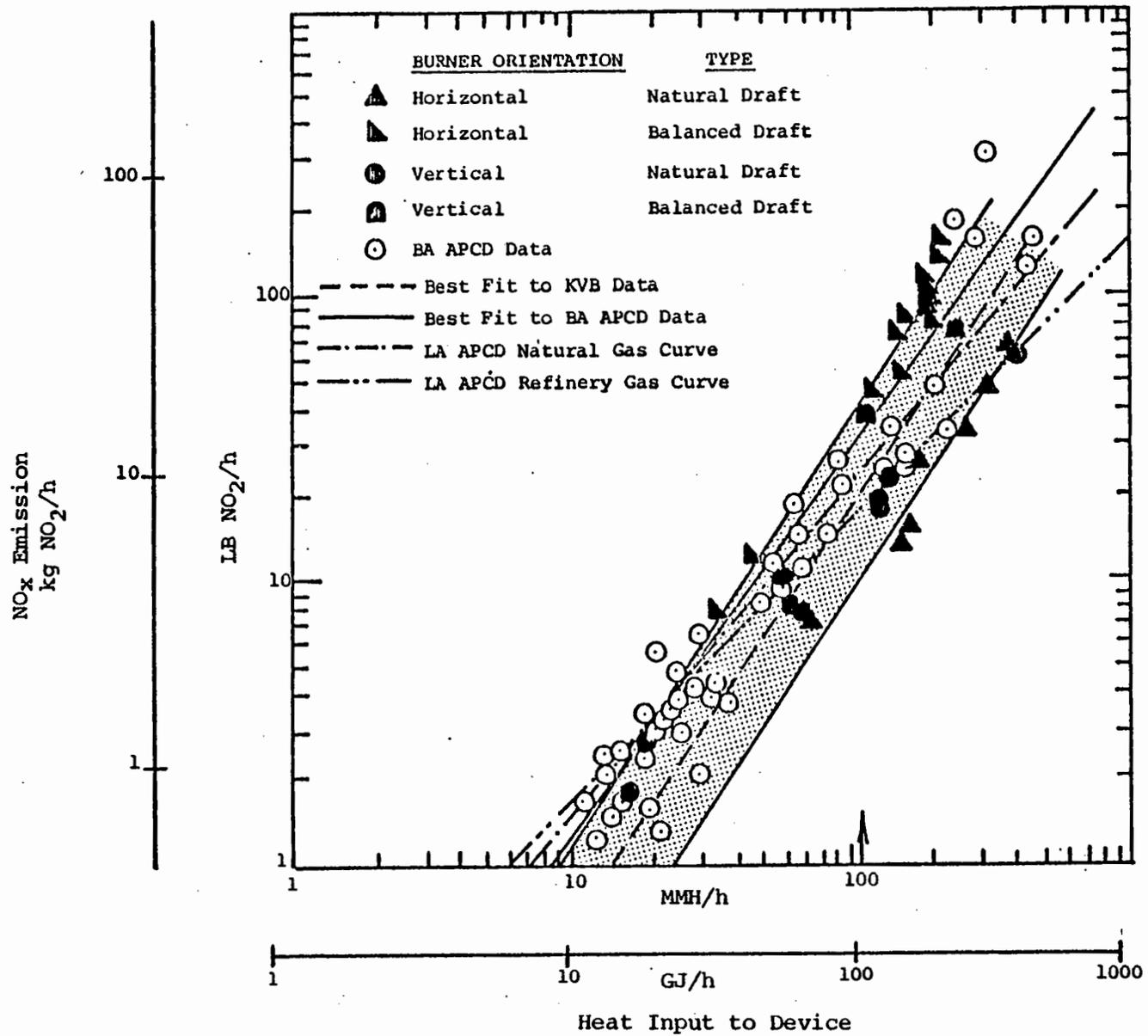


Figure A-10.12-1. Total emissions of nitrogen oxide for refinery heaters and boilers operating on refinery gas.

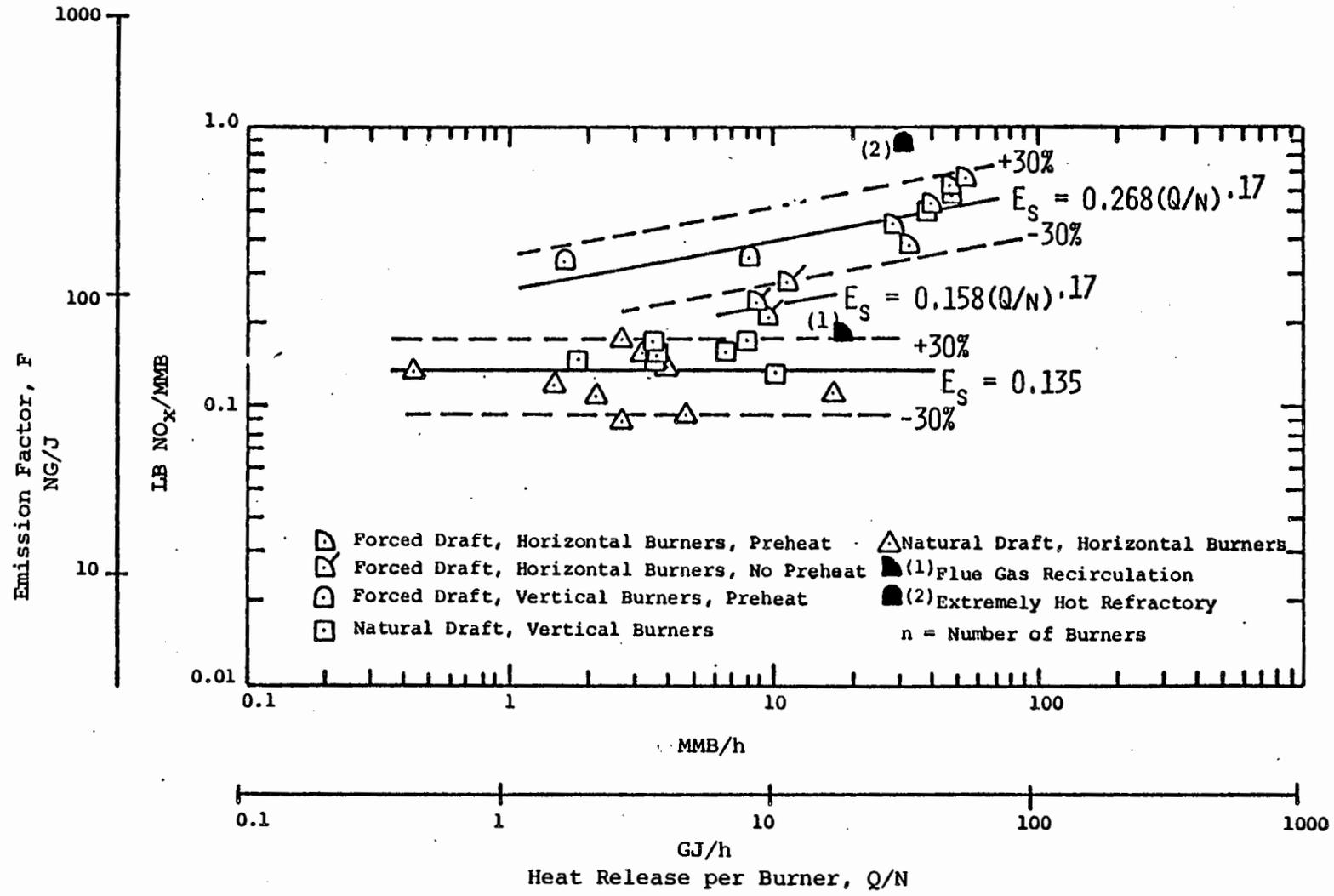


Figure A-10.12-2. Emission factor for heaters and boilers with refinery gas fuel.

H<sub>2</sub>S per cubic meter but variations from 3.0 to 5600 mg H<sub>2</sub>S/m<sup>3</sup> are observed. Sulfur content is regulated to 50 grains H<sub>2</sub>S per 100 cubic feet (1144 mg H<sub>2</sub>S/m<sup>3</sup>) in that area. No data are available for other areas of the U.S.

Table A-8-1 presents the estimated total emissions from refinery heaters in the United States based on NEDS data. The NO<sub>x</sub> emissions are significantly higher than for the other categories. However, the presence of only 2818 data records in NEDS relative to an estimated 7000 total heater count indicates that the NEDS emissions data may be low.

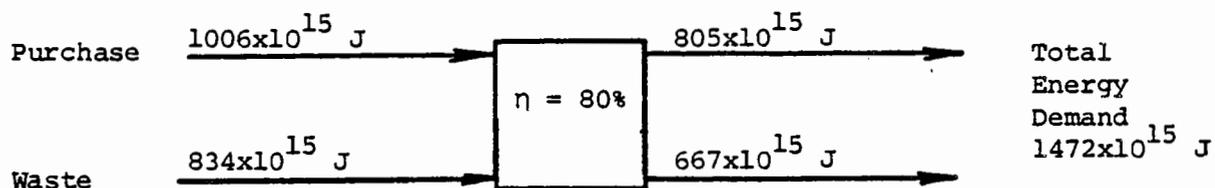
SECTION A-11.0

POTENTIAL FUEL SAVINGS IN PULP, PAPER AND PAPERBOARD INDUSTRY

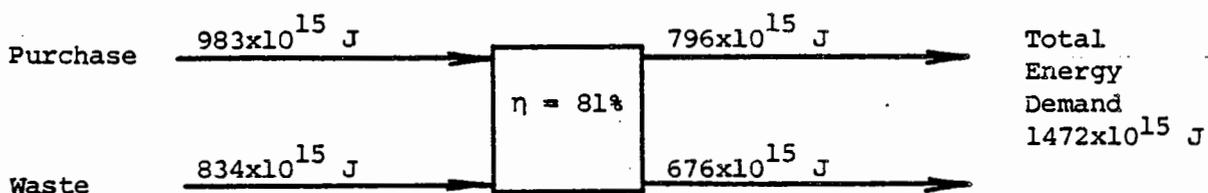
Reference A-11-1 indicates that the estimated 1975 fossil fuel energy utilization in this industry was:

Purchased:	$1006 \times 10^{15}$ J	(excluding steam and electricity)
+ Waste Recovery:	$834 \times 10^{15}$ J	
Consumed:	$1840 \times 10^{15}$ J	(excluding steam and electricity)

Consider that the purchased and waste recovery fuels were combusted in a "device" with an efficiency of 80%. The following situation would develop:



Now consider the situation if the "device" efficiency was increased to 81%. The waste energy input of  $834 \times 10^{15}$  J would still be used as it is available "free" and purchased fuel would be reduced to meet the same total energy demand.



Therefore, the amount of purchased fossil fuel has decreased by 2.3%, or a savings of  $23 \times 10^{15}$  J. This can be translated into a yearly savings in residual oil amounting to:

$$\frac{23 \times 10^{15} \text{ J}}{41.8 \times 10^9 \text{ J/m}^3} = 0.55 \times 10^6 \text{ m}^3 \text{ residual oil (} 3.46 \times 10^6 \text{ Barrels)}$$

or approximately 5% of the industries yearly purchase of residual oil.

## REFERENCES

- A-2-1 Bieser, C. O., "Identification And Classification of Combustion Source Equipment," Processes Research, Inc., No. EPA-R2-73-174, February 1973.
- A-2-2 Anon., "National Emissions Data System (NEDS) - Emissions By Source Classification Code," EPA computer file created on September 17, 1975.
- A-2-3 Anon., "Fuels And Electric Energy Consumed - 1972 Census Of Manufactures," U.S. Department of Commerce, Bureau of the Census, MC 72 (SR)-6, July 1973.
- A-4-1 Anon., "U.S. Pulp, Paper And Paperboard Industry Estimated Fuel And Energy Use (For) First Six Months - 1975," American Paper Institute, Inc.
- A-7-1 Ketels, P. A., et al., "A Survey of Emissions Control and Combustion Equipment Data in Industrial Process Heating," Institute of Gas Technology, EPA-600/2-76-022, NTIS No. PB 263-453/AS, June 1976.
- A-10.2-1 Anon., "Energy Conservation Potential In The Cement Industry," prepared by Portland Cement Association, FEA Conservation Paper No. 26, June 1975.
- A-10.2-2 Anon., "Summary Of 1975 Energy Report - U.S. Cement Industry," Portland Cement Association, March 1, 1976.
- A-10.2-3 Anon., "U.S. Portland Cement Industry: Plant Information Summary," Portland Cement Association, December 31, 1975.
- A-10.3-1 Schorr, J. R., et al., "Final Report On Industrial Energy Study To Federal Energy Administration (Sponsor) And Department Of Commerce (Project Monitor)," Battelle Columbus Laboratories, Report No. FEA/B-75-385, December 1, 1974.
- A-10.3-2 Anon., "American Glass Review - 1975 Glass Factory Directory Issue," February 28, 1975.
- A-10.4-1 Anon., Steam - Its Generation And Use, 38th edition, The Babcock and Wilcox Co., 1972.
- A-10.4-2 Private communication from B. N. Thorson (Babcock and Wilcox) to S. S. Cherry (KVB), April 13, 1976.
- A-10.4-3 Private communication from A. H. F. Barlow (Combustion Engineering) to S. S. Cherry (KVB), April 28, 1976.

- A-10.5-1 de Lorenzi, O. (Editor), Combustion Engineering, 1st edition, Combustion Engineering, Inc., 1955.
- A-10.6-1 McGannon, H. E. (Editor), The Making, Shaping And Treating of Steel, eighth edition, United States Steel Corp., August 1964.
- A-10.6-2 Private communication between J. A. van Ackeren (Koppers Co., Inc.) and S. S. Cherry (KVB), April 1976.
- A-10.6-3 Allen, K. C., Directory Of Iron And Steel Works Of The United States and Canada, 33rd edition, American Iron and Steel Institute, July 1974.
- A-10.6-4 Anon., "Blast Furnaces, Steel Works, And Rolling And Finishing Mills - SIC Industry Group 331 - 1972 Census of Manufactures," U.S. Department of Commerce, Bureau of the Census, MC 72(2)-33A, February 1975.
- A-10.9-1 Private communication between Mr. Frank Vereecke (Surface Combustion) and S. S. Cherry (KVB), April 28, 1976.
- A-10.9-2 Anon., "Compilation Of Air Pollutant Emission Factors - Second Edition," EPA Publication No. AP-42, March 1975.
- A-10.10-1 "Diesel & Gas Turbine Progress," Vol. 42, No. 4, page 49, April 1976.
- A-10.10-2 Private communication between Mr. S. Youngblood (Aerotherm Div. of Acurex) and S. S. Cherry (KVB), May 12, 1976.
- A-10.10-3 Taylor, C. F., and Taylor, E. S., The Internal Combustion Engine, second edition, International Textbook Co., p. 176, 1970.
- A-10.11-1 Sawyer's Gas Turbine Catalog - 1975 Edition, published by Gas Turbine Publications, Inc., Stamford, Conn.
- A-10.11-2 Roessler, W. U., Muraszew, A., and Kopa, R. D., "Assessment Of The Applicability Of Automotive Emission Control Technology To Stationary Engines," Aerospace Corp., Report no. EPA-650/2-74-051, July 1974.
- A-10.11-3 Sawyer's Gas Turbine Catalog - 1974 Edition, published by Gas Turbine Publications, Inc. Stamford, Conn.

- A-10.11-4 Private communication between Paul Canty (Solar Div. International Harvester) and S. S. Cherry (KVB), May 14, 1976.
- A-10.11-5 Private communication between Mr. Warren Will (FPC) and S. S. Cherry (KVB), May 20, 1976.
- A-10.11-6 "Electrical World," a McGraw-Hill publication, March 15, 1976.
- A-10.11-7 Private communication between Bill Hayes (Electrical World, McGraw-Hill, Inc.) and S. S. Cherry (KVB), May 20, 1976.
- A-10.12-1 Nelson, W. L., Petroleum Refinery Engineering, McGraw-Hill Book Co., Fourth Edition, 1969.
- A-10.12-2 Bartz, D. R., et al., "Control of Oxides of Nitrogen from Stationary Sources in the South Coast Air Basin of California," NTIS PB 237 688/7WP, Sept. 1974.
- A-10.12-3 Cantrell, A., "Annual Refining Survey," Oil and Gas Journal, pp. 124, March 29, 1976.
- A-10.12-4 Grace, E. C., "Achievements to Date in Using Heat Transfer Equipment to Conserve Energy," API preprint 03-76, May 11, 1976.
- A-10.12-5 Federal Energy Administration, Office of Industrial Programs, "Voluntary Industrial Energy Conservation, Progress Report 3," April 1976.
- A-10.12-6 Devorkin, H. and Steigerwald, B. J., "Emissions of Air Contaminants From Boilers and Process Heaters," Joint District, Federal, and State Project for the Evaluation of Refinery Emissions, Report No. 7, June 1958, (Published by Los Angeles Air Pollution Control District).
- A-11-1 Anon., "U.S. Pulp, Paper And Paperboard Industry Estimated Fuel And Energy Use (For) First Six Months - 1975," American Paper Institute, Inc.

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## APPENDIX B

### GASEOUS AND PARTICULATE EMISSIONS TEST METHODS AND INSTRUMENTATION

#### B.1.0 SAMPLE COLLECTION AND ANALYSIS

The emission measurements were made with instrumentation carried in a mobile laboratory trailer. A plan view of this laboratory trailer is shown in Figure B-1. Exterior and interior views are shown in Figure B-2. The gaseous species measurements, except sulfur trioxide, are made with analyzers maintained in the mobile laboratory, while the particulate, smoke spot and sulfur oxides measurements are conducted with portable analyzers carried to the sample port. The weighing and titration operations which are part of the latter analyses are conducted in or near the laboratory trailer. The trailer also includes a work area which can be used for in-field laboratory analyses, meetings and day-to-day review of the test plans and results.

The emission measurement instrumentation used on the project is summarized in Table B-1.

#### B.1.1 Gas Sampling and Conditioning System

A flow schematic of the flue gas sampling and analyzing system is shown in Figure B-3. This system is mounted on and behind the control console. Cylinders of certified calibration gas are also located in this area. The sampling system uses three pumps to continuously draw flue gas from the boiler into the laboratory. A high capacity positive displacement diaphragm pump is used to draw a high volume of flue gas into the unheated portion of the system to provide adequate system response. The pump pulls from a manifold connected to 24 unheated sample lines. Selector valves allow composites of up to 12 points to be sampled at one time. The probes are connected to the sample manifold with 0.95 cm (3/8") nylon line. Stainless steel quick-disconnect couplings are provided to facilitate the connection between the sample lines and the instrumentation laboratory. The sample from each line then passes through a glass

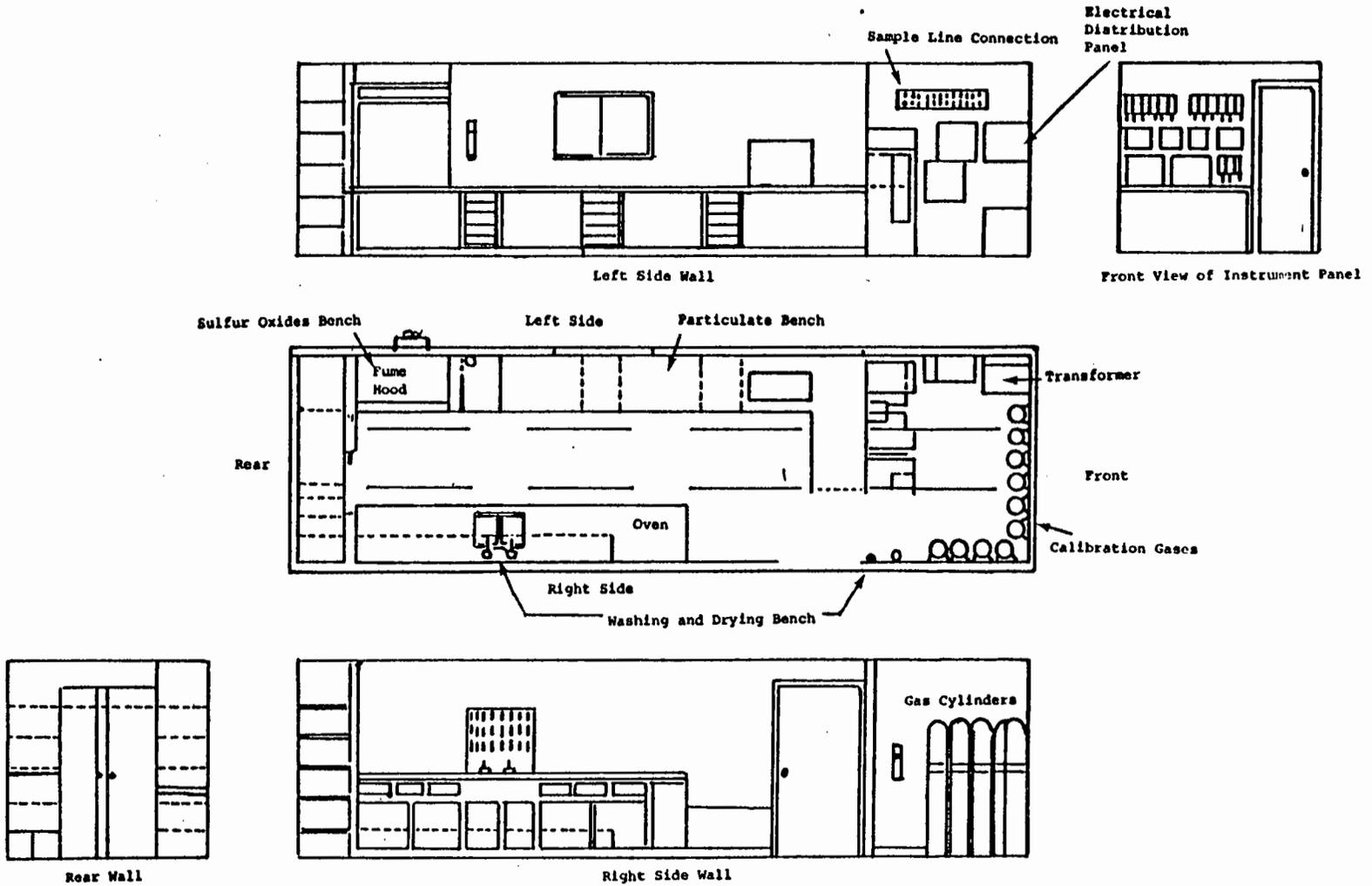


Figure B-1. Instrumentation trailer floor plan and side wall elevation.

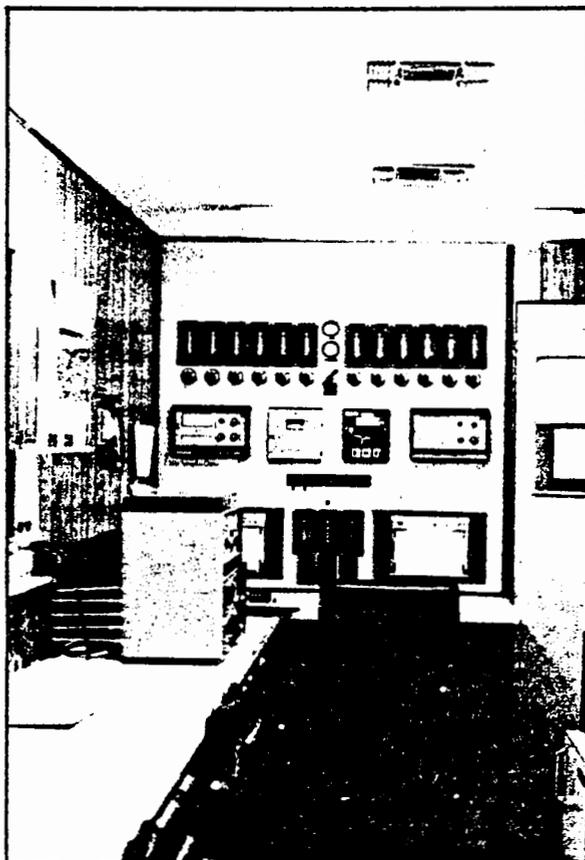


Figure B-2. Exterior and interior views of mobile air pollution reduction laboratory. This laboratory has been used in previous EPA-sponsored field-test programs.

TABLE B-1. SUMMARY OF EMISSION MEASUREMENT INSTRUMENTATION

Emission Parameter	Symbol	Measurement Method	Equipment Manufacturer
Nitric oxide	NO	Chemiluminescent	Thermo Electron
Oxides of nitrogen	NO <sub>x</sub>	Chemiluminescent	Thermo Electron
Carbon monoxide	CO	Nondispersive infrared	Beckman
Carbon dioxide	CO <sub>2</sub>	Nondispersive infrared	Beckman
Oxygen	O <sub>2</sub>	Polarographic	Teledyne
Hydrocarbons	HC	Flame ionization	Beckman
Sulfur dioxide	SO <sub>2</sub>	UV spectrometry	Du Pont
Sulfur dioxide Sulfur trioxide	SO <sub>2</sub> SO <sub>3</sub>	Absorption/titration	Shell-Emeryville Absorption train
Total particulate matter	PM	<u>EPA Std. Method 5</u>	Joy Mfg. Co.
Particulate size distribution		Cascade impactor, electro-balance	Anderson, Brink, Cahn
Smoke spot		Field service type smoke tester	
Opacity		EPA Std. Method 9	

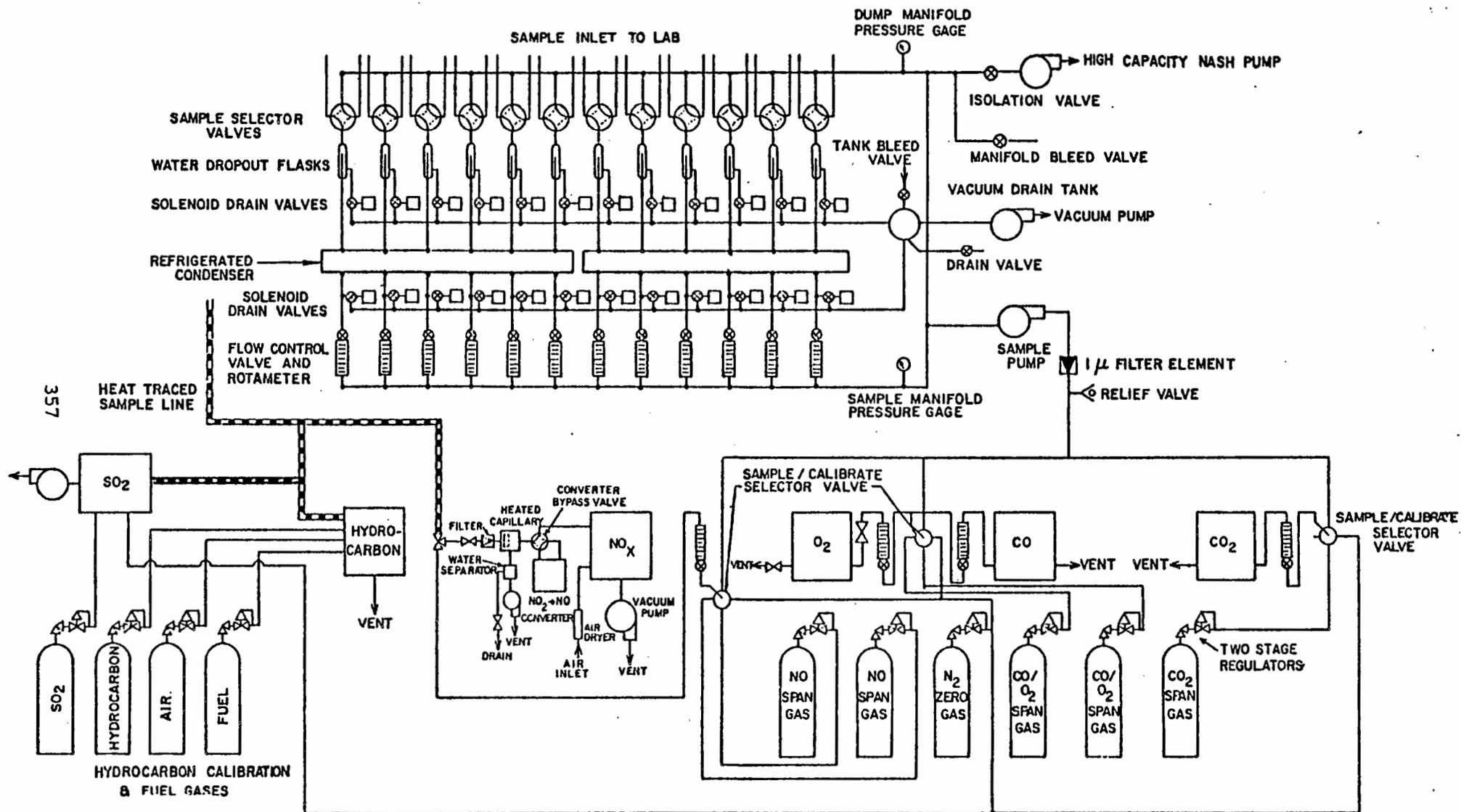


Figure B-3. Flue gas sampling and analyzing system.

bubbler to remove water condensate. Drain valves are provided for emptying the traps. A positive displacement diaphragm sample pump draws a small portion of the unheated sample gas from the high volume line, and transfers it through a refrigerated condenser to reduce the dew point to 275 K (35 °F), a rotameter with flow control valve, the sample pump, and a 1 micron filter, as it passes to instrumentation for measurement of O<sub>2</sub>, NO, CO, and CO<sub>2</sub>. Flow to the individual analyzers is measured and controlled with rotameters and flow control valves. Excess sample is vented to the atmosphere.

Since heavy hydrocarbons may be condensable, and NO<sub>2</sub> and SO<sub>2</sub> are soluble in water, a heated sample line must be used to obtain samples for the analysis of these components. For this reason a separate, electrically-heated, sample line is used to bring the sample into the laboratory for analysis. The line is 0.95 cm (3/8 inch) stainless steel line, electrically traced and thermally insulated. A heated metal bellows pump is used to provide sample to both the hydrocarbon, NO<sub>x</sub>, and SO<sub>2</sub> analyzers.

#### B.1.2 INSTRUMENTAL CONTINUOUS MEASUREMENTS

The laboratory trailer is equipped with analytical instruments to continuously measure concentrations of NO, NO<sub>2</sub>, CO, CO<sub>2</sub>, O<sub>2</sub>, SO<sub>2</sub>, and hydrocarbons. All of the continuous monitoring instruments and sample handling system are mounted in the self-contained mobile laboratory. The entire system requires only connection to on-site water, power, and sampling lines to become fully operational. The instruments themselves are shock mounted on a metal console panel. The sample flow control measurement and selection, together with instrument calibration, are all performed from the console face. Three-pen recorders provide a continuous permanent record of the data taken. The sample gas is delivered to the analyzers at the proper condition and flow rate through the sampling and conditioning system described in the previous section. The following sections below describe the analytical instrumentation.

#### B.1.2.1 Nitric Oxide (NO) and Total Nitrogen Oxides (NO<sub>x</sub>)

Both the total nitrogen oxides (NO<sub>x</sub>) and nitric oxide (NO) concentrations are measured from a sample gas obtained using a heated sample line at 394 K (250 °F). In addition, the nitric oxide concentrations are measured sequentially from samples obtained using the unheated sample line that is connected to the same analyzer in the laboratory trailer. In the latter case, water is first removed from the sample gas by a drop-out bottle and refrigeration unit. The analytical instrument used for these measurements is the Thermo Electron Model 10A chemiluminescent gas analyzer.

For NO analyses, the sample gas is passed directly into the reaction chamber where a surplus of ozone is maintained. The reaction between the NO and the ozone produces light energy proportional to the NO concentration which is detected with a photomultiplier and converted to an electrical signal. Air for the ozonator is drawn from ambient through an air dryer and a 10-micron filter element. Flow control for the instrument is accomplished with a small bellows pump mounted on the vent of the instrument downstream of a separator which insures that no water collects in the pump.

The chemiluminescent reaction with ozone is specific for NO. To detect NO<sub>2</sub>, a thermal converter has been designed to dissociate the NO<sub>2</sub> to NO by the bi-molecular reaction:  $2 \text{NO}_2 \xrightarrow{\Delta} 2 \text{NO} + \text{O}_2$ . A Model 700 thermal converter is used in conjunction with the chemiluminescent gas analyzer as shown in Figure B-4. The converter is a coil of resistance-heated stainless steel tubing drives the NO<sub>2</sub>/NO ratio to its chemical equilibrium value at the converter temperature and pressure. The unit is designed to operate at 923 K (1200 °F) and 1.3 kPa (10 torr). For these conditions and typical stack gas O<sub>2</sub> concentrations, the equilibrium NO<sub>2</sub> concentration is 0.2% of the total NO<sub>x</sub> concentration. Therefore, when a gas sample containing NO<sub>2</sub> is passed through the converter, essentially all NO<sub>2</sub> would be converted to NO. The resulting total NO is then measured using the chemiluminescent analyzer and the difference between the actual NO and the "total NO" would be the sample NO<sub>2</sub> concentration. The "total NO" is interpreted as NO<sub>x</sub>.

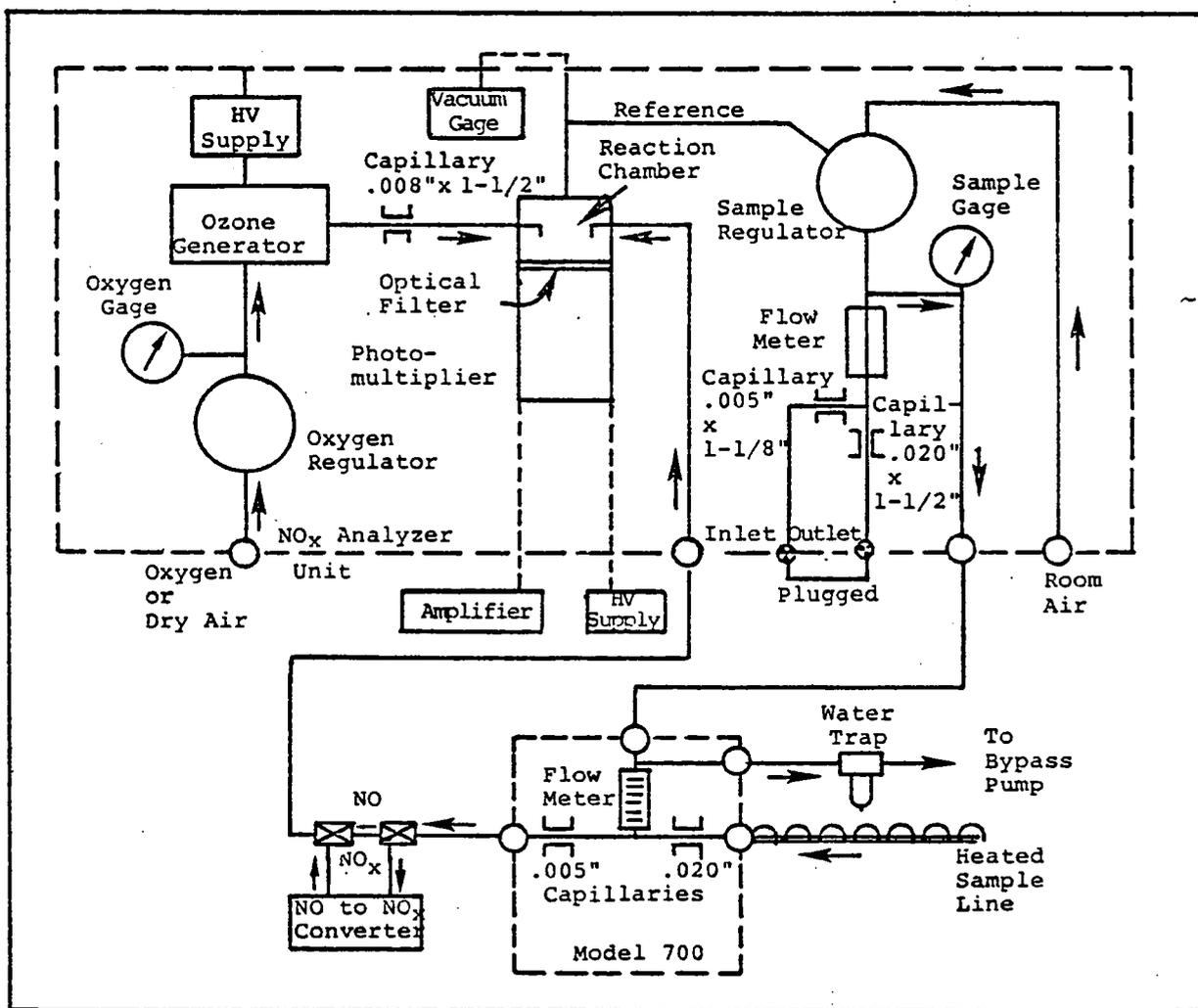


Figure B-4. Schematic of  $\text{NO}_x/\text{NO}$  chemiluminescent analysis system.

NO<sub>2</sub> may react upon contact with H<sub>2</sub>O (liquid phase) to form HNO<sub>3</sub> (nitric acid). Under field test conditions, the exhaust gas may contain significant H<sub>2</sub>O (depending upon the process and the ambient meteorological conditions) and it is necessary to convert the NO<sub>2</sub> to NO before the H<sub>2</sub>O is allowed to condense in the sampling system. By using the heated sample line and the Thermo Electron Model 700 heated NO<sub>x</sub> module, NO<sub>2</sub> concentrations will effectively be measured. In reference to Figure B-4, the sample is maintained above the H<sub>2</sub>O dew point up to and through the 127 μm (0.005 in.) capillary in the heated module. Downstream of this capillary, the flow network is maintained at 1.3 kPa (10 torr), where the partial pressure of the H<sub>2</sub>O in the sample is sufficiently low to prevent any condensation at ambient temperature.

When using the heated system, NO, NO<sub>2</sub>, and NO<sub>x</sub> are measured on a wet basis. When not using the heated system, a condenser is placed upstream of the analyzer and NO is measured on a dry basis.

#### Specifications

Accuracy: 1% of full scale

Span stability: ± 1% of full scale in 24 hours

Zero stability: ± 1 ppm in 24 hours

Power requirements: 115 ± 10V, 60 Hz, 1000 watts

Response: 90% of full scale in 1 sec (NO<sub>x</sub> mode);  
0.7 sec (NO mode)

Output: 4-20 ma

Sensitivity: 0.5 ppm

Linearity: ± 1% of full scale

Vacuum detector operation

Range: 2.5, 10, 25, 100, 250, 1000, 2500, 10,000 ppm  
full scale

#### B.1.2.2 Carbon Monoxide and Carbon Dioxide (CO and CO<sub>2</sub>)

Carbon monoxide and carbon dioxide concentrations are measured using Beckman Model 864 and 865 short pathlength nondispersive infrared analyzers (see Figure B-5). These instruments measure the differential in infrared

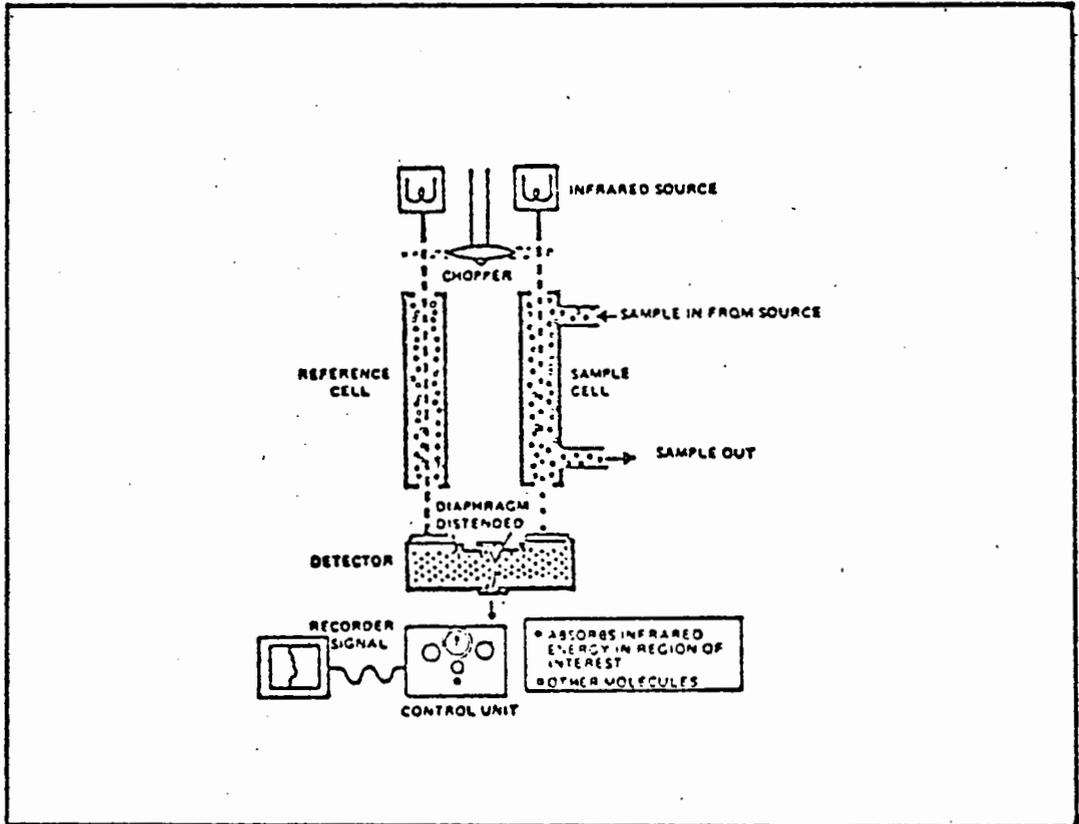


Figure B-5. Schematic of NDIR analyzer.

energy absorbed from energy beams passed through a reference cell (containing a gas selected to have minimal absorption of infrared energy in the wavelength absorbed by the gas component of interest) and a sample cell through which the sample gas flows continuously. The differential absorption appears as a reading on a scale of 0% to 100% and is then related to the concentration of the specie of interest by calibration curves supplied with the instrument. A linearizer is supplied with each analyzer to provide a linear output over the range of interest. The operating ranges for the CO analyzer are 0-100 and 0-2000 ppm, while the ranges for the CO<sub>2</sub> analyzer are 0-5% and 0-20%.

#### Specifications

Span stability:  $\pm 1\%$  of full scale in 24 hours

Zero stability:  $\pm 1$  ppm in 24 hours

Ambient temperature range: 273 to 322 K (32 °F to 120 °F)

Line voltage: 115  $\pm$  15V rms

Response: 90% of full scale in 0.5 or 2.5 sec

Linearity: Linearizer board installed for one range

Precision:  $\pm 1\%$  of full scale

Output: 4-20 ma

#### B.1.2.3 Oxygen (O<sub>2</sub>)

A Teledyne Model 326A oxygen analyzer is used to automatically and continuously measure the oxygen content of the flue gas sample. The analyzer utilizes a micro-fuel cell which is specific for oxygen, has an absolute zero, and produces a linear output from zero through 25% oxygen. The micro-fuel cell is a sealed electrochemical transducer with no electrolyte to change or electrodes to clean. Oxygen in the flue gas diffuses through a Teflon membrane and is reduced on the surface of the cathode. A corresponding oxidation occurs at the anode internally and an electric current is produced that is proportional to the concentration of oxygen. This current is measured and conditioned by the instrument's electronic circuitry to give an output in percent O<sub>2</sub> by volume for operating ranges of 0% to 5%, 0% to 10%, and 0% to 25%.

### Specifications

Precision: + 1% of full scale

Response: 90% in less than 40 sec

Sensitivity: 1% of low range

Linearity: + 1% of full scale

Ambient temperature range: 273 K to 325 K (32 to 125 °F)

Fuel cell life expectancy: 40,000+hrs

Power requirement: 115 VAC, 50-60 Hz, 100 watts

Output: 4-20 ma

#### B.1.2.4 Total Hydrocarbons (HC)

Hydrocarbon emissions are measured using a Backman Model 402 high-temperature hydrocarbon analyzer. The analyzer utilizes the flame ionization method of detection which is a proven technique for a wide range of concentrations (0.1 to 120,000 ppm). A flow schematic of the analyzer is presented in Figure B-6. The sensor is a burner where a regulated flow of sample gas passes through a flame sustained by regulated flows of air and a premixed hydrogen/nitrogen fuel gas. Within the flame the hydrocarbon components of the sample stream undergo a complex ionization that produces electrons and positive ions. Polarized electrodes collect these ions, causing current to flow through electronic measuring circuitry. Current flow is proportional to the rate at which carbon atoms enter the burner.

The analysis occurs in a temperature controlled oven. The sample is extracted from the stack with a stainless steel probe which has been thermally treated and purged to eliminate any hydrocarbons existing in the probe itself. An insulated, heat traced teflon line is used to transfer the sample to the analyzer. The entire heated network is maintained at a temperature to prevent condensation of heavier hydrocarbons.

The flame ionization detector is calibrated with methane and the total hydrocarbon concentration is reported as the methane equivalent. FID's do not respond equally to all hydrocarbons but generally provide a measure of the carbon - hydrogen bonds present in the molecule. The FID does not detect pure carbon or hydrogen.

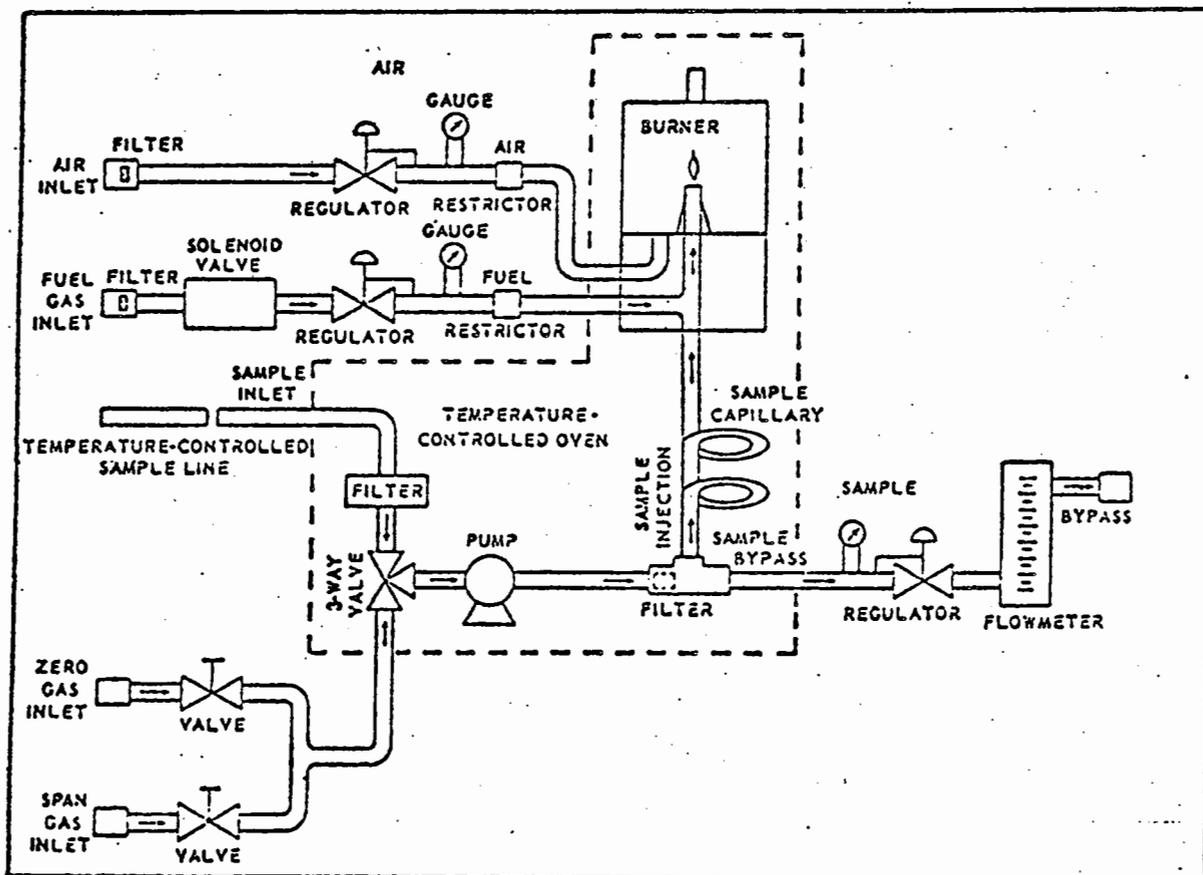


Figure B-6. Flow schematic of hydrocarbon analyzer (FID).

### Specifications

Full scale sensitivity: adjustable from 5 ppm CH<sub>4</sub> to 10% CH<sub>4</sub>

Ranges: Range multiplier switch has 8 positions: X1, X5, X10, X50, X100, X500, X1000, and X5000. In addition, span control provides continuously variable adjustment within a dynamic range of 10:1

Response time: 90% full scale in 0.5 sec

Precision: + 1% of full scale

Electronic stability: + 1% of full scale per 24 hours with ambient temperature change of less than 10 °F

Reproducibility: + 1% of full scale for successive identical samples

Analysis temperature: ambient

Ambient temperature: 273 K to 317 K (32 °F to 110 °F)

Output: 4-20 ma

Air requirements: 250 to 400 cc/min of clean, hydrocarbon-free air, supplied at  $2.07 \times 10^5$  to  $1.38 \times 10^6$  n/m<sup>2</sup> (30 to 200 psig)

Fuel gas requirements: 75 to 80 cc/min of fuel consisting of 100% hydrogen supplied at  $2.07 \times 10^5$  to  $1.38 \times 10^6$  n/m<sup>2</sup> (30 to 200 psig)

Electric power requirements: 120 V, 60 Hz

Automatic flame indication and fuel shut-off valve

#### B.1.2.5 Sulfur Dioxide (SO<sub>2</sub>)

A Dupont Model 400 photometric analyzer is used for measuring SO<sub>2</sub>. This analyzer measures the difference in absorption of two distinct wavelengths (ultraviolet) by the sample. The radiation from a selected light source passes through the sample and then into the photometer unit where the radiation is split by a semi-transparent mirror into two beams. One beam is directed to a phototube through a filter which removes all wavelengths except the "measuring" wavelength, which is strongly absorbed by the constituent in the sample. A second beam falls on a reference phototube, after passing through an optical filter which transmits only the

"reference" wavelength. The latter is absorbed only weakly, or not at all, by the constituent in the sample cell. The phototubes translate these intensities to proportional electric currents in the amplifier. In the amplifier, full correction is made for the logarithmic relationships between the ratio of the intensities and concentration or thickness (in accordance with Beer's Law). The output is therefore linearly proportional, at all times, to the concentration and thickness of the sample. The instrument has a lower detection limit of 2 ppm and full scale ranges of 0-500 and 0-5000 ppm.

#### Specifications

Noise: Less than 1/4%

Drift: Less than 1% full scale in 24 hours

Accuracy: ( $\pm 1\%$  of analyzer reading) + ( $\pm 1/4\%$  of full scale range)

Sample cell: 304 stainless steel, quartz windows

Flow rate: 6 CFH

Light source: Either mercury vapor, tungsten, or "Osram" discharge type lamps

Power rating: 500 watts maximum, 115 V, 60 Hz

Reproducibility: 1/4% of scale

Electronic response: 90% in 1 sec

Sample temperature: 378 K (220 °F)

Output: 4-20 ma d.c.

### B.1.3 INTEGRATED AND SEMI-CONTINUOUS MEASUREMENTS

#### B.1.3.1 Oxides of Sulfur (SO<sub>2</sub> and SO<sub>3</sub>)

The Absorption-Titration Method for the Determination of Oxides of Sulfur in Stack Gases published by the Shell Development Company (62/69) will be used for SO<sub>2</sub> and SO<sub>3</sub> measurements (see Figures B-7 and B-8). KVB has utilized this procedure on a number of previous test programs.

The gas sample is withdrawn from the flue by a single probe made of 5mm ID Vycor glass tubing inserted approximately one-third to one-half way into the duct. The inlet end of the probe has a section 50mm long by 15mm OD to hold a quartz wool filter to prevent particulate matter from being drawn into the sampling train. The entire probe is maintained above the dew point of the flue gas during sampling (minimum temperature of 260°C). The portion of the probe extending out of the stack is insulated to prevent it from cooling to the point where SO<sub>3</sub> condenses as sulfuric acid. Provision is made to heat the exposed probe if necessary to prevent condensation. Insulating putty is used to provide a seal between the exposed end of the glass probe and support tube. The glass probe terminates in a Vycor glass ball joint to provide a gas tight connection to the absorber train.

The sample gas is passed through an absorption train consisting of two lamp sulfur absorbers and a spray trap as described by ASTM D1266, and a secondary absorber as described by ASTM D1551. All joints are ground glass or glass butt joints held together by vinyl tubing. All glass-vinyl joints are made gas tight by using metal hose clamps. An ice bath is provided for the first SO<sub>3</sub> absorber to cool the incoming gas and prevent excessive evaporation of the absorbing solutions. A trap with an ice bath is inserted between the train and the sample pump to prevent any liquid from reaching the pump or test meter. The sample is drawn with a total transfer diaphragm pump. A dry gas test meter is used to measure the sample volume to  $0.28 \times 10^{-4} \text{ m}^3$  (0.001 cubic feet).

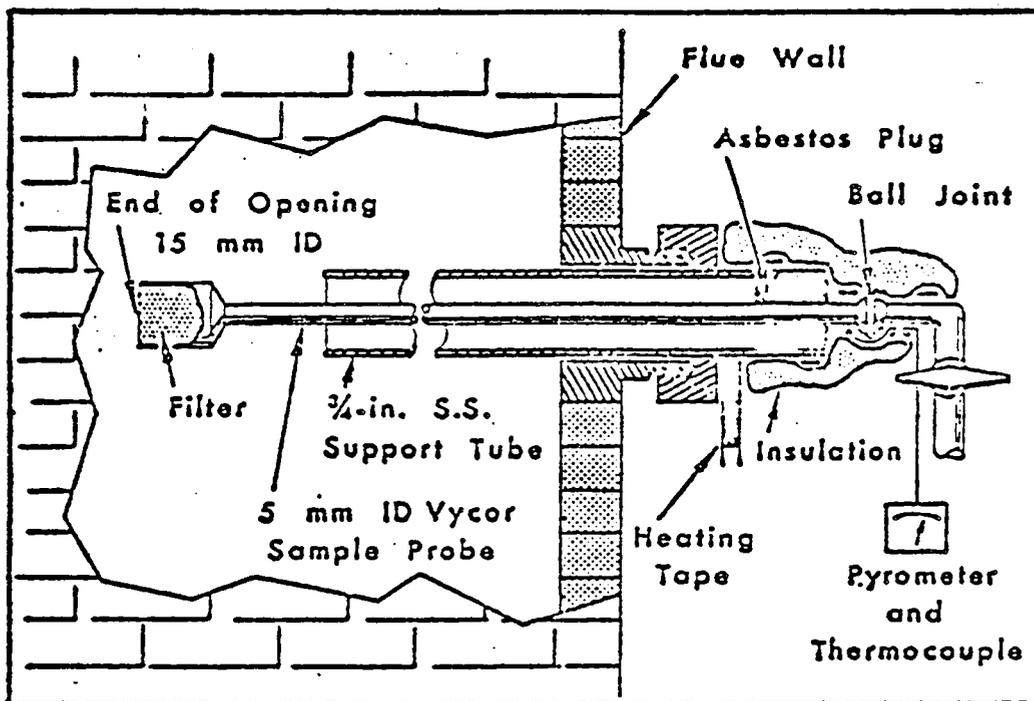


Figure B-7.  $\text{SO}_2/\text{SO}_3$  Sampling Probe Configuration.

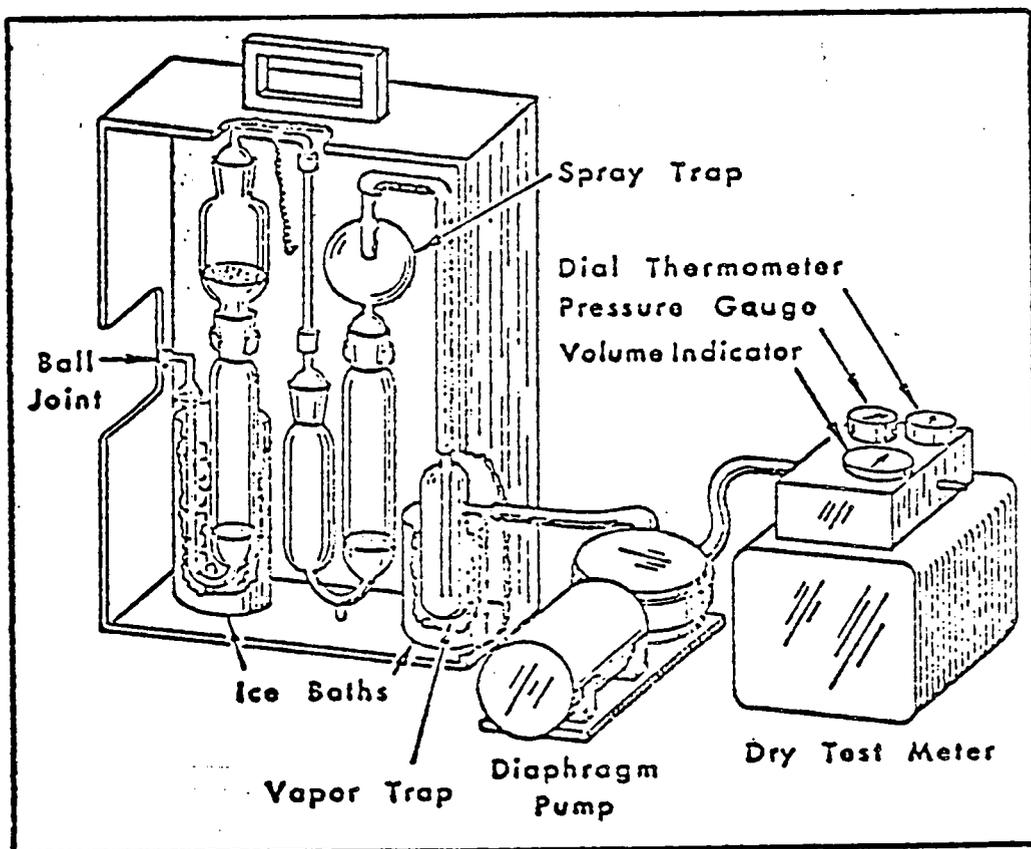


Figure B-8.  $\text{SO}_2/\text{SO}_3$  Absorption Train.

The result of passing the sample through the absorber train is to separate and then convert both  $\text{SO}_3$  and  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$  (sulfuric acid). The first two absorbers contain 80% (by volume) 2-propanol (isopropyl alcohol) in water. The  $\text{SO}_3$  in the sample is absorbed into the solution and upon contact with the solution, the  $\text{SO}_3$  is converted to  $\text{H}_2\text{SO}_4$  (sulfuric acid). Some of the sulfur trioxide is removed in the first absorber. The remainder passes through as sulfuric acid mist, is completely removed by the secondary absorber mounted above the first. Most of the  $\text{SO}_2$  passes through the first two absorbers and is oxidized to  $\text{H}_2\text{SO}_4$  by 3% hydrogen peroxide with water in the third absorber. The isopropyl alcohol in the first two absorbers prevents the  $\text{SO}_2$  from oxidizing to  $\text{SO}_3$ . After the sample is taken, the absorber train is purged with nitrogen. The nitrogen carries any  $\text{SO}_2$  which was dissolved in the first two absorbers over to the third absorber. This procedure assures complete separation of  $\text{SO}_3$  and  $\text{SO}_2$ . The  $\text{H}_2\text{SO}_4$  that is produced is titrated in both cases with  $\text{Pb}(\text{ClO}_4)_2$  (lead perchlorate) to a Sulfonazo III (3,6 bis (orthosulfophenylazo) 4, 5 dihydroxy 2, 7 (naphthelene disulfonic acid) end point.

The concentration of the  $\text{Pb}(\text{ClO}_4)_2$  titrant must be accurately known. This concentration is determined by titrating it against a standardized  $\text{H}_2\text{SO}_4$  solution to a Sulfonazo III indicator end point. The  $\text{H}_2\text{SO}_4$  solution is standardized by titrating it against a standard NaOH (sodium hydroxide) solution to a phenolphthalein end point. The standard NaOH solution is obtained commercially.

$\text{SO}_2$  and  $\text{SO}_3$  concentrations are calculated using the following equation:

$$\text{SO}_x \text{ (ppm by volume)} = \frac{(A-B) \times (N) \times (F) \times (460 + T) \times (24)}{V (P + p)}$$

where:

A = ml of lead perchlorate solution used for titration of the SO<sub>2</sub> or SO<sub>3</sub> samples

B = ml used for blank

N = normality of lead perchlorate titrant

F = dilution factor

T = average temperature of dry test meter, degrees Fahrenheit

V = uncorrected volume of gas sample, cubic feet

P = barometric pressure, inches of mercury

p = average pressure in the dry test meter, inches of mercury

The SO<sub>x</sub> is reported on a dry basis.

#### B.1.3.2 Particulate Matter Total Mass Concentration

Particulate matter is collected by filtration and wet impingement in accordance with US-EPA Method No. 5. Nomograph techniques are utilized to select the proper nozzle size and to set the isokinetic flow rates.

Gas samples for particulate sampling can be taken from the same sample port as those for gas analysis and passed through the Joy Manufacturing Company Portable Effluent Sampler. This system, which meets the EPA design specifications for Test Method 5, Determination of Particulate Emissions from Stationary Sources (Federal Register, Volume 36, No. 27, page 24888, December 24, 1971, and revisions thereof) is used to perform both the initial velocity traverse and the particulate sample collection.

Dry particulates are collected in the heated case that may contain a cyclone to separate particles larger than 5 μm and a 125 mm glass-fiber filter to retain particles as small as 0.3 μm. Condensible particulates are collected in four Greenburg-Smith impingers immersed in a chilled water bath.

The sampling probe is positioned through an exhaust port and attached to the sampling box. The probe consists of a sampling nozzle, heated probe, gaseous probe, thermocouple, and pitot tube. The ball joint from the heated probe connects to the cyclone and glass filter holder assembly. These assemblies are positioned in the heated sampling box which is maintained at 433 K (320 °F) above the predicted SO<sub>3</sub> dew point, in order to eliminate condensation. The sample then passes from the heated section to four Greenburg-Smith impingers immersed in an ice bath. Only the second impinger has the original tip, the other three have had the tip removed to decrease the pressure drop through them. The first and second impingers are filled with 250 and 150 milliliters of distilled/deionized water, respectively. The third impinger is left dry. The fourth impinger is filled with approximately 200 grams of indicating silica gel to remove entrained water. The use of silica gel assures that a dry sample is delivered to the meter box. After sampling, the spent silica gel is discarded and not used for any further analysis.

An umbilical cord connects the last impinger, the pitot tube, and the heating elements to the meter box which is located in a convenient place within 15 m of the sampling ports. The meter box contains a vacuum pump, regulating valves, instantaneous and integrating flow meters, pitot tube manometers, vacuum gauge, and electrical controls.

Particulate matter (solids and condensibles) is collected in three discrete portions by the sampling train: the probe and glassware upstream of the filter; the filter; and the wet impingers. The probe and glassware are brushed and rinsed with acetone; the matter is captured for gravimetric analysis. The probe and glassware are then rinsed with distilled water and the rinsings transferred to a second container for analysis. The filter is desiccated and analyzed gravimetrically. The combined impinger liquid is heated to drive off uncombined water and the residue retained for analysis. The particulate matter analysis is illustrated schematically in Figure B-9.

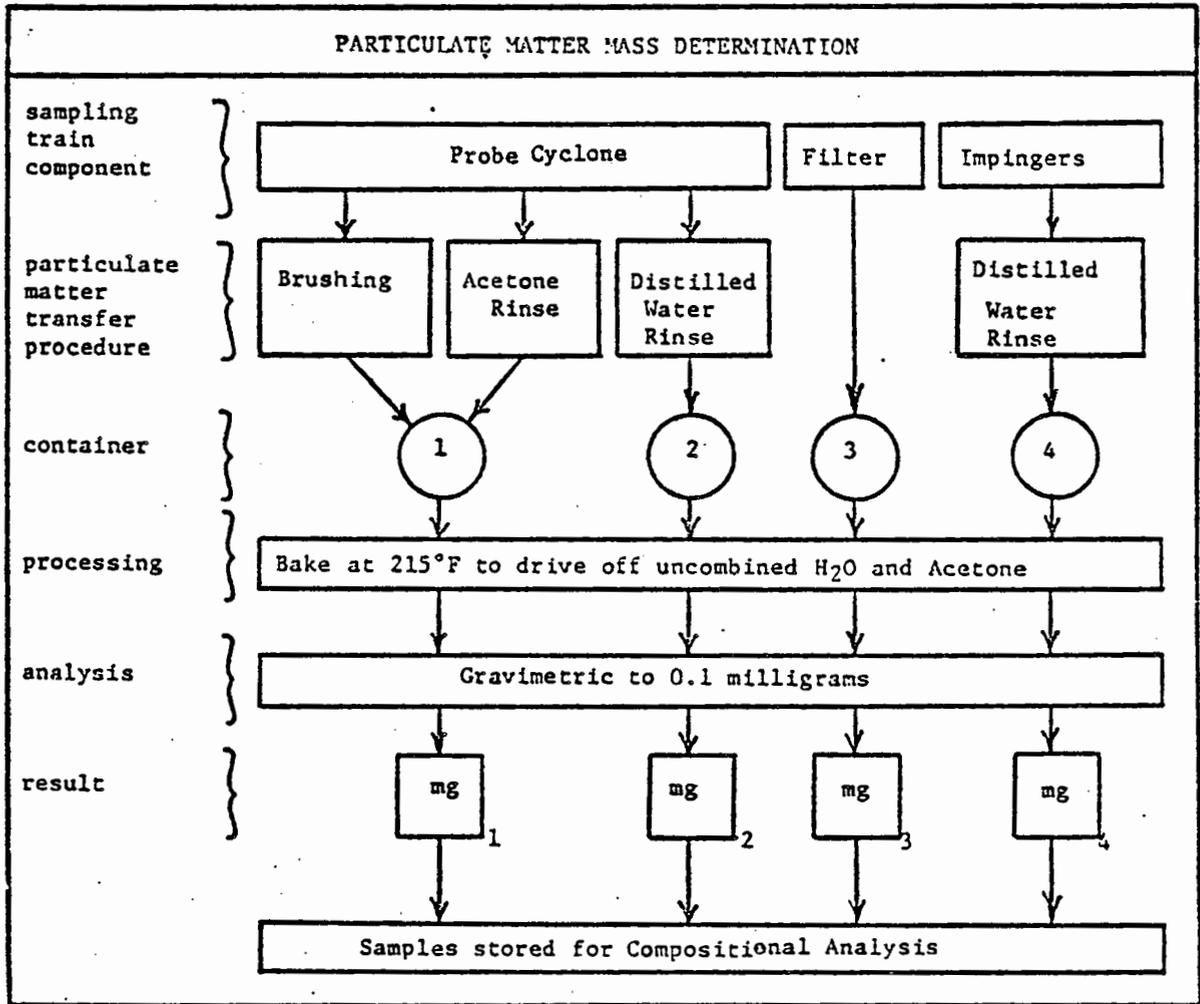


Figure B-9. Processing and analyzing particulate matter.

US EPA method 5 considers the particulate matter captured in containers (1) and (3); the filter, probe brushing, and probe acetone rinse. Since EPA source standards are based on only solid particulates, care is taken to differentiate between solid and the total (solid and condensable) particulates. The water wash is performed because KVB's test experience has shown that a significant amount of water soluble material may sometimes be captured by the probe.

The dry sample volume is determined with a dry test meter at a measured temperature and pressure and then converted to standard conditions. The volume of condensed water in the impingers is measured in milliliters and the corresponding volume of water vapor is then computed at standard conditions. The dry sample volume and water vapor volume are then summed to give the total sample volume. The dry sample volume is used in the data reduction procedures.

A point of interest is the method chosen to calculate particulate emissions in ng/J or lb/10<sup>6</sup>Btu from the experimental data. The particulate sampling train, properly operated, yields particulate mass per unit flue gas volume. Having measured g/m<sup>3</sup>, it is necessary to establish the flue gas volume per unit heat input if emissions in ng/J are desired. The original Method 5 involved determining a velocity traverse of the stack, the cross sectional area, the flue flow rate, and fuel heating value. A revised and more accurate method has been promulgated by the Environmental Protection Agency that utilizes a fuel analysis (carbon content, hydrogen content, high heating value, etc.) and the measured excess O<sub>2</sub> in the exhaust to calculate the gas volume generated in liberating 1.055 GJ (a million Btu's). The velocity traverse approach generally results in a 20 to 30% higher value and is believed to be less accurate.

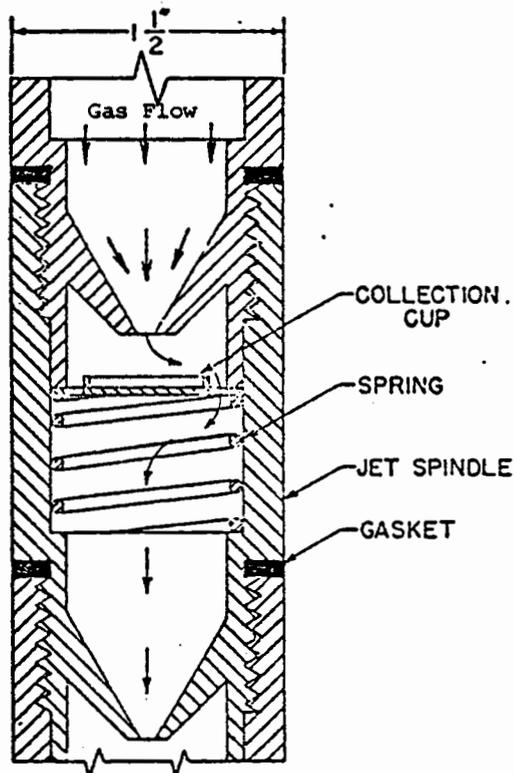
### B.1.3.3 Particulate Size

Particulate matter size distribution is determined using a cascade impactor to collect the sample and a Cahn Model G-2 Electrobalance to weigh the sample. When light fuels, i.e., No. 2 oil, are used and the flue gas is relatively clean, a high volume type impactor, the Anderson 2000 Mark III, is used. When the grain loading of the flue gas is heavy, as when coal is burned, a low volume impactor, the Brink as shown in Figure B-10 is used.

To improve the accuracy of the weighing, lightweight substrate made of aluminum foil or glass fiber are placed in or on each steel collection stage. The particles are collected on these lightweight discs, and the original steel collection stages are used only as a backing for these substrata.

A common problem with impactors is that the particles do not adhere to the stage surface, but strike it, rebound, and are re-entrained in the flow through the slots down to the next stage. Re-entrainment has not proved to be a problem with the cascade impactor measurements KVB currently is making. The flue gas flow rate has been reduced from the nominal  $46.7 \times 10^{-6} \text{ m}^3/\text{s}$  (2.8 liters per minute) to  $33 \times 10^{-6} \text{ m}^3/\text{s}$  (2.0 LPM) or less. Visual examination of the collection stages has found no evidence of scouring or re-entrainment. One set of stages was further examined under an electron microscope and there was no sign of a significant number of particulates that were larger than the aerodynamic diameter cut point ( $D_{50}$ ) of the preceding stage. There was, however, a considerable amount of sponge-like material that appeared to be an agglomeration of small particles.

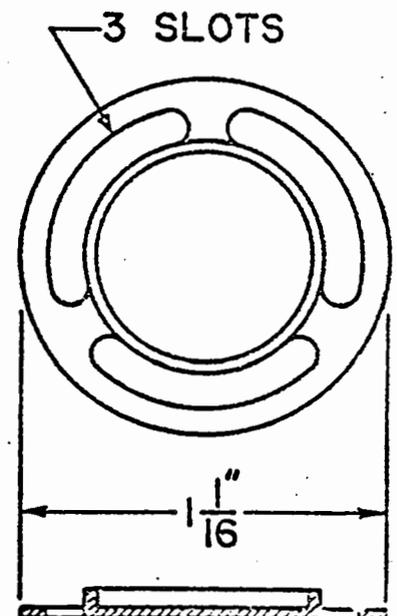
If rebound proves to be a problem that cannot be solved by reducing the throughput, the substrate is coated with an adhesive. Workers in the field currently are using a solution of 5% polyethelene glycol 3000 in benzene as the substrate coating substance. If a coating is used the substrates are baked at 473 K (200 °C) for two hours or until the volatiles have vaporized, and the weight ceases to change. At least one additional substratum is processed as a blank.



The in-line impactor has five stages. Particles in the range of 0.3 to 3.0 microns are collected by successive impingement

Dimensions of Cascade Impactor Jets		
Dimensions, Cm.		
Jet No.	Jet diam.	Spacing of jet opening*
1	0.249	0.747
2	0.1775	0.533
3	0.1396	0.419
4	0.0946	0.282
5	0.0731	0.220

\* From collection cup surface.



Collection cups are positioned so that the distance from the jet decreases as the jet diameter becomes smaller. Annular slots around cup minimize turbulence

Figure B-10. Design of a single stage from a Brink type cascade impactor.

Back-up filters are used on all impactors to collect the material that passes the last impaction stage. Binderless, glass-fiber filter material, such as high-purity Gelman Type A Glass Fiber-Filter Webb are employed for this purpose. For the Brink brand of impactor, 25 mm diameter circular filters are placed under the last spring in the outlet stage of the impactor. The filter is protected by a Teflon O-ring and a second filter disc placed behind the actual filter which acts as a support. The Andersen brand impactor uses 625 mm diameter filter discs placed above the final "F" stage.

For accurate weighing of collected material, a Cahn G-2 Electro-balance with a sensitivity of 0.05 micrograms is used. This sensitivity is needed for the lower stages of the high loading impactors where collection of 0.3 mg or less is not uncommon. KVB currently is using this balance in the field and has found it to be insensitive to vibration.

The flow through the impactor is measured to determine the cut points of the individual stages. The flow is maintained by monitoring the flow through the impactor assembly with the pressure gauges on the EPA train control box. The pump on the control box is used to maintain the flow. This technique is being used successfully in the field by KVB, Inc. at present.

To ensure proper measurement by dry gas meter and to protect the vacuum pumps from damage by water condensing from the flue gas, the sample stream will be chilled and the water dropped out by a commercially available condenser of the type available for use with the Western Precipitation, Inc. EPA Train.

If the stack pressure is less than the ambient pressure it is possible for backflow to occur through the impactor when the pump is turned off. This can cause the collected material to be blown off the collection substrates and onto the underside of the jet plate above. KVB avoids this problem by ensuring that no gas flow through the impactor takes place, except when sampling, by using a check valve to close off the impactor from the pump while removing the impactor from the duct.

The impactor is carefully loaded with the stage cups and the pre-weighed stage substrates. The Andersen type impactor requires extra attention for the substrate stage and stage-to-stage alignments to ensure that the jets of one stage are above the collection surface of the next stage. After all stages are loaded and the cap and nozzle are added, the assembled Brink is tightened with wrenches to make certain the high temperature No. 116 asbestos gaskets are seated. Hand tightening suffices for the Andersen impactor.

KVB has found that supplemental heating of the impactor is not necessary to prevent the condensation of flue gas water inside the case. If it is found with industrial combustion equipment that heating is necessary to prevent water vapor from condensing in the impactor, heating tape and the necessary insulation will be employed. A thermocouple mounted in the sample gas flow immediately downstream of the impactor outlet is used to monitor and control the impactor temperature. This measurement also yields the temperature needed for calculating impactor cut points.

The impactor will be preheated for at least 30 minutes before sampling. The inlet nozzle will be pointed downstream of the flow field during this heating phase to prevent the premature accumulation of particulates in the impactor.

A predetermined flow rate will be established immediately and will be maintained constant throughout the test. Attempts to modulate flow to compensate for changes in the duct flow rate and to maintain isokinetic sampling would destroy the utility of the data by changing the cut points of the individual stages. Establishment of the correct flow rate quickly is especially important for the short sampling times typical of coal fuels. If a non-standard flow is necessary, the true cut points will be calculated for the actual flue gas temperature and impactor pressure drop.

KVB has found that the post-test procedure is very important in obtaining accurate measurements. The crucial part is to make sure the collected material stays where it originally impacted. After the test, the impactor will be carefully removed from the duct without jarring, unscrewed from the probe, and allowed to cool. Proper disassembly is critical as discussed below.

1. Brink Impactor: Careful disassembly of a Brink impactor is necessary for obtaining good stage weights. If a precollector cyclone has been used, all material from the nozzle to the outlet of the cyclone is included with the cyclone catch. All of this material is brushed onto a small 3 cm x 3 cm aluminum foil square and saved for weighing. Cleaning the nozzle is also important, especially if it is a small bore nozzle.

All material between the cyclone outlet and the second stage nozzle will be included with material collected on the first collection substrate. All adjacent walls will be brushed off, as well as around the underside of the nozzle where a halo frequently occurs on the upper Brink stages. All material between the second stage nozzle and third stage nozzle will be included with that on the second collection substrate. This process will be continued down to the last collection substrate. Finally, care will be exercised in taking out the filter.

2. Andersen Impactor: The foil to hold the stage 1 substrate will be laid out. Next the nozzle and entrance cone will be brushed out and onto the foil. Then the material on stage 0 will be brushed off. Next, any material on the top O-ring and bottom of stage 0 will be brushed onto the foil. The stage 1 filter substrate material will then be placed on the foil and, finally, the top of the stage 1 plate O-ring and cross peice will be brushed off. Depending on how tightly the impactor was assembled, some filter material may stick to the O-ring edge contacting the substrate. This will be carefully brushed onto the appropriate foil. This process will be continued through the lower stages and the filter.

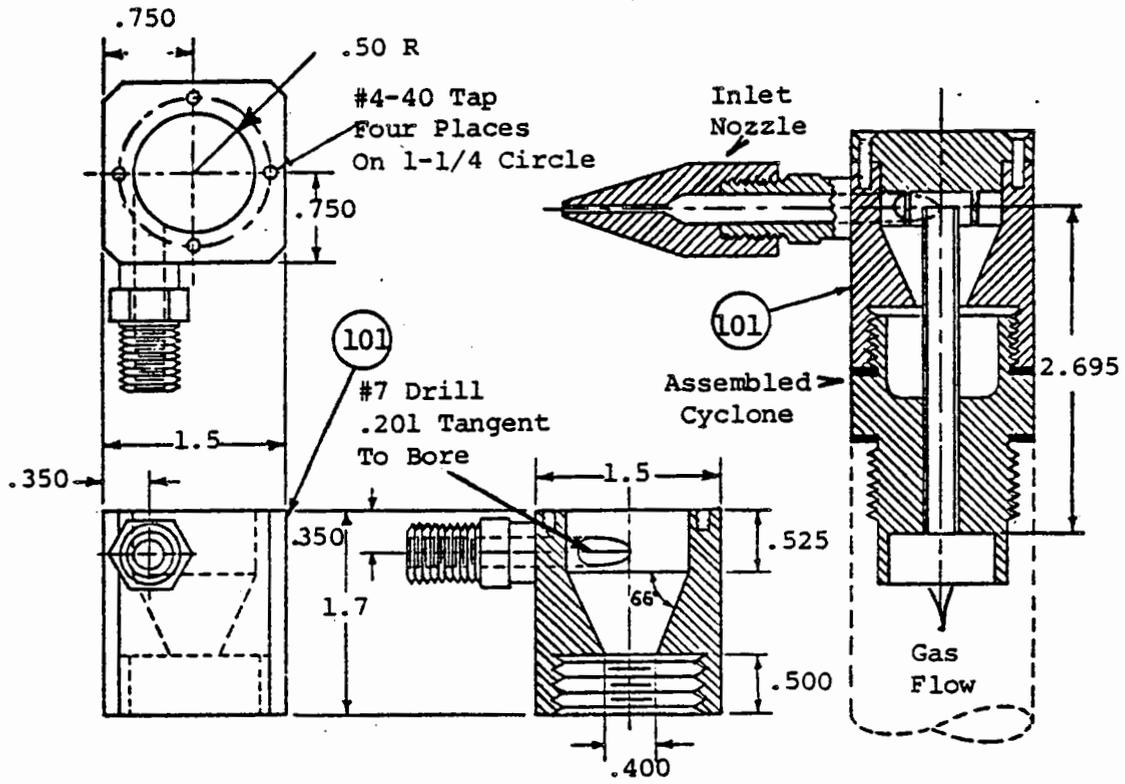
All substrates, the backup filter, and the control blanks are cooled to room temperature in a desiccator and weighed to  $\pm 0.01$  mg. The weighing chamber of the balance also will be desiccated. Samples and blanks are returned to the desiccator overnight and reweighed until constant weight is established. The substrates are weighed soon after the end of the test so that the data will be available for setting up the following test.

Upon their arrival, the field test crew undertakes the combustion modification testing, including total particulate measurement. While this initial testing is being done an estimate of the grain loading and particle size is made. The data used to select an isokinetic nozzle for the EPA Train is also used to select a nozzle for the impactor. In no case is an impactor nozzle of less than two millimeters diameter to be used.

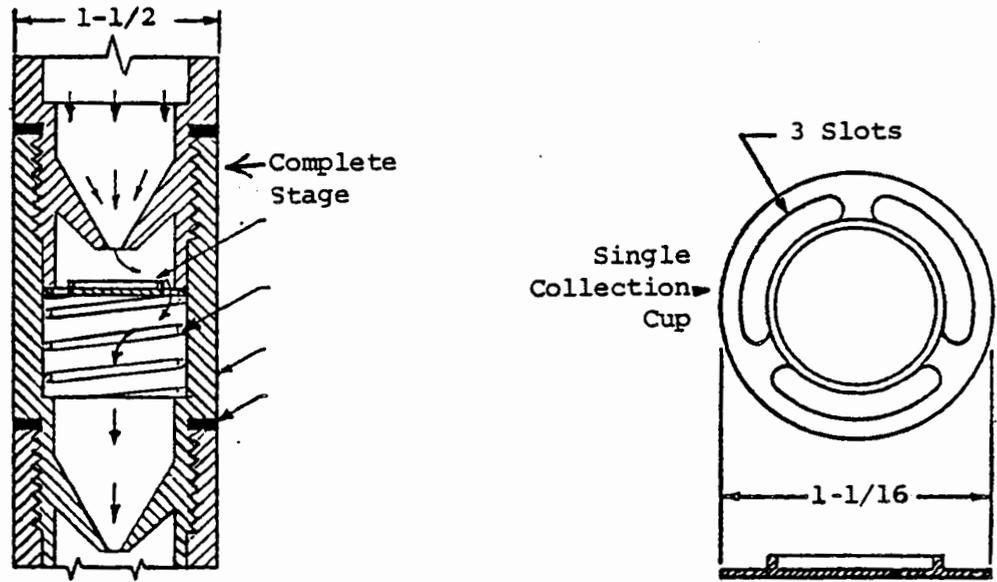
Measurements are made at a sufficient number of points across the flue or smoke stack, as specified by EPA Method 5, to make certain that a representative sample of particulates is obtained. Whenever possible, the impactor is oriented vertically so that the flow through it is directed downward. This will minimize the tendency of the particulates to fall off the stages. When horizontal orientation is unavoidable, extra care will be taken not to jar the impactor against the flue during removal and cause particulates to fall from the stages.

When coal fuel is fired and sampling is done upstream of the dust collector, the percentage (by weight) of material larger than ten micrometers is appreciable. In such cases a precutter cyclone, such as that shown in Figure B-11 and currently used with the Brink impactor, is used to prevent the upper impactor stages from overloading. A precutter cyclone is used during the preliminary orientation run, and if the weight of material obtained by the precutter is comparable to that on the first stage, the precollector is used on subsequent runs.

The length of the sampling is dictated by grain loading and the particulate size distribution. An estimate can be made from the following typical data gathered during previous KVB test programs.



PRECUTTER CYCLONE



STAGE

Figure B-11. Detail of one stage and of precutter cyclone for cascade impactor.

<u>Fuel and/or Burner</u>	<u>Sampling Duration (min.)</u>
No. 6 oil	120-240
Spreader stoker	59
No. 2 oil	300

The flow rate and nozzle size are closely coupled, and requirements for isokinetic or near-isokinetic nozzle flow sometimes force a compromise on nozzle selection. The general order of priorities used by investigators to determine nozzle size in the field is (1) nozzle diameter (minimum only), (2) last stage jet velocity, (3) isokinetic flow rate required, and (4) nozzle diameter if greater than 2.0 mm.

The largest nozzle diameter should be used to minimize sampling errors resulting from nozzle inlet geometry. Investigators have reported that when very small nozzles have been used with the Brink impactor, there have been some cases in which large amounts of material were retained in the nozzle or the nozzle has been completely blocked. The smallest diameter nozzle KVB uses is 2.0 mm. In some instances, a 90-degree elbow may be necessary due to port location and gas flow direction, but these situations will be avoided when possible. Problems in cleaning elbows may occur as well as difficulties in determining the size interval(s) from which the deposited material originated. When these problems cannot be avoided, nozzle bends will be made as smooth as possible and of sufficiently large radius to minimize the disturbance of the flow.

For light oil fuel, 300 minutes was required to collect a measurable sample. On the other hand, with coal, only 59 minutes was required. The long test time for No. 2 oil was necessary because a low-flow-rate Brink brand impactor was used. To avoid long test time KVB used a high-flow-rate impactor when the flue gas grain loading was low. However, in no case will the test duration be less than 60 minutes in order to allow for short-term variations in the operation of the combustion device.

#### B.1.3.4 Smoke Spot

On combustion equipment where smoke numbers normally are taken, such as oil-fired boilers, KVB, Inc. determines the smoke number using test procedures according to ASTM Designation: D 2156-65. The smoke number is determined at each combustion modification setting of the unit. Examples are baseline, minimum excess air, low load, etc., and whenever a particulate concentration is measured.

Smoke spots are obtained by pulling a fixed volume of flue gas through a fixed area of a standard filter paper. The color (or shade) of the spots that are produced are visually matched with a standard scale. The result is a "Smoke Number" which is used to characterize the density of smoke in the flue gas.

The sampling device is a hand pump similar to the one shown in Figure B-12. It is a commercially available item that can pass  $36,900 \pm 1650$  cu cm of gas at  $16^{\circ}\text{C}$  and 1 atmosphere pressure through an enclosed filter paper for each 6.5 sq cm effective surface area of the filter paper.

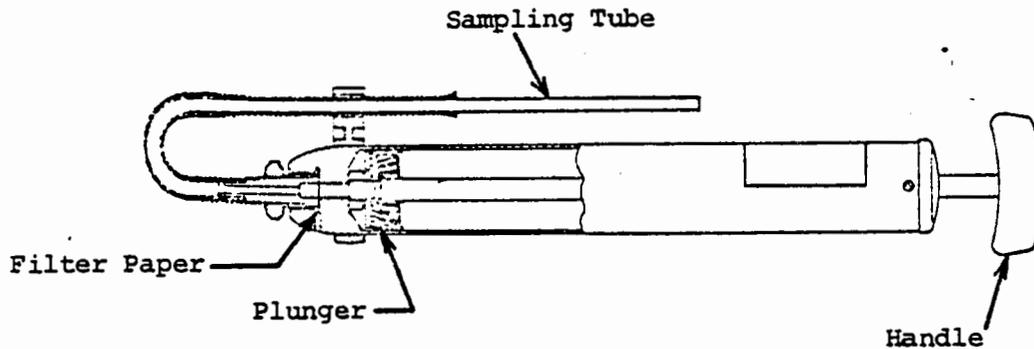


Figure B-12. Field service type smoke tester.

KVB 6002-471

The smoke spot sampler is provided with a motor-driven actuator to ensure a constant sampling rate independent of variations in stroke rate that can occur when the sampler is operated manually.

The required smoke scale consists of a series of ten spots numbered consecutively from 0 to 9, and ranging in equal photometric steps from white through neutral shades of gray to black. The spots are imprinted or otherwise processed on white paper or plastic stock having an absolute surface reflectance of between 82.5 and 87.5%, determined photometrically. The smoke scale spot number is defined as the reduction (due to smoke) in the amount of light reflected by a soiled spot on the filter divided by 10.

Thus the first spot, which is the color of the unimprinted scale, will be No. 0. In this case there will be no reduction in reflected incident light directed on the spot. The last spot, however, is very dark, reflecting only 10% of the incident light directed thereon. The reduction in reflected incident light is 90%, and this spot is identified as No. 9. Intermediate spot numbers are similarly established. Limits of permissible reflectance variation of any smoke scale spot shall not exceed  $\pm 3\%$  relative reflectance.

The test filter paper is made from white filter paper stock having absolute surface reflectance of 82.5 to 87.5%, as determined by photometric measurement. When making this reflectance measurement, the filter paper will be backed by a white surface having absolute surface reflectance of not less than 75%.

When clean air at standard conditions is drawn through clean filter paper at a flow rate of 47.6 cu cm per sec per sq cm effective surface area of the filter paper, the pressure drop across the filter paper will fall between the limits of 1.7 and 8.5 kPa (1.3 and 6.4 cm of mercury).

The sampling procedure is specified in D 2156. A clean, dry, sampling pump will be used. It will be warmed to room temperature to prevent condensation on the filter paper. When taking smoke measurements in the flue pipe, the intake end of the sampling probe is placed at the center line of the flue. When drawing the sample, the pressure in the flue gas stream and the sampler is allowed to equalize after each stroke.

The smoke density is reported on the Mobile Lab Data Sheet as Smoke Spot Number on the standard scale most closely corresponding to test spot. Differences between two standard Smoke Spot Numbers will be interpolated to the nearest half number. Smoke Spot Numbers higher than 9 will be reported as "Greater than No. 9."

This procedure is deemed to be reproducible to within  $\pm 1/2$  of a Smoke Spot Number under normal conditions where no oily stain is deposited on the disk.

KVB's field experience with industrial boilers has been that the human factor involved in the interpretation of the smoke spot by an experienced observer does not cause a significant lack of precision.

#### B.1.3.5 Opacity

Opacity readings are taken by a field crew member who is a certificated graduate of a U.S. Environmental Protection Agency approved "Smoke School". Observations are made when particulate measurements are made. Additional observations are made when necessary to gather the maximum amount of information. The procedures set forth in EPA Method 9, "Visual Determinations of the Opacity of Emissions for Stationary Sources" are followed.

Observations are made and recorded at 15 second intervals while particulate concentration is being measured and at other times after the unit has stabilized. Before beginning observations, the observer determines that the feedstock or fuel is the same as that from which the sample was taken for the fuel analysis.

Before beginning opacity observations, the observer makes arrangements with the combustion unit operator to obtain the necessary process data for the standard KVB Control Room Data Sheet. The control room data are recorded for the entire period of observations, as is customarily done by KVB during an emissions test. The process unit data that are obtained include:

- a. Production rates
  - 1. maximum rated capacity
  - 2. actual operating rate during test
- b. Control device data
  - 1. recent maintenance history
  - 2. cleaning mechanism and cycle information.

The observer requests the appropriate plant personnel to briefly review and comment on the opacity measurements and process data and the observer will comment on:

- a. the basis for choosing the observation periods used;
- b. why it is believed the periods chosen constitute periods of greatest opacity;
- c. why the observations span a time period sufficient to characterize the opacity.

Consideration is given to postponing the EPA Method 5 particulate tests during periods of cloudy or rainy weather because of the inability of the observer to monitor the smoke.

APPENDIX C

TRACE SPECIES AND ORGANICS  
SAMPLING AND ANALYSIS PROCEDURES

Table of Contents

	<u>Page</u>
C-1.0 INTRODUCTION	389
C-2.0 PREPARATION OF XAD-2 RESIN	392
C-3.0 PREPARATION FOR A SAMPLING RUN	395
C-4.0 SAMPLING PROCEDURES	402
C-5.0 TRAIN DISASSEMBLY AND SAMPLE RECOVERY	406
C-6.0 SUPPLEMENTARY REFERENCE MATERIAL	411
C-7.0 SAMPLE PREPARATION AND ANALYSIS	417

Note: Units for values in this Appendix are given in the actual English or metric units as used or measured on field equipment. Alternate English to metric, or metric to English conversions are not listed to avoid confusion, as the Appendix is intended for direct field use. A table of conversion factors is given in Section 7.0.

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## C-1.0 INTRODUCTION

Sampling and analysis procedures for trace species and organics emissions used in the current program were based on procedures developed by the EPA Industrial Environmental Research Laboratory at Research Triangle Park, NC. The IERL-RTP procedures are defined in a procedures manual prepared for EPA by TRW Systems Group (Ref. C-1) that relates the procedures in terms of a multi-media Level I stream prioritization sampling and a Level II detailed assessment sampling. Although those sampling procedures were adapted for the current program, this program was not formulated in the specific Level I-Level II framework. Level I sampling is intended to show the presence or absence and, within a factor of  $\pm 2$  to 3, the emission rates of all inorganic elements, selected inorganic anions and classes of organic compounds. The current program objective is to obtain qualitative and quantitative data for a large number of elements (approximately 60) by use of spark source mass spectrometry. This objective is similar to the Level I philosophy. A second objective of the current program, more related to the Level II definition, is to more accurately quantify the emissions of the elements, species, and organics as shown in Table C-1, and to relate the emissions of these species, by mass balance, to the amounts input with fuel or process materials. In addition to total quantities, information is required on the relationship of particulate species emissions to particulate size.

The referenced Level I procedures manual refers to several multi-media sampling procedures. The current program is more narrowly concentrated on exhaust emissions from the stacks of industrial combustion devices. Therefore Chapter III "Gaseous Streams Containing Particulate Matter" of the referenced manual is that portion pertinent to the current program. That chapter discusses sampling with a "Source Assessment Sampling System" (SASS). The features of that

TABLE C-1. TRACE SPECIES AND ORGANICS TO BE IDENTIFIED

<u>Elements</u>		
Antimony	Cobalt	Selenium
Arsenic	Copper	Tellurium
Barium	Fluorine	Tin
Beryllium	Iron	Titanium
Cadmium	Lead	Vanadium
Calcium	Manganese	Zinc
Chlorine	Mercury	
Chromium	Nickel	
<u>Species</u>		
Total sulfates		
Total nitrates		
<u>Organics</u>		
Total polychlorinated biphenyls (PCB)		
Total polycyclic organic matter (POM)		
Specific POM compounds:		
7, 12 - dimethylbenz (a) anthracene		
Dibenz (a,h) anthracene		
Benzo (c) phenanthrene		
3-Methylcholanthrene		
Benzo (a) pyrene		
Dibenzo (a,h) pyrene		
Dibenzo (a,i) pyrene		
Dibenzo (c,g) carbazole		

sampling train are presented in the referenced manual and will not be repeated here. The remainder of this appendix presents the specifics of the referenced procedures as adopted for the current program. SASS sampling and analytical procedures are updated continuously. The techniques used for this study were approved at the time, but may have changed afterwards.

The SASS sampling train and samples obtained are shown schematically in Figure C-1.

391

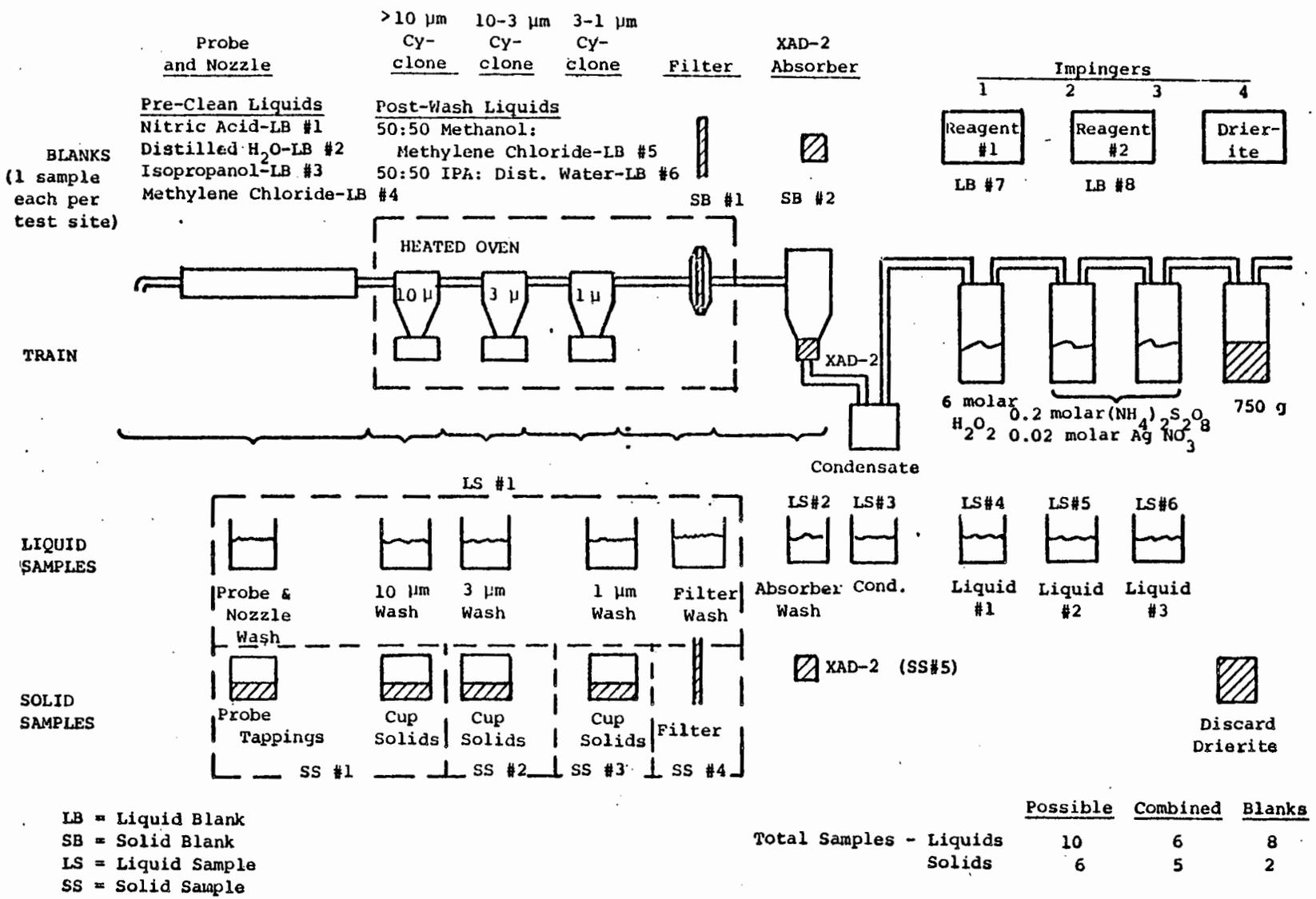


Figure C-1. SASS train schematic.

## C-2.0 PREPARATION OF XAD-2 RESIN

### C-2.1 General Procedure

The XAD-2 resin to be used in the SASS train sorbent trap must be cleaned prior to use. The resin as obtained from the supplier is soaked with an aqueous salt solution. This salt solution plus residual monomer and other trace organics must be removed before the resin can be used for sampling trace organics.

Clean-up is normally achieved in a giant Soxhlet extractor. Any other continuous extractor working on the same principle of circulating distilled solvent would be adequate.

The wet XAD-2 resin is charged into the extractor thimble and extracted in sequence with refluxing solvent as follows:

1. Water, 20-24 hours
2. Methanol, 20-24 hours
3. Anhydrous ether, 8 hours (during day only)
4. Pentane, 20-24 hours

Methanol is used primarily to remove the water from the resin. Ether removes a substantial portion of the organics--overnight reflux is acceptable if apparatus is secure to the hazards of ether. Pentane is used as the final stage because it is the solvent used to extract the resin after sample collection.

A commercial giant extractor has a dumping volume of 1500 ml and thus about 2.5 l of solvent is required in a 3 l flask.

After the final pentane extraction, the resin is transferred to a clean flask and dried under vacuum aided by mild heat from a heat lamp. Care should be taken (traps) to prevent backstreaming from vacuum systems.

### C-2.2 Soxhlet Cleaning of XAD-2

Follow the general procedure given above. However, the following procedural details may be helpful to those not familiar with operating the Soxhlet extractors. These recommendations and comments are based on our recent experience in preparing XAD-2 for EPA SASS tests.

1. Quality of solvents \*

Water: Arrowhead distilled

Methanol: Anhydrous methyl alcohol, Mallinckrodt, AR grade

Anhydrous ether: anhydrous (ethyl) ether, Mallinckrodt,  
AR grade

Pentane: Mallinckrodt, spectr. AR grade

2. The use of paper (cellulose) thimbles was recommended by ADL. With a soft lead pencil, mark on the outside of the thimble the desired fill line which corresponds to the entrance level of the syphon tube when the thimble is inserted into the extractor. Handle the thimble with plastic gloves.
3. Fill (i.e., "charge") the thimble with XAD-2 using a stainless steel spoon. Intermittently moisten the XAD-2 with distilled water (from a plastic wash bottle) to compact the XAD-2 in the thimble. Excess water will flow through the walls of the thimble. In this manner, add XAD-2 up to the pencil fill line.
4. Install the charged thimble in the extractor, place approximately 300 ml of distilled water in the Soxhlet flask and assemble the Soxhlet extractor. Room temperature tap water is adequate for the condenser cooling.  
  
\*When inserting the charged thimble into the Soxhlet, make a small indent at the bottom of the thimble to avoid obstructing the inlet to the syphon tube.
5. Bring the water to a boil and allow the extractor to syphon several times (one hour of operation is adequate). Discard the flask contents, refill with fresh distilled water and continue the extraction. By discarding the initial water, most of the salt originally contained in the raw XAD-2 is removed from the system. This will prevent salt carryover back into the XAD-2 and will "even out" the boiling.
6. The methanol solvent should also be replaced in a similar fashion. This assures complete removal of the water. (Any water remaining during the ether extraction stage will "plug" the XAD-2 pores thereby interfering with the ether extraction.) Three hundred to four hundred ml of methanol in the extraction flask is adequate for all-night operation. Use room temperature tap water for the condenser.

\*Mention of trade names does not constitute approval by U.S. EPA.

7. For the ether and pentane extraction, a circulating ice bath should be used for condenser cooling to minimize vapor loss through the top of the condenser. Three hundred to four hundred ml of solvent is adequate for all-night pentane operation. To avoid condensing water (from the air) on the inside of the condenser during startup, operate the Soxhlet for several minutes without condenser cooling (until solvent vapors purge out the air) before turning on the circulating water.
8. Use extreme caution when handling ether and pentane. Both are extremely volatile and highly flammable. Make sure all heating mantles, electrical equipment, etc. are off while containers are open.
9. The Soxhlet reflux rate can be judged by observing the drip rate from the condenser onto the XAD-2. One to Two drops per second is desirable. This is accomplished by adjusting the power to the heating mantle. For this condition, the water may be boiled vigorously but no boiling (bubbling) will be observed for the other three solvents.
10. When changing over from one solvent to another, residual solvent remaining in the thimble and extractor should be removed to as high degree as practical (i.e., do not desiccate or vacuum dry). One approach which works quite well is to apply suction to the discharge end of the Soxhlet syphon tube. The use of a plastic "filtering pump" (an aspirator pump operated by tap water from the faucet) has proved adequate.
11. While drying the XAD-2 in the vacuum desiccator, heat to approximately 120°F using heating lamps. Do not use vacuum grease on the desiccator. Protect the vacuum pump from pentane vapors with a carbon trap. The XAD-2 may be left in the paper thimbles while drying in the desiccator. Use a filter (i.e., cotton in a flask) between the carbon trap and the desiccator to prevent backflow of carbon into the XAD-2 in the event of a rapid loss of desiccator vacuum.

### C-3.0 PREPARATION FOR A SAMPLING RUN

#### C-3.1 Containers, Chemicals, and Laboratory Equipment

Table C-2 lists the samples to be recovered from the SASS train and the recommended containers used for sample storage and shipping. In some cases more than one container may be required. All containers should be cleaned prior to use according to the procedure used for cleaning the train as described in Section C-2.2.

#### Laboratory Equipment--

All sample recovery operations, sample weighing, and chemical cleaning of train components and containers should be performed in a clean area specially set aside for this work. In the field, this "clean room" should consist of at least a clean enclosed work bench or table top and every attempt should be made to observe the following general recommendations:

1. Avoid drafts and areas with high foot traffic
2. Keep floors swept to minimize air borne dust
3. Use plastic table cloths
4. Inlet filters on air conditioners should be in place
5. Use common sense to avoid contaminating samples with hair, fingerprints, perspiration, cigarette smoke or ashes, etc.
6. Use plastic gloves or forceps when handling tared containers; stainless steel tweezers when handling filters

In addition to sample containers listed in Table C-2, the following clean room accessories will be required:

SASS train tool kit  
stainless steel tweezers (2)  
stainless steel spatulas (2)  
disposable plastic gloves  
teflon or "guth" unitized wash bottles (3)  
teflon policeman (optional)  
110°C drying oven  
weighing balance 160 gram capacity required  
assorted powder and liquid funnels  
assorted graduated cylinders, 250 ml to 1000 ml  
1/2-gal mixing jugs (3)

TABLE C-2. SAMPLE STORAGE/SHIPPING CONTAINERS

Train Component	Sample Type	Container Required*
Probe and nozzle	solid tappings solvent wash	Tared 4 oz. LPE <sup>†</sup> 500 ml amber glass (16 oz)
10 $\mu$ cyclone	cup solids solvent wash	Add to probe and nozzle tappings. Add to probe and nozzle wash.
3 $\mu$ cyclone	cup solids solvent wash	Tared 4 oz. LPE 500 ml amber glass (16 oz)
1 $\mu$ cyclone	cup solids solvent wash	Tared 4 oz. LPE 500 ml amber glass (16 oz)
Filter holder and filter	solid tappings and filter solvent wash	Tared 150 mm glass petri dish 500 ml amber glass (16 oz)
XAD-2 Module:		
(1) XAD-2 resin	solid adsorbent	500 ml amber glass (wide mouth) (16 oz)
(2) Condensate	contents of condensate cup	1 liter LPE
(3) All surfaces	solvent wash	500 ml amber glass (16 oz)
Impinger #1	contents rinses	1 liter LPE, with pressure relief cap 500 ml amber glass (16 oz)
Impinger #2	contents rinses	1 liter LPE 500 ml amber glass (16 oz)
Impinger #3	contents rinses	1 liter LPE 500 ml amber glass (16 oz)

\*All glass containers must have teflon cap liners.

<sup>†</sup>Linear polyethylene (same as "high density" or "type 3" polyethylene).

Additional sample bottles must be provided for all fuel, process materials, and ashes to be collected. For train washes and liquids, particularly the condensate, several bottles may be required.

## Quality of Chemicals--

An underlying concern in selecting chemicals for impinger solution and washes is to avoid introducing trace compounds similar to those being analyzed. Although "blanks" of impinger solutions will be analyzed, it is preferable to minimize chemical impurities when possible by using highest quality chemicals rather than adjust the final sample analyses results. The following chemical grades were used:

Chemical	Quality
<b>Impinger Solution:</b>	
distilled water	Commercial distilled
ammonium per(oxydi)sulfate [(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ]	AR
0.1N silver nitrate (AgNO <sub>3</sub> )	
30% hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> )	AR
<b>Train Precleaning:</b>	
distilled water	Commercial distilled
isopropyl alcohol [CH <sub>3</sub> CH(OH)CH <sub>3</sub> ]	Spectr AR
methylene chloride (CH <sub>2</sub> Cl <sub>2</sub> )	Spectr AR
<b>Sample Recovery:</b>	
distilled water	commercial distilled
methylene chloride (CH <sub>2</sub> Cl <sub>2</sub> )	Spectr AR
methanol (CH <sub>3</sub> OH)	Spectr AR
isopropyl alcohol [CH <sub>3</sub> CH(OH)CH <sub>3</sub> ]	Spectr AR

If higher grade (lower impurity levels) of chemicals are available they should be used.

### C-3.2 Cleaning the SASS Train

Newly purchased or previously unused train components and sample containers should be washed with tap water and a plastic scouring pad. All surfaces in the sampling train which come in contact with sample, as well as all sample containers and impingers, should be prepassivated by one-hour standing contact with a 50:50% volume solution of pure nitric acid and distilled water. Remove any remaining traces of acid by rinsing with tap water, then continue with the solvent cleaning procedure below.

Prior to sampling, all SASS train components and sample containers are cleaned in two or three successive stages (in the order listed) using a different solvent in each stage:

<u>All Except Impinger Sample Bottles</u>	<u>Impinger Sample Bottles</u>
1. distilled water	1. distilled water
2. isopropyl alcohol	2. isopropyl alcohol
3. methylene chloride ( $\text{CH}_2\text{Cl}_2$ )	

The distilled water may be dispensed in plastic wash bottles; the isopropyl alcohol and  $\text{CH}_2\text{Cl}_2$  should be dispensed using teflon or glass wash bottles. After each part is washed with  $\text{CH}_2\text{Cl}_2$ , it should be dried in a filtered stream of dry air or nitrogen.

Any solid residues adhering to the internal surfaces should be removed with tap water and a plastic scouring pad before proceeding with the solvent cleaning procedure.

After cleaning, assemble and cap off the cyclone assembly. (All caps should be previously cleaned according to the above 3-solvent procedure.) Cap off other sections of the train including the probe, XAD-2 module, filter housing, impinger trains, and interconnecting hoses.

C-3.3 Impinger Solutions

Impinger	Reagent	Quantity	Purpose
#1	6 M $H_2O_2$	750 ml	Trap reducing gases such as $SO_2$ to prevent depletion of oxidative capability of trace element collecting impingers 2 and 3
#2	0.2 M $(NH_4)_2 S_2 O_8$ + 0.02 M $AgNO_3$	750 ml	Collection of volatile trace elements by oxidative dissolution.
#3	0.2 M $(NH_4)_2 S_2 O_8$ + 0.02 M $AgNO_3$	750 ml	Collection of volatile trace elements by oxidative dissolution.
#4	Drierite (color indicating)	750 g	Prevent moisture from reaching pumps

Suggested Formulas for Preparing Impinger Solutions--

Impinger #1 (6 M  $H_2O_2$ )

To prepare 750 ml of 6M  $H_2O_2$  dilute 465 ml of standard 30% (by weight)  $H_2O_2$  with distilled water.

Impingers #2 and #3 [0.2 M  $(NH_4)_2 S_2 O_8$  + 0.02M  $AgNO_3$ ]

To prepare 1500 ml of solution combine:

1. 68.46 gm crystalline  $(NH_4)_2 S_2 O_8$
2. 300 ml 0.1 N  $AgNO_3$  solution

and dilute to 1500 ml using distilled water.

Additional solution should be prepared for at least 1 liter of solution as a blank.

#### Impinger #4 (color indicating Drierite)

Use 750 gm or approximately 750 cc of 8 mesh color indicating Drierite ( $\text{CaSO}_4$ )

When installing the top on the impinger bottle, avoid forcing Drierite up into the center tube as this results in increased pressure drop. Lay impinger on side while inserting top.

It may be necessary to replace the Drierite several times during a SASS run. A marked decrease in Impinger #4 outlet temperature (moisture absorption by Drierite produces heat) may signal Drierite depletion if the Drierite color change is difficult to detect.

The spent Drierite is not kept for analysis and can be discarded or, preferably, rejuvenated for future use by heating in a drying oven at 220°F to 250°F to blueness.

#### C-3.4 Filter Preparation

More than one filter will be required when particulate grain loading is high (i.e., pulverized coal units, cement kilns, etc.). Using stainless steel tweezers, place each filter in a clean, numbered 150 mm glass petri dish. Bake at 220°F for at least three hours in a drying oven, then immediately transfer to a desiccator to cool.

Weigh the petri dish (plus filter). Weigh a second time, preferably several hours later, to confirm the initial weighing. This is the tare weight used to determine the mass particulate catch on the filter.

The type of filter used is a Gelman type A/E binderless glass fiber filter (142 mm diameter), purchased through Scientific Products.

#### C-3.5 SASS Train Assembly

Transport each separate train component to the sample port area with all sealing caps in place. When removing caps for connection of components, make certain no foreign matter enters the components. If the ambient dust level is high, the train should be covered with plastic drop cloths. Before installing the probe nozzle and with the probe capped, turn on the vacuum pump and leak check the system. Leakage rate should be held to 0.05 cfm at 20 "Hg pump suction. Avoid over-tightening fittings and clamps.

C-3.6 SASS Chemical "Blanks"

- a. Blanks from impingers #2 and #3 should be prepared in the field with the same distilled water used in preparing the impinger solution. To prepare a 1000 ml blank, mix the following ingredients and dilute to 1000 ml with distilled water:
  1. 45.7 gm crystalline  $(\text{NH}_4)_2 \text{S}_2\text{O}_8$
  2. 200 ml 0.1 N  $\text{AgNO}_3$
- b. Blanks of impinger #1 can be prepared in the field with the same  $\text{H}_2\text{O}_2$  and distilled water used for the impinger solution.
- c. Blanks of the wash solutions should be obtained in the field (i.e., IPA, 50:50 meth. chlor. - methanol,  $\text{H}_2\text{O}$ ).
- d. At least one filter blank should be processed in the same manner as sample filters; one blank per test site.
- e. At least one blank sample of the XAD-2 resin should be preserved for each test site.

#### C-4.0 SAMPLING PROCEDURES

The SASS train is basically a high volume Method 5 system modified to collect trace metal and organic compounds which would normally pass through the standard Method 5 train. The major design differences apparent in Figure C-1 are the XAD-2 adsorbent module, multiple cyclone assembly, and new impinger solutions. The SASS train is operated in much the same fashion as a Method 5 train, but there are a number of modifications as discussed below.

##### C-4.1 Sample Flow and Isokinetic Conditions

To preserve the cyclone "cut-off" points, the sampling flow rate is adjusted to maintain approximately 4.0 awcfm (actual wet cubic feet per minute) at the required 400°F cyclone oven temperature conditions. Since isokinetic sampling is also still required, both these constraints are satisfied to the highest degree possible by selecting the optimum probe nozzle diameter.

After stack velocities, temperatures, and oxygen levels are established by the preliminary stack traverse, the nomogram, Section C-5, may be used to select the proper nozzle diameter and "rough in" the required sampling rate (but see STEP 5 below). However, if stack conditions are encountered that are not covered by the nomogram, the following computational procedure may be used for each sampling location.

##### EQUATIONS:

$$d = 0.1192 \sqrt{T_s/V_s} \quad (1)$$

$$Q_{cy} = 281.4 (V_s) (d^2)/T_s \quad (2a)$$

$$V_s = [Q_{cy} (T_s)]/[281.4 (d^2)] \quad (2b)$$

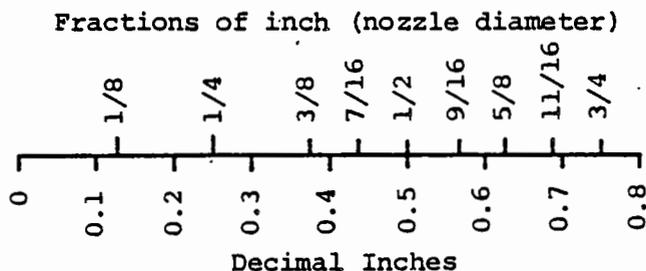
$$Q_m = Q_{cy} (T_m/860) [1 - (\%H_2O/100)] \quad (3)$$

$d$  = nozzle diameter (inches)  
 $T_s$  = stack temperature ( $^{\circ}R$ )  
 $V_s$  = stack velocity (ft/sec)  
 $Q_{cy}$  = sample flow rate at cyclones (awcfm)  
 $Q_m$  = sample flow rate at meter (adcfm)  
 $T_m$  = meter temperature ( $^{\circ}R$ )  
 $\%H_2O$  = sample moisture content (% by volume)

These equations are valid only when an oven (cyclone) temperature of  $400^{\circ}F$  is maintained and when the pressure of the stack and dry test meter are roughly the same (i.e.,  $\pm 1$ " Hg).

STEP 1:

Select the nozzle size closest to the value computed from Equation (1). Use this value in the following step:



STEP 2:

Compare the cyclone flow rate from Equation (2a) to the desired rate of 4.0. If the values compare to within  $\pm 10\%$ , proceed to next step. Otherwise, calculate a stack velocity from Equation (2b) using a value for  $Q_{cy}$  which is within 10% of 4.0 [i.e., use 3.6 or 4.4, whichever is closest to the value obtained from Equation (2a)]. This calculated stack velocity should be within 10% of the actual stack velocity. If not, stack conditions are very unusual and greater than 10% "tolerances" are necessary (i.e., deviations from isokinetic conditions a/o deviations from 4.0 cfm conditions at the cyclone will be necessary).

STEP 3:

Calculate the meter flow rate from Equation (3) using the cyclone flow determined in the previous step.

STEP 4:

Determine the approximate orifice  $\Delta H$  corresponding to the flow rate from the previous step. Use the nomogram plot of  $\Delta H$  versus flow rate determined experimentally for the particular control box and orifice. This is based on the mid-size orifice of the three in the control box.

STEP 5:

The value of  $\Delta H$  determined in the previous step (or from the nomograph) will be adequate to "rough in" the flow rate when the SASS train is first turned on. However, as soon as possible, obtain more accurate settings using the actual measured meter temperature and the actual meter flow rate obtained from the meter readout and a stopwatch.

C-4.2 Organic Adsorber Module Operation

When the XAD-2 module is operated "cold" to condense moisture from the sample, the following procedure may be used to transfer condensate from the condensate cup at the base of the module to the condensate collection flask. This is necessary to avoid overfilling the condensate cup which would result in condensate carryover into the impingers.

This transfer procedure can be accomplished without interrupting the sampling. The procedure should be performed frequently at the start of a test until the actual condensate collection rate is established.

STEP 1:

Inspect the condensate collection flask and interconnecting tube to confirm that all fittings are tight.

STEP 2:

Partially close off the large (1/2-inch) ball valve at the inlet to the XAD-2 module until the vacuum gage on the pump increases by about 2 in. of mercury.

STEP 3:

Open the condensate drain valve at the bottom of the module. Since the collecting flask is initially at a higher pressure than the inside of the module, air will flow from the flask into the module (bubbling through the collected condensate) until pressures are equalized.

STEP 4:

After a few seconds, to allow the equilibration of pressures, open the 1/2-inch ball valve. This raises the pressure in the module relative to the collection flask, forcing any condensate into the bottle.

STEP 5:

After all the condensate has been transferred, close the drain valve.

C-4.3 Drierite

See Section C-2.3 for comments on Drierite depletion and renewal (Impinger #4).

C-4.4 Filter Changes

When sampling combustion effluents with high particulate loading, plugging of the filter may occur before adequate sample volume is obtained. In this event, it will be necessary to shut the train down and install a new filter.

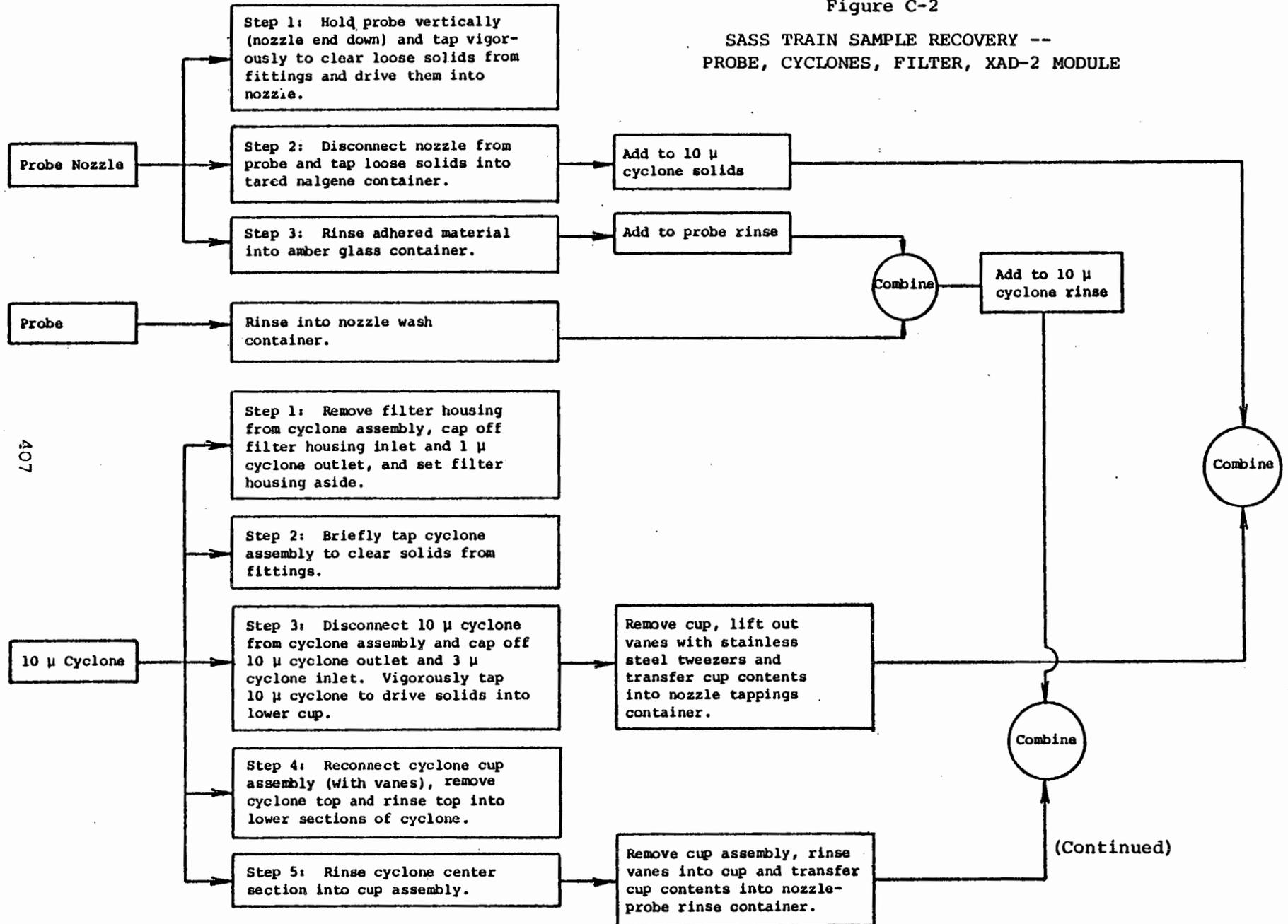
The rate of filter plugging is evident by the gradual increase in sample pump vacuum required to maintain sample flow. To minimize filter changes, the train may be operated with pump vacuums of 15 to 20 "Hg or until desired sample flow cannot be maintained.

#### C- 5.0 TRAIN DISASSEMBLY AND SAMPLE RECOVERY

1. After turning off train and withdrawing probe from stack, open the cyclone oven to expedite cooling (turn oven cooling fan on).
2. Disconnect probe and cap off both probe ends and inlet to 10 $\mu$  cyclone.
3. Disconnect the line joining the cyclone oven to the XAD-2 module at the exit side of the filter and cap off the filter holder exit and the entrance to the joining line which was disconnected from the filter holder exit point.
4. Disconnect the line joining the XAD-2 module to the impinger system at the point where it exits the XAD-2 module. Cap off the exit of the XAD-2 module and the entrance to the joining line leading to the impinger system.
5. Disconnect the line exiting the Drierite impinger at the point where it leaves the impinger and cap off the impinger exit. Discard ice and water from the impinger box to facilitate carrying.
6. Carry the probe, cyclone-filter assembly, XAD-2 module (plus joining line and condensate collection flask) and impinger train (plus joining line) to the clean room for sample recovery. Before entering the clean room, clean off all loose particles from the exterior surfaces of the train components using compressed air, brushes, etc.
7. Procedure for transferring samples from the various portions of the SASS train into storage containers is outlined in the flow diagrams on Figures C-2, C-3, and C-4. Place copies of these diagrams in an easily visible location in the clean room for quick reference during the sample recovery and transfer operations.

Figure C-2

SASS TRAIN SAMPLE RECOVERY --  
PROBE, CYCLONES, FILTER, XAD-2 MODULE



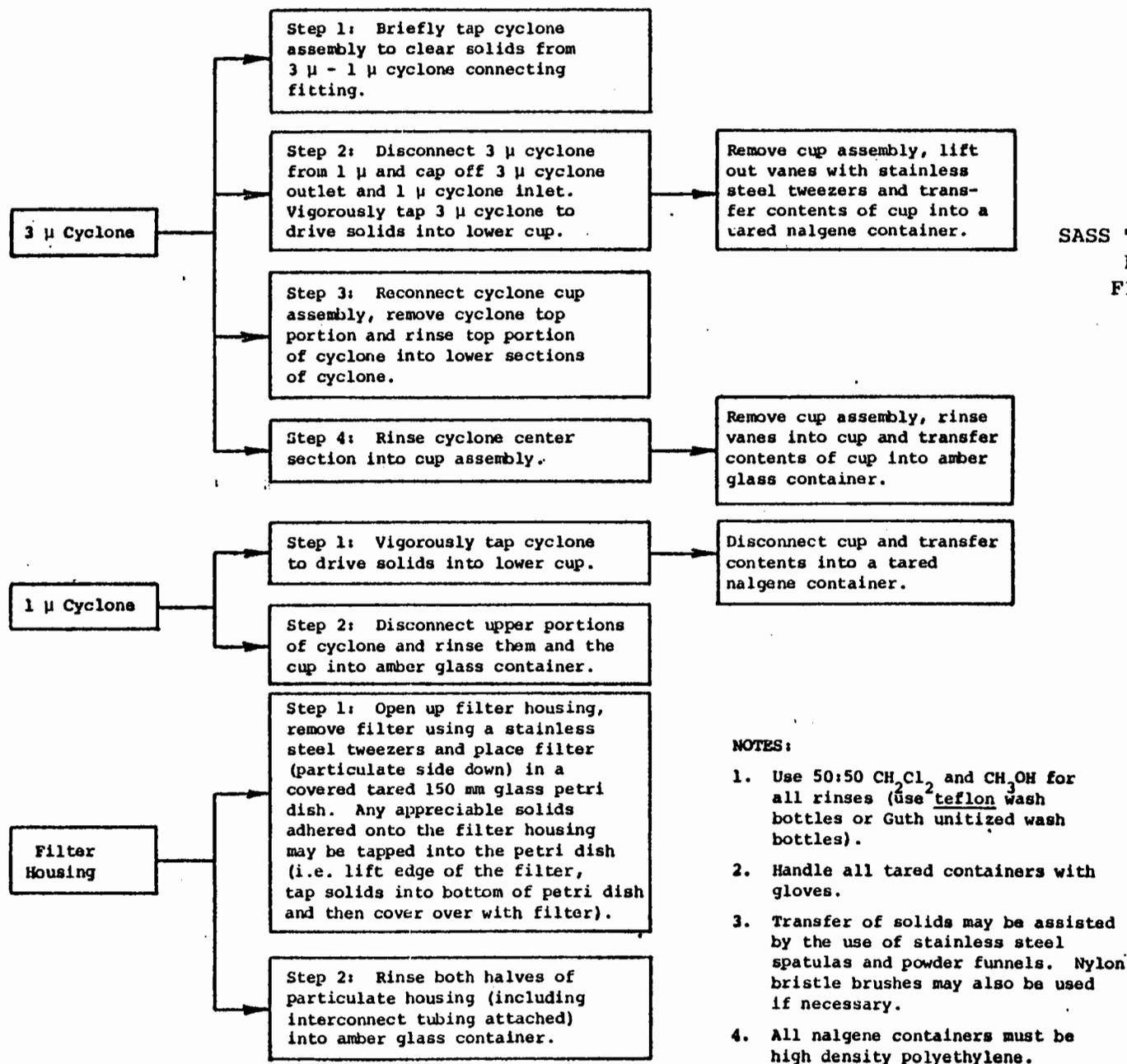
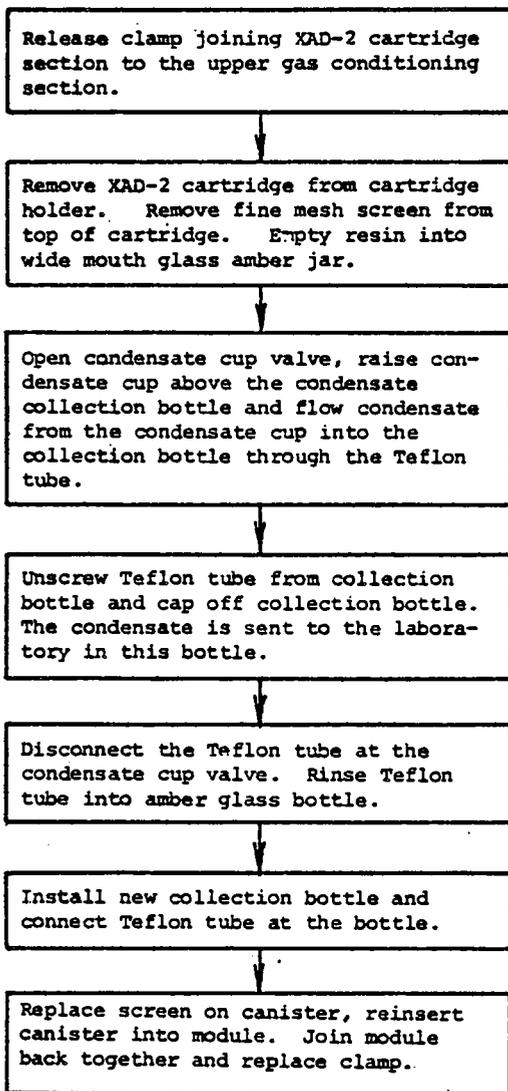


Figure C-2  
(Continued)

SASS TRAIN SAMPLE RECOVERY--  
PROBE, CYCLONES,  
FILTER, XAD-2 MODULE

SASS TRAIN SAMPLE RECOVERY -- XAD-2 MODULE

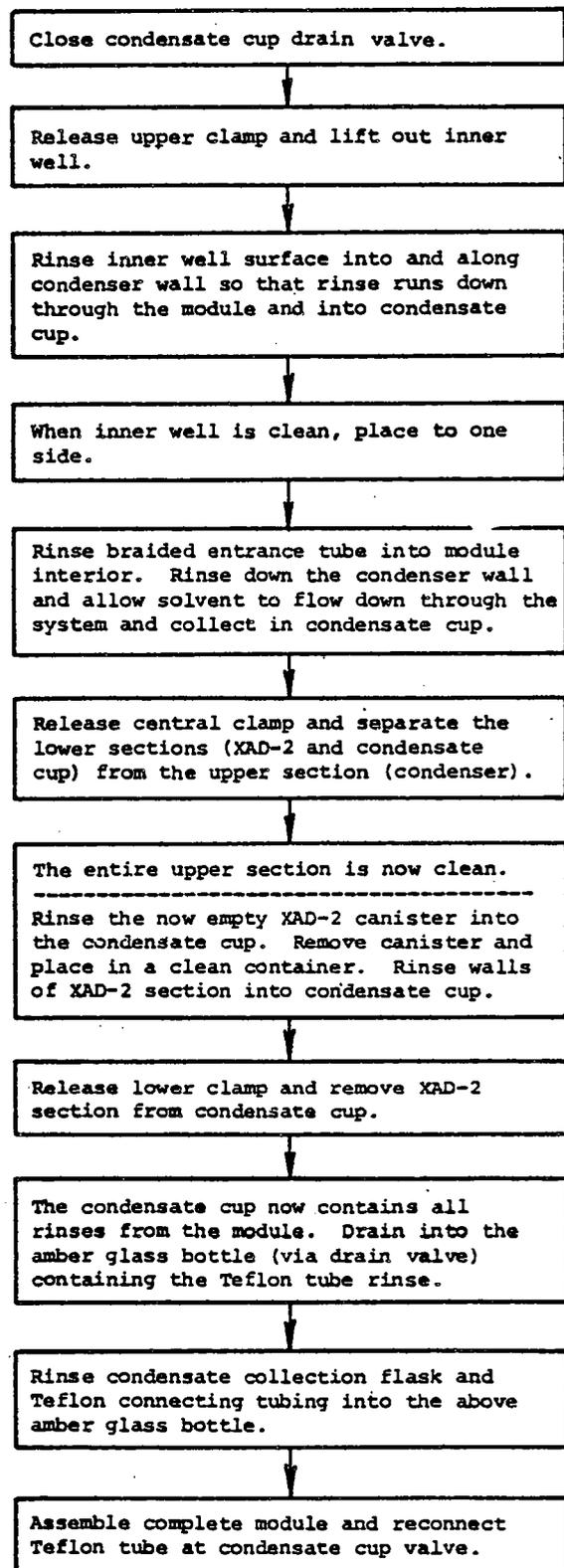
STEP NO. 1, XAD-2  
AND CONDENSATE REMOVAL



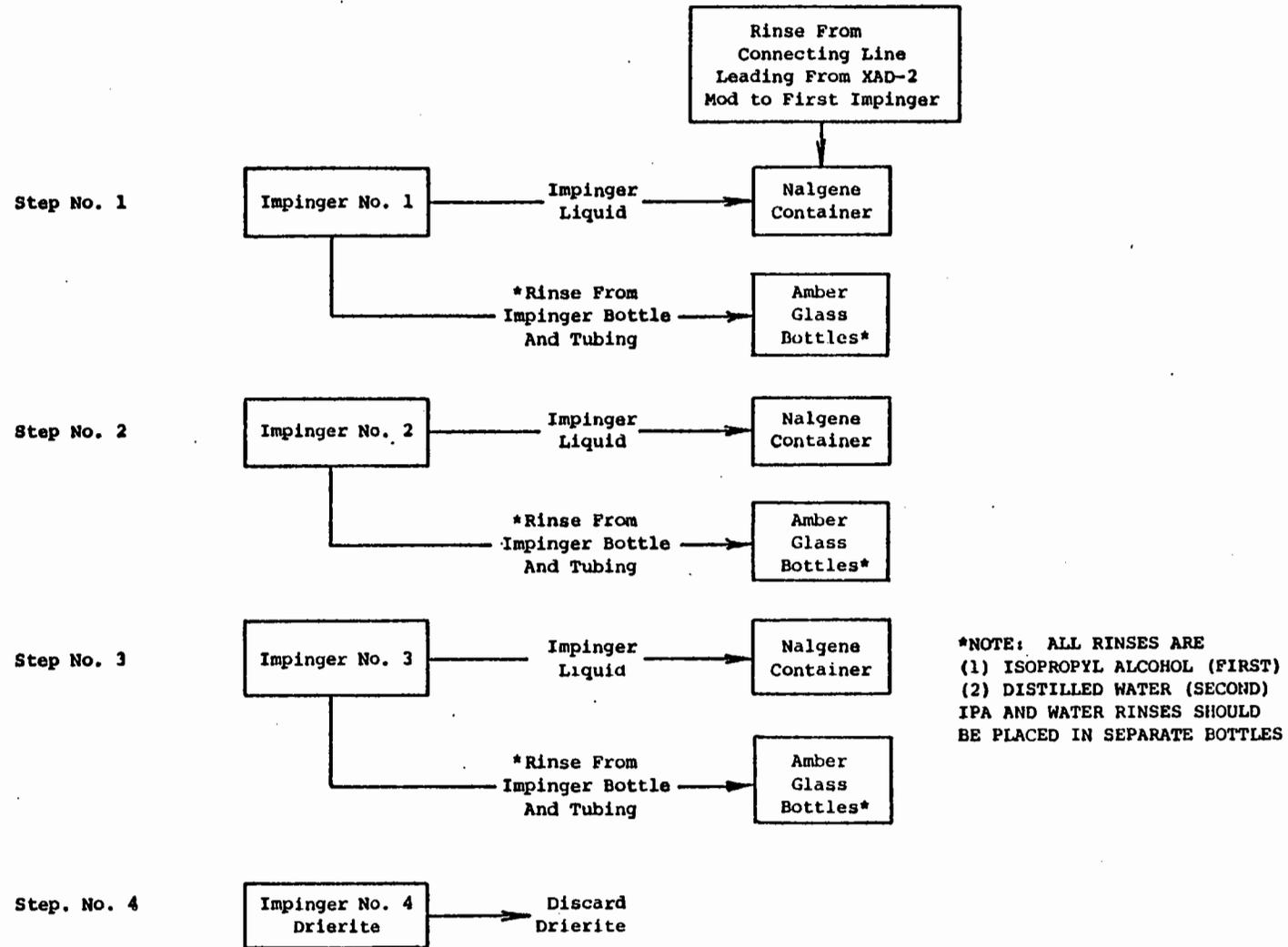
NOTE: USE 50:50  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{OH}$   
FOR ALL RINSES.

Figure C-3.

STEP NO. 2, XAD-2  
MODULE RINSE



### SASS TRAIN SAMPLE RECOVERY -- IMPINGERS



410

Figure C-4.

C-6.0 SUPPLEMENTARY REFERENCE MATERIAL

Physical Properties of SASS Chemicals, Figure C-5

Physical Properties of XAD-2, Table C-3

SASS Train Nomogram, Figure C-6

Miscellaneous Data, Table C-4

PHYSICAL CONSTANTS OF ORGANIC COMPOUNDS

No.	Name	Synonyms and Formula	Mol. wt.	Color, crystalline form, specific rotation and $\lambda_{max}$ (log $\epsilon$ )	m.p. °C	b.p. °C	Density	$n_D$	Solubility						Ref.
									w	al	eth	ace	bz	other solvents	
Q m252	—dichloro—	Methylenechloride. CH <sub>2</sub> Cl <sub>2</sub> .	84.93	$\lambda^{max}$ < 200	-95.1	40 <sup>100</sup>	1.3266 <sup>20</sup>	1.4242 <sup>20</sup>	$\delta$	$\infty$	$\infty$	.....	.....	.....	B1 <sup>2</sup> , 13
Q p1588	2-Propanol*	Isopropanol. Isopropyl alcohol. CH <sub>3</sub> CH(OH)CH <sub>3</sub> .	60.11	$\lambda^{max}$ 181 (2.79)	-89.5	82.4 <sup>100</sup>	0.7855 <sup>20</sup>	1.3776 <sup>20</sup>	$\infty$	$\infty$	$\infty$	s	v	.....	B1 <sup>2</sup> , 1439
Q m349	Methanol*	Carbinol. Methyl alcohol. Wood alcohol. CH <sub>3</sub> OH	32.04	$\lambda^{max}$ 183.3 (2.18)	-93.9	64.96 <sup>100</sup> 15 <sup>73</sup>	0.7914 <sup>20</sup>	1.3288 <sup>20</sup>	$\infty$	$\infty$	$\infty$	$\infty$	v	chl s	B1 <sup>2</sup> , 1147

PHYSICAL CONSTANTS OF INORGANIC COMPOUNDS

No.	Name	Synonyms and Formulae	Mol. wt.	Crystalline form, properties and index of refraction	Density or spec. gravity	Melting point, °C	Boiling point, °C	Solubility, in grams per 100 cc		
								Cold water	Hot water	Other solvents
a236	Ammonium peroxydisulfate	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	228.18	col. monoc. 1.498, 1.502, 1.587	1.982	d 120	.....	58.2°	v s	.....
b63	Hydrogen oxide	Water. H <sub>2</sub> O	18.0153	col liq or hex cr. liq 1.333, sol 1.309, 1.313	1.000 <sup>1</sup>	0.000	100.000	.....	.....	= al
b64	Hydrogen oxide, per	H <sub>2</sub> O <sub>2</sub>	34.01	col liq; 1.414 <sup>18</sup>	1.4422 <sup>18</sup>	-0.41	150.2 <sup>100</sup>	=	.....	s al, eth; i pet eth
a119	Nitric acid	HNO <sub>3</sub>	63.01	col liq, corr. pois. 1.397 <sup>14</sup>	1.5027 <sup>18</sup>	-42	83	=	=	d al, viol; s eth
a167	Silver nitrate	AgNO <sub>3</sub>	169.87	col, rhomb. 1.729, 1.744, 1.788	4.352 <sup>18</sup>	212	d 444	122°	952 <sup>100</sup>	s eth, glyce; v al s abs al

Figure C-5. Physical properties of SASS chemicals.

TABLE C-3. XAD-2 RESIN

XAD-2 is available from:

Fluid Process Department  
Rohn and Haas  
Philadelphia, Pa.

A contact for questions is:

Mr. Charles Dickert  
(215) 592-3000

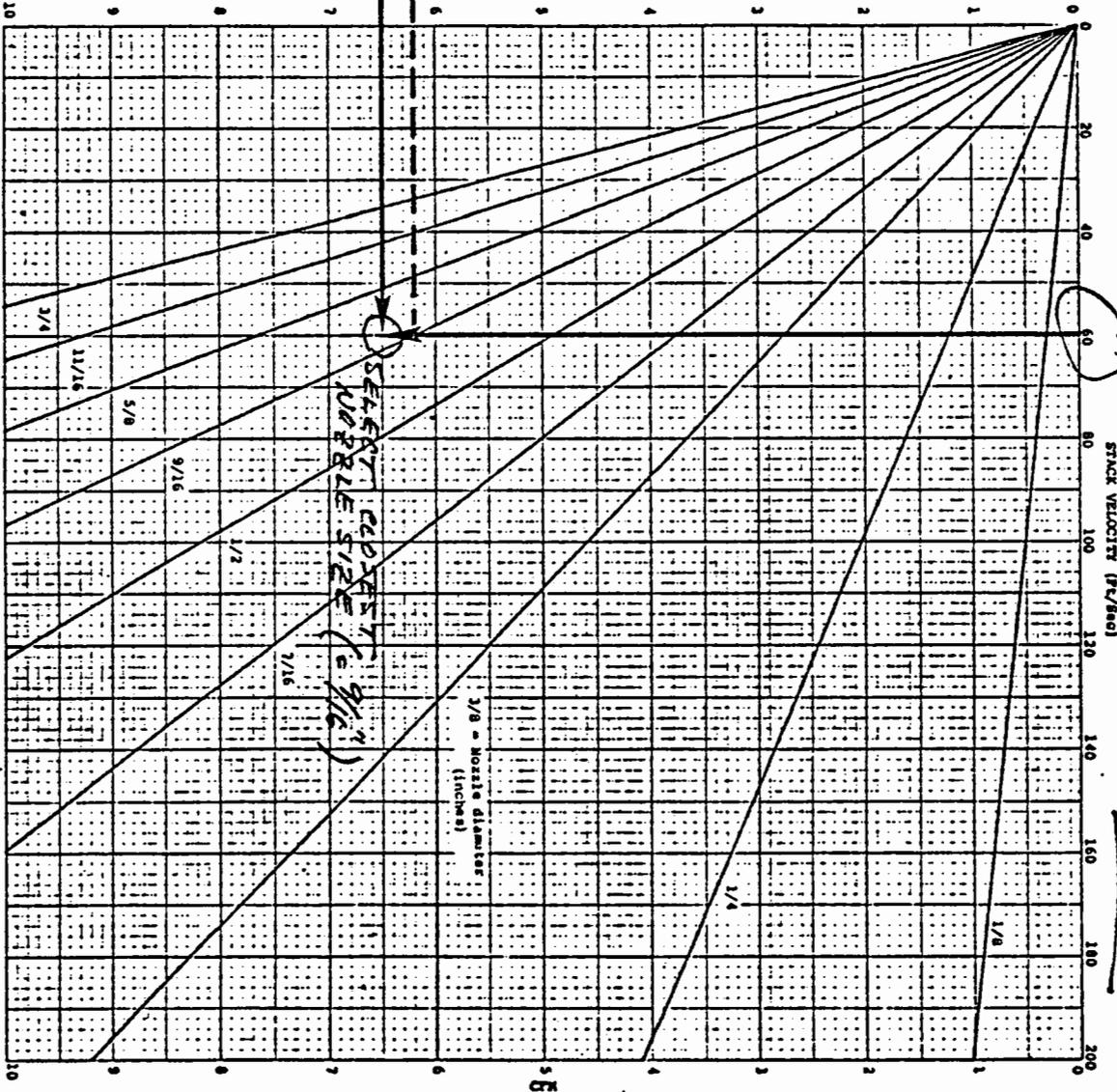
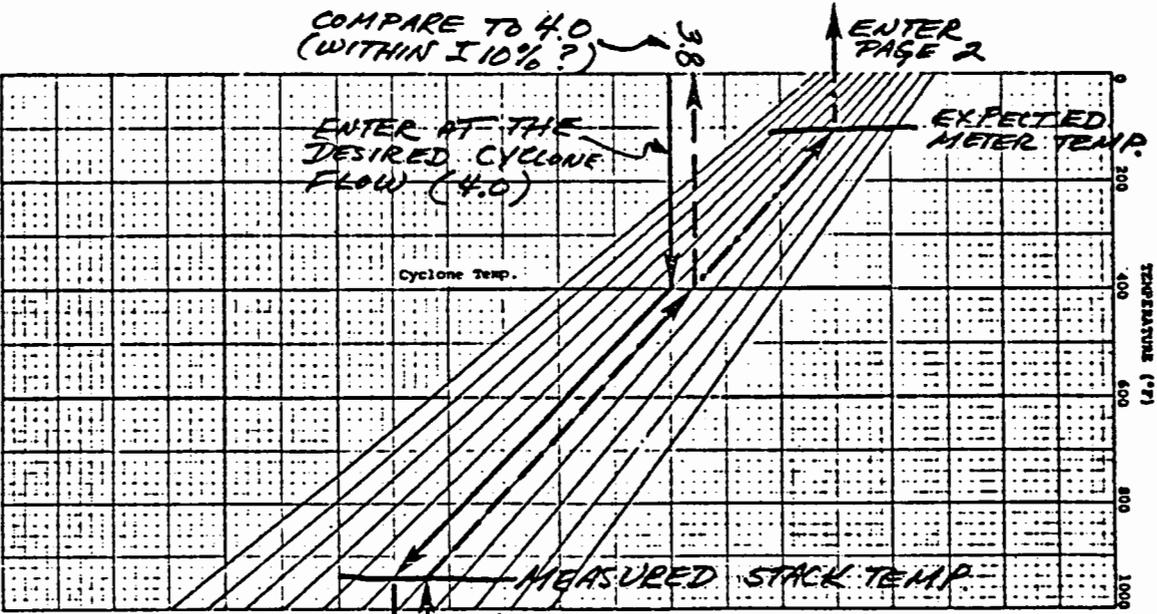
The material is a styrene/divinylbenzene copolymer and the material is supplied wet with a salt solution.

Some relevant parameters are:

mesh range:	20-50
surface area:	300-350 m <sup>2</sup> /g
avg. pore dia.:	90A
specific density:	1.02 g/cc
bulk density:	0.4 g/cc
pore volume:	0.85 cc/g

Costs were \$96.50/cu. ft.

<i>Property</i>	<i>Amberlite XAD-2</i>
Appearance	Hard, Spherical opaque beads.
Solids	51 to 55
Porosity (ml.pore/ml.bead--dry basis)	0.40 to 0.45
Surface Area (m. <sup>2</sup> /g.--dry basis)	330
Effective Size (mm.)	0.30 to 0.45
Harmonic Mean Particle Size (mm.)	0.45 to 0.60
Average Pore Diameter (Å--dry basis)	90
True Wet Density indistilled water (g./ml.)	1.02
Skeletal Density (g./ml.)	1.07
Bulk Density (lbs./ft. <sup>3</sup> )	40 to 44
(g./cc.)	0.64 to 0.70



ENTER AT STACK MEASURED VELOCITY

PAGE 1

Figure C-6. SASS operating nomogram.

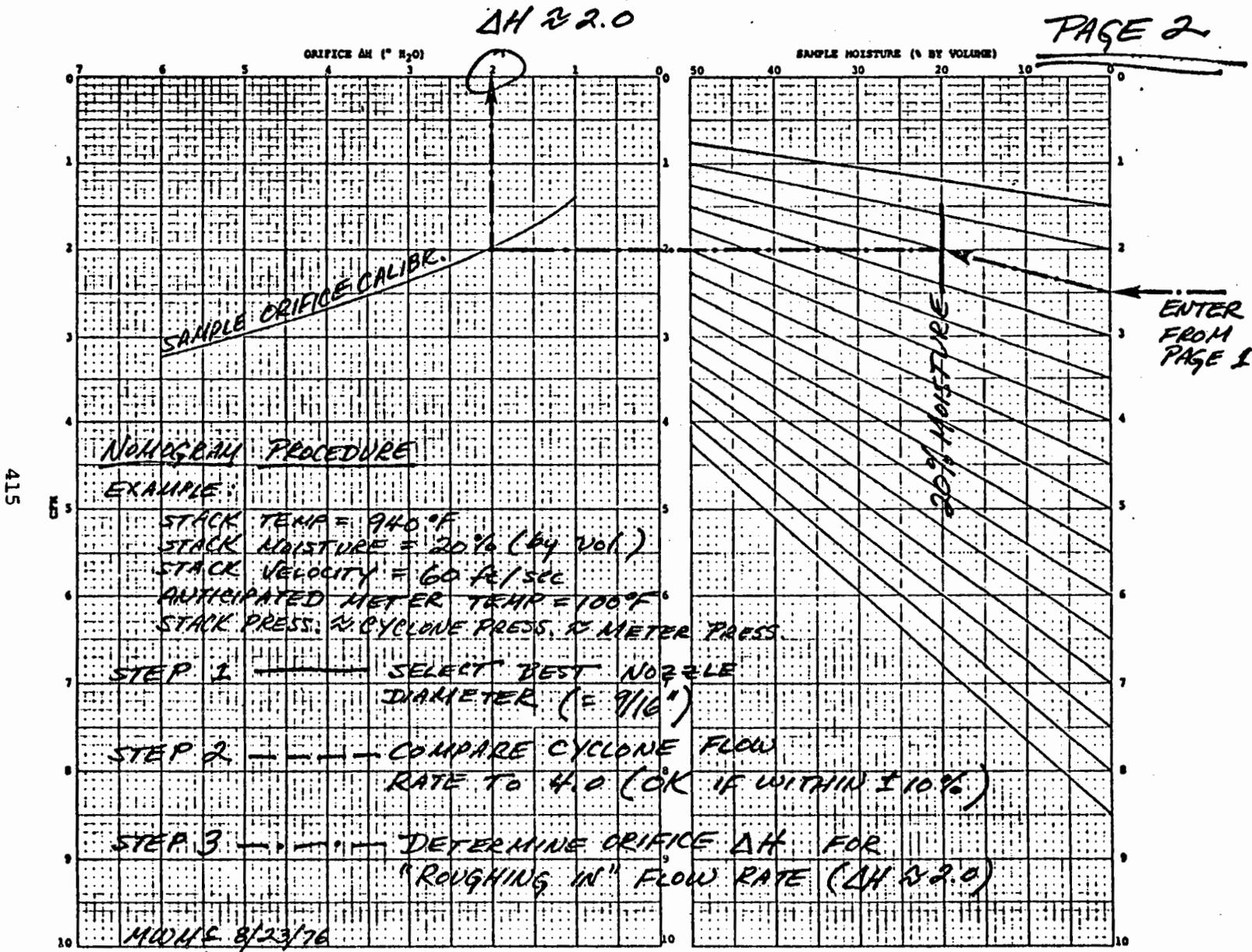


Figure C-6. (Continued) SASS operating nomogram.

TABLE C-4. MISCELLANEOUS DATA

Cyclone cup capacities:  $3\mu$  and  $10\mu = 370$  cc;  $1\mu = 20$  cc

XAD-2 canister volume = 402 cc

S-type pitot tube factor =  $0.85 \pm 0.02$

Screen for XAD-2 canister:

316 stainless steel

80 mesh x 0.055 wire diameter

Purchase from:

Cambridge Wire Cloth Co.

3219 Glendale Blvd

Los Angeles, California

(213) 660-0600

Condensate container volume = 700 cc

XAD-2 module temperature =  $68^{\circ}\text{F}$  ( $20^{\circ}\text{C}$ )

## C-7.0 SAMPLE PREPARATION AND ANALYSIS

Samples were analyzed by Calspan Corp., Buffalo, NY, by atomic absorption, gas chromatography and wet chemistry. Spark source mass spectrographic (SSMS) analyses were performed by Commercial Testing and Engineering, Golden, CO, as a subcontract to Calspan's work. Calspan and CTE analyzed preselected samples that include base samples, blanks, and duplicates. Additional samples were submitted to Battelle Memorial Institute, Columbus, OH for analysis of POM by gas chromatography/mass spectrometry.

### C-7.1 Sample Size

The sample size required for analysis is dependent on how much sample can be obtained from the SASS train. Table C-5 lists the detection limit and sensitivity for all sample components to be analyzed. For metal analysis, 200 ml of impinger liquids are necessary. For solid samples, 4 to 5 grams are necessary. Analysis for chloride, fluoride, sulfate, and nitrate requires up to 200 ml of liquid sample and 5 grams of solid sample. PCB and POM analysis requires 10 to 50 grams of solids and as much liquid as can be obtained (> 500 ml). Additional sample is required for SSMS analysis.

The sample amounts given are desired amounts. Analysis can be achieved on much smaller samples but with a sacrifice in detection capability for desired components. The detection of individual components, however, cannot be greater than the detection limits and sensitivities given in the table. Detection limits may also be higher for certain types of sample matrix.

### C-7.2 Sample Preparation

Analysis of SASS train samples involves pretreatment of the samples after collection to place them in a form suitable for chemical analysis. Atomic absorption requires that each sample be predissolved or be in the liquid phase. The technique for solubilization of the

TABLE C-5. DETECTION LIMITS AND SENSITIVITY VALUES

Pollutant	Detection Limit		Sensitivity	
	Solids ( $\mu\text{g/g}$ ) *	Liquids ( $\mu\text{g/ml}$ )	Solids ( $\mu\text{g/g}$ ) *	Liquids ( $\mu\text{g/ml}$ )
Antimony	10	0.2	25	0.5
Arsenic	0.10	0.002	0.5	0.01
Barium	1.5	0.03	20	0.4
Beryllium	0.25	0.005	1.25	0.025
Cadmium	0.10	0.002	1.25	0.025
Calcium	0.15	0.003	4	0.08
Chromium	1.0	0.02	5	0.1
Cobalt	1.5	0.03	10	0.2
Copper	0.5	0.01	5	0.1
Iron	1.0	0.02	5	0.1
Lead	2.5	0.05	25	0.5
Manganese	0.5	0.01	2.5	0.05
Mercury	0.01	0.0002	0.05	0.001
Nickel	1.0	0.02	7.5	0.15
Selenium	0.1	0.002	0.1	0.002
Tellurium	10	0.2	50	1
Tin	5	0.1	200	4
Titanium	15	0.3	100	2
Vanadium	10	0.2	40	0.8
Zinc	0.25	0.005	1	0.02
Chloride	5.0	1	250	5
Fluoride	5	0.1	12.5	0.25
PCB	0.1	0.002	0.50	0.01
POM	50	0.1	100	2
Sulfates	50	1	250	5
Nitrates	5	0.1	10	0.2

\*Values given are for 1 gram of material dissolved in 50 ml of solution.

metals is based on methods utilized by the National Bureau of Standards (Ref. C-2) for solubilizing both highly organic materials such as coal and inorganic materials such as fly ash prior to sample analysis. The outlined techniques allow for wet chemical ashing of material that prevents loss of volatile elements like mercury, arsenic, and selenium. The methods given use concentrated mineral acids, and a strong oxidizing acid, perchloric ( $\text{HClO}_3$ ), to decompose organic materials.

One gram of highly organic material (coal, tar residue, fuel oil, etc.) is transferred to a Teflon beaker. The sample is slowly digested for several hours in 25 ml of  $\text{HNO}_3$  and cooled. A mixture of 5 ml of HF and 10 ml of  $\text{HClO}_4$  is added and the digestion is continued at low heat. Extreme care is necessary, because excessive temperatures can cause decomposition and explosion. Digestion is continued until all carbonaceous material has been destroyed. The solution is then transferred to a 50 ml volumetric flask and diluted to a calibrated volume.

Low organic samples (fly ash, bottom ash, cement kiln dust, etc.) are accurately weighed to one gram in a Teflon beaker. A mixture of 5 ml of  $\text{HNO}_3$  and 5 ml of HF is added. The beaker is covered and the sample digested for one hour. After complete cooling, 10 ml of  $\text{HClO}_4$  is added and the digestion is continued until all carbonaceous material has been destroyed. The cover is then removed and the sample evaporated to dryness and baked until the solids turn brown around the edges. A mixture of 2 ml of HCl and 35 ml of distilled water is added and the solution heated slightly until all solids dissolve. The solution is then transferred to a 50 ml volumetric flask and diluted to a calibrated volume.

Liquid samples from the SASS train are stabilized with 1 ml of concentrated nitric acid to every 200 ml of impinger liquid. Whenever possible, liquids are concentrated by boiling to one-half their received volume to concentrate trace elements.

Both predissolved and concentrated liquids are analyzed using atomic absorption spectroscopy using the most sensitive aspiration techniques available. Analysis for both PCB and POM will involve extraction and concentration prior to analysis. The PCB and POM are coextracted by liquid-liquid or liquid-solid extraction.

Solid samples (~ 50 grams) are extracted with benzene using a Soxhlet extractor. The extract is concentrated using a Kuderna-Danish evaporator to reduce the extract volume to 10 ml. Aliquots 2 to 5 µl are injected directly into a gas chromatograph for PCB and POM analysis after liquid-solid column separation and clean-up.

Both POM and PCB, after extraction with benzene, are isolated as a class using adsorption chromatography by a technique called the Rosen separation (Refs. C-3 and C-4). This technique entails adsorption of the total sample on a silica gel column. The initial effluent from the column when washed with pentane will contain an aliphatic hydrocarbon fraction. The aromatic hydrocarbon fraction is eluted with benzene. The benzene fraction which contains all POM and PCB is analyzed using gas chromatography employing FID and EC detectors.

Detection and measurement of POM and PCB are accomplished by using a gas chromatograph employing a flame ionization detector (FID) and an electron capture (EC) detector equipped with Ni-63 source. Confirmation is performed by comparing to POM standards and PCB standards of known concentration and literature relative retention time data.

### C-7.3 Analysis Procedures

Analysis for chlorine, fluorine, nitrates, and sulfates all involve wet chemical processing prior to actual measurement. Since all chlorides, nitrates and most sulfates are water soluble, they can be extracted from solid samples using a Soxhlet extractor. The extraction scheme to be used has been effectively used by the Bay Area Air Pollution Control District, San Francisco (Refs. C-5 and C-6).

Fluorides, however, are not sufficiently soluble to allow for effective aqueous extraction. Solid samples are fused with sodium hydroxide to convert all fluorides to soluble sodium fluoride. The fused melt is dissolved in 4 M HCl and the resulting liquid analyzed as a soluble fluoride.

Liquid samples analyzed for chlorine, fluorine, nitrates, and sulfates are analyzed directly by techniques specific for each anion.

Solubilized chloride is analyzed by adding dilute mercuric nitrate solution to an acidified sample in the presence of mixed diphenylcarbozone-bromophenol blue indicator. The end point of the titration is the formation of a blue-violet mercury, diphenylcarbozone complex (Ref. C-7).

An alternative method involves direct measurement of chloride with a specific ion electrode. Both methods are used and checked to obtain the best sensitivity on the submitted samples.

Analysis for fluoride in liquid samples or solubilized fusion products is performed by prior Bellack Distillation to remove interfering substances. After distillation, the fluoride is determined potentiometrically using a selective ion fluoride electrode (Ref. C-8).

The analysis for nitrate is based upon the reaction of the nitrate ion with brucine sulfate in a 13N  $H_2SO_4$  solution at 100°C. The color of the resulting complex is measured at 410 nm (Ref. C-8).

Sulfate analysis is performed by converting sulfate ion to barium sulfate suspension under controlled conditions. The resulting turbidity is determined on a spectrophotometer and compared to a curve prepared from standard sulfate solutions (Ref. C-8).

Metal analyses are performed on liquid and solid samples after pretreatment and solubilization of materials as outlined earlier. A Perkin-Elmer Model 460 atomic absorption spectrometer with microcomputer electronics is used in conjunction with conventional aspiration and time integration techniques. The Model 460 is a relatively new, highly sensitive instrument that allows accurate measurement of metal concentrations. In addition, conventional hollow cathode source lamps, electrodeless discharge lamps (EDL), are available for lead, mercury, arsenic, and selenium. These special lamps are more stable and provide for more initial energy to allow accurate detection of difficult-to-analyze elements.

Mercury is analyzed by the cold vapor technique developed by Hatch and Ott (Ref. C-9). Arsenic and selenium are to be analyzed by conversion of these elements with hydrogen to arsenic hydride and selenium hydride vapor. Each of the vapor techniques allows for low-level detection and quantization for each of these elements.

A listing of the detection limits and sensitivity for each element in liquid and solid samples is given in Table C-5. In the table, detection limit is defined as the concentration that produces a signal equivalent to twice the magnitude of the background. Sensitivity is defined as the concentration in micrograms per milliliter of solution to produce a one percent change in absorption or one percent change in the recording chart readout.

The detection limits for solid samples are based on a one gram sample dissolved or extracted into 50 ml volumes of analysis solution. Each value given is conservative and is based on the possibility of interference between components present. If the sample is relatively "clean", i.e., no interfering or high background substances, detection limits may be even lower.

Polychlorinated biphenyls (PCB) and polycyclic organic materials (POM) are analyzed using a Hewlett-Packard Model 5700 gas chromatograph equipped with a flame ionization and an electron capture detector. The electron capture detector contains a radioactive source, Ni-63, and is highly sensitive to chlorinated and highly conjugated organic compounds. The flame ionization detector is sensitive to all hydrocarbons. The gas chromatographic column used in separation of components is four feet long, packed with a substrate coated with 2.5% by weight of a liquid crystal.

The analysis column used is the one suggested by Janini (Ref. C-10) specifically for POM separations. Gas chromatographic column parameters are summarized below:

Column length:	4' x 1/8" OD
Column material:	Stainless steel
Stationary phase:	2.5% BMBT*
Support:	Chromosorb W HP, 100/120 mesh
Flow:	40 ml/min helium
Temperature:	235°C, isothermal

\*N, N-bis [p-methoxybenzylidene]- a, a' - bi-p-toluidine

The gas chromatograph is operated in the isothermal temperature mode. This is necessary due to the extreme temperature sensitivity of the electron capture detector. Any attempt to temperature program would result in a gross baseline drift.

Alternate chromatographic methodology and retention time data has been obtained from an analytical method of Gouw, et al. (Ref. C-11) and Lao, et al. (Ref. C-12). Literature column retention time data is available for all the desired POM listed in the request for proposal with the exception of the dibenzo[c,g]carbazole.

Four of the eight POM are commercially available and are used in fixing retention times and in calibrating the instrument response factors for the various components. The 7,12 dimethylbenz[a]anthracene, benzo[a]pyrene, dibenz[a,b]anthracene, and 3-methylcolanthrene POM are obtained from the Eastman Kodak Company in the pure form. The other POM listed are not available from any commercial source known, so literature relative retention time data of the other POM is utilized to fulfill analyses requirements.

The quantization of total POM is made by taking the total area of all POM and reporting the response area as if it were 9-methylanthracene ( $C_{15}H_{12}$ , Mol. Wt. 192.26). If PCB is found to be present, the concentration is subtracted from the total hydrocarbon response area. The standards used in measuring PCB response and retention times are known (Aroclor) standards. The eight individual POM specifically required for identification are analyzed separately, and reported as such. The eight materials are also included in the total POM reported values.

#### C-7.4 Quality Control

Quality control is maintained by two principal modes. Throughout this study a number of samples are analyzed in duplicate to assure precision of results. More importantly, however, carefully prepared analytical standards and blanks are utilized in preparing suitable calibration curves, thereby assuring accurate measurement of data. To test the accuracy, known additions are made to samples that can be obtained in large enough quantity to test for quantitative recoveries.

REFERENCES FOR APPENDIX C

- C-1 Hamersma, J. W., Reynolds, S. L., and Maddalone, R. F., "IERL-RTP Procedures Manual: Level I Environmental Assessment," EPA Report EPA-600/2-76-160a, NTIS No. PB 257 850, June 1976.
- C-2 Private communication with Theodore C. Rains, U. S. Dept. of Commerce, National Bureau of Standards, Washington, DC (1974).
- C-3 Rosen, A. A., and Middleton, F. M., Anal. Chem. 27, 790 (1955).
- C-4 Moore, G. E., Thomas, R. S., and Monkman, J. L., J. Chromatogr. 26, 456 (1967).
- C-5 Levaygi, D. A., et al., J. Air Pollution Association 26 (6), 554 (1976).
- C-6 Sandberg, J. S., et al., J. Air Pollution Association 26 (6), 559 (1976).
- C-7 ASTM Standards, Part 23, Water & Atmospheric Analysis, p. 273, Method 512-67, Referee Method A (1973).
- C-8 Methods of Chemical Analysis of Waters and Wastes, US EPA, EPA-625/6-74-003 (1974).
- C-9 Hatch, W. R., and Ott, W. L., "Determination of Sub-Microgram Quantities of Mercury in Solution by a Flameless Atomic Absorption Technique," Atomic Absorption Newsletter 6, 101 (1967).
- C-10 Janini, G. M., Hohnston, R., and Zrelinski, W., Anal. Chem. 47, (1975).
- C-11 Gouw, T. H., Whittemore, I. M., and Jentoft, R. E., "Capillary Column Separation of Various Poly Cyclic Aromatic Materials," Anal. Chem. 42, 1394 (1970).
- C-12 Lao, R. C., Thomas, H., Oja, H., and Dubois, L., "Application of Gas Chromatograph-Mass Spectrometer Data Processor Combination to the Analysis of the Polycyclic Hydrocarbon Content of Airborne Pollutants," Anal. Chem. 45, 908 (1973).

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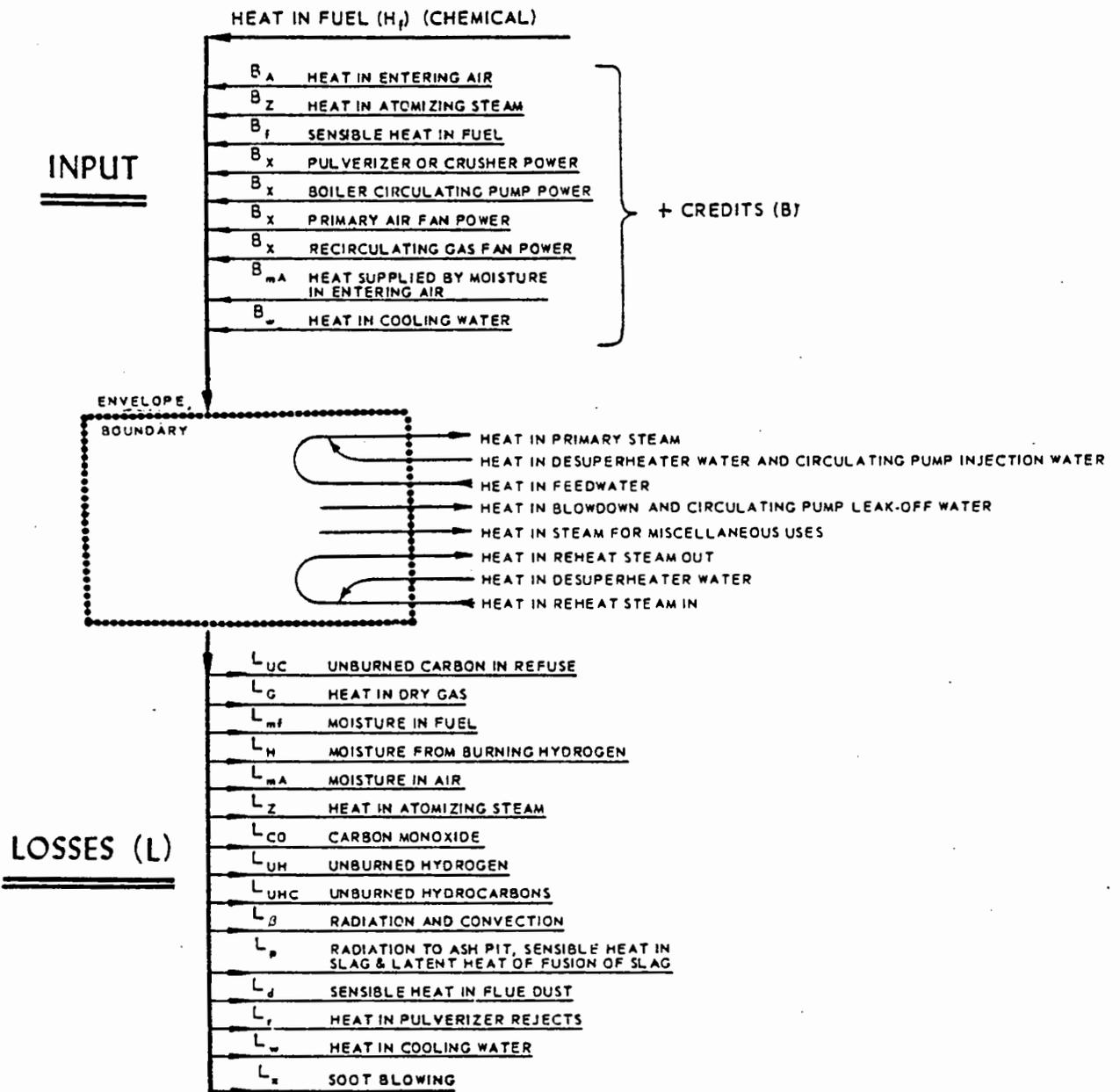
## APPENDIX D

### EFFICIENCY MEASUREMENTS

#### D.1 EFFICIENCY

Unit efficiencies for boilers are calculated and reported according to the ASME Power Test Codes. These codes present instructions for two acceptable methods of determining thermal efficiency. One method is the direct measurement of input and output and requires the accurate measurement of the quantity and high-heating value of the fuel, heat credits and the heat absorbed by the working fluids. The second method involves the direct measurements of heat losses and is referred to as the heat loss method. This method requires the determination of losses, heat credits and ultimate analysis and high-heat value of the fuel. Some of the major heat losses include losses due to heat in dry flue gas, losses due to fuel moisture content, losses due to combustible material in refuse and flue gas, and radiation losses. Heat credits are defined as those amounts added to the process in forms other than the chemical heat in the fuel "as fired". These include quantities such as sensible heat in the fuel, heat in the combustion air, and heat from power conversion in a pulverizer or fan. The relationships between input, output, credits and losses for a steam generator are illustrated in Figure D-1.

KVB's experience has shown the heat-loss efficiency determination method to be the most reliable when working with industrial combustion devices. However, methods developed for boilers must be modified for other types of industrial equipment. Accurate fuel input measurements are rarely possible on industrial units due to the lack



$$\text{OUTPUT} = \text{INPUT} - \text{LOSSES}$$

$$\text{DEFINITION: EFFICIENCY (PERCENT)} = \eta_g (\%) = \frac{\text{OUTPUT}}{\text{INPUT}} \times 100 = \frac{\text{INPUT} - L}{H_f + B} \times 100$$

$$\text{HEAT BALANCE: } H_f + B = \text{OUTPUT} + L \text{ OR } \eta_g (\%) = \left[ 1 - \frac{L}{H_f + B} \right] \times 100$$

Figure D-1. Heat balance of steam generator.

of adequate instrumentation thus making the input-output method undesirable. The accuracy of the efficiency based on the heat loss method is determined primarily by the accuracy of the flue gas temperature measurement immediately following the last heat removal station, the stack gas excess  $O_2$  level, the fuel analysis, the ambient temperature, and proper identification of the combustion device external surfaces (for radiation losses). Determination of the radiation and other associated losses may appear to be a rather imposing calculation but in practice it can be accomplished by utilizing standard efficiency calculation procedures. Inaccuracies in determining efficiency occasionally occur even with the heat loss method primarily because of out-of-calibration unit instrumentation such as the stack gas exit temperature. However, this problem has been resolved by KVB test engineers through the use of portable instrumentation and separate temperature readings.

The abbreviated efficiency test procedure which considers only the major losses and the chemical heat in the fuel as input will be followed. Tables D-1 and D-2 are the ASME Test Forms for Abbreviated Efficiency Tests on steam generators which exemplify the type of forms to be used for recording the necessary data and performing the required calculations.

These efficiency procedures have been developed primarily for steam generators and were used for steam generators tested in this program. For other industrial combustion devices, there are no set standards for efficiency computation. Methods for efficiency determination for those devices were developed separately after inspection of the devices and based on discussions with the device operators, and were based primarily on stack loss calculations.

TABLE D-1

SUMMARY SHEET

ASME TEST FORM  
FOR ABBREVIATED EFFICIENCY TEST

PTC 4.1-a (1964)

		TEST NO	BOILER NO.	DATE
OWNER OF PLANT		LOCATION		
TEST CONDUCTED BY		OBJECTIVE OF TEST		DURATION
BOILER MAKE & TYPE		RATED CAPACITY		
STOKER TYPE & SIZE				
PULVERIZER, TYPE & SIZE		BURNER, TYPE & SIZE		
FUEL USED	MINE	COUNTY	STATE	SIZE AS FIRED
PRESSURES & TEMPERATURES			FUEL DATA	
1	STEAM PRESSURE IN BOILER DRUM	psia		COAL AS FIRED PROX. ANALYSIS
2	STEAM PRESSURE AT S. H. OUTLET	psia	37	MOISTURE
3	STEAM PRESSURE AT R. H. INLET	psia	38	VOL MATTER
4	STEAM PRESSURE AT R. H. OUTLET	psia	39	FIXED CARBON
5	STEAM TEMPERATURE AT S. H. OUTLET	F	40	ASH
6	STEAM TEMPERATURE AT R. H. INLET	F		TOTAL
7	STEAM TEMPERATURE AT R. H. OUTLET	F	41	Btu per lb AS FIRED
8	WATER TEMP. ENTERING (ECON.) (BOILER)	F	42	ASH SOFT TEMP.* ASTM METHOD
9	STEAM QUALITY % MOISTURE OR P. P. M.			COAL OR OIL AS FIRED ULTIMATE ANALYSIS
10	AIR TEMP. AROUND BOILER (AMBIENT)	F	43	CARBON
11	TEMP AIR FOR COMBUSTION (This is Reference Temperature) †	F	44	HYDROGEN
12	TEMPERATURE OF FUEL	F	45	OXYGEN
13	GAS TEMP. LEAVING (Boiler) (Econ.) (Air Htr.)	F	46	NITROGEN
14	GAS TEMP. ENTERING AH (If conditions to be corrected to guarantee)	F	47	SULPHUR
UNIT QUANTITIES			40	ASH
15	ENTHALPY OF SAT. LIQUID (TOTAL HEAT)	Btu/lb	37	MOISTURE
16	ENTHALPY OF (SATURATED) (SUPERHEATED) STM.	Btu/lb		TOTAL
17	ENTHALPY OF SAT. FEED TO (BOILER) (ECON.)	Btu/lb		TOTAL
18	ENTHALPY OF REHEATED STEAM R. H. INLET	Btu/lb	48	GRINDABILITY INDEX*
19	ENTHALPY OF REHEATED STEAM R. H. OUTLET	Btu/lb	49	FINENESS % THRU 50 M*
20	HEAT ABS. LB OF STEAM (ITEM 16 - ITEM 17)	Btu/lb	50	FINENESS % THRU 200 M*
21	HEAT ABS. LB R. H. STEAM (ITEM 19 - ITEM 18)	Btu/lb	64	INPUT-OUTPUT EFFICIENCY OF UNIT %
22	DRY REFUSE (ASH PIT + FLY ASH) PER LB AS FIRED FUEL	lb/lb		HEAT LOSS EFFICIENCY
23	Btu PER LB IN REFUSE (WEIGHTED AVERAGE)	Btu/lb	65	HEAT LOSS DUE TO DRY GAS
24	CARBON BURNED PER LB AS FIRED FUEL	lb/lb	66	HEAT LOSS DUE TO MOISTURE IN FUEL
25	DRY GAS PER LB AS FIRED FUEL BURNED	lb/lb	67	HEAT LOSS DUE TO H <sub>2</sub> O FROM COMB OF H <sub>2</sub>
HOURLY QUANTITIES			68	HEAT LOSS DUE TO COMBUST. IN REFUSE
26	ACTUAL WATER EVAPORATED	lb/hr	69	HEAT LOSS DUE TO RADIATION
27	REHEAT STEAM FLOW	lb/hr	70	UNMEASURED LOSSES
28	RATE OF FUEL FIRING (AS FIRED wt)	lb/hr	71	TOTAL
29	TOTAL HEAT INPUT (Item 28 x Item 41) / 1000	kB/hr	72	EFFICIENCY = (100 - Item 71)
30	HEAT OUTPUT IN BLOW-DOWN WATER	kB/hr		
31	TOTAL HEAT OUTPUT (Item 26 + Item 20) + (Item 27 + Item 21) + Item 30 / 1000	kB/hr		
FLUE GAS ANAL. (BOILER) (ECON) (AIR HTR) OUTLET				
32	CO <sub>2</sub>	% VOL		
33	O <sub>2</sub>	% VOL		
34	CO	% VOL		
35	N <sub>2</sub> (BY DIFFERENCE)	% VOL		
36	EXCESS AIR	%		

\* Not Required for Efficiency Testing

† For Point of Measurement See Par. 7.2.8.1-PTC 4.1-1964

TABLE D-2

PTC 4.1-b (1964)

ASME TEST FORM  
CALCULATION SHEET FOR ABBREVIATED EFFICIENCY TEST Revised September, 1965

OWNER OF PLANT	TEST NO.	BOILER NO.	DATE
30	HEAT OUTPUT IN BOILER BLOW-DOWN WATER = LB OF WATER BLOW-DOWN PER HR x $\frac{\text{ITEM 15} - \text{ITEM 17}}{1000}$ = $\frac{\dots - \dots}{1000}$ = .....		lb/hr
24	<p>If impractical to weigh refuse, this item can be estimated as follows</p> <p>DRY REFUSE PER LB OF AS FIRED FUEL = <math>\frac{\% \text{ ASH IN AS FIRED COAL}}{100 - \% \text{ COMB. IN REFUSE SAMPLE}}</math></p> <p>CARBON BURNED PER LB AS FIRED FUEL = <math>\frac{\text{ITEM 43}}{100} - \left[ \frac{\text{ITEM 22} \times \text{ITEM 23}}{14,500} \right] = \dots</math></p>		NOTE: IF FLUE DUST & ASH PIT REFUSE DIFFER MATERIALLY IN COMBUSTIBLE CONTENT, THEY SHOULD BE ESTIMATED SEPARATELY. SEE SECTION 7, COMPUTATIONS.
25	<p>DRY GAS PER LB AS FIRED FUEL = <math>\frac{11\text{CO}_2 + 8\text{O}_2 + 7(\text{N}_2 + \text{CO})}{3(\text{CO}_2 + \text{CO})} \times (\text{LB CARBON BURNED PER LB AS FIRED FUEL} + \frac{3}{8} \text{S})</math></p> <p>= <math>\frac{11 \times \frac{\text{ITEM 32}}{\dots} + 8 \times \frac{\text{ITEM 33}}{\dots} + 7 \left( \frac{\text{ITEM 35}}{\dots} + \frac{\text{ITEM 34}}{\dots} \right)}{3 \times \left( \frac{\text{ITEM 32}}{\dots} + \frac{\text{ITEM 34}}{\dots} \right)} \times \left[ \frac{\text{ITEM 24}}{\dots} + \frac{\text{ITEM 47}}{267} \right] = \dots</math></p>		
36	<p>EXCESS AIR = <math>100 \times \frac{\text{O}_2 - \frac{\text{CO}}{2}}{.2682\text{N}_2 - (\text{O}_2 - \frac{\text{CO}}{2})} = 100 \times \frac{\text{ITEM 33} - \frac{\text{ITEM 34}}{2}}{.2682(\text{ITEM 35}) - (\text{ITEM 33} - \frac{\text{ITEM 34}}{2})} = \dots</math></p>		
<b>HEAT LOSS EFFICIENCY</b>			
65	HEAT LOSS DUE TO DRY GAS = $\frac{\text{LB DRY GAS PER LB AS FIRED FUEL}}{\text{AS FIRED FUEL}} \times C_p \times (t_{\text{vg}} - t_{\text{air}}) = \frac{\text{ITEM 25}}{\dots} \times 0.24 \times ((\text{ITEM 13}) - (\text{ITEM 11})) = \dots$	Btu/lb AS FIRED FUEL	LOSS % $\frac{65}{41} \times 100 = \dots$
66	HEAT LOSS DUE TO MOISTURE IN FUEL = $\frac{\text{LB H}_2\text{O PER LB AS FIRED FUEL}}{\text{AS FIRED FUEL}} \times [(\text{ENTHALPY OF VAPOR AT 1 PSIA \& T GAS LVG}) - (\text{ENTHALPY OF LIQUID AT T AIR})] = \frac{\text{ITEM 37}}{100} \times [(\text{ENTHALPY OF VAPOR AT 1 PSIA \& T ITEM 13}) - (\text{ENTHALPY OF LIQUID AT T ITEM 11})] = \dots$		$\frac{66}{41} \times 100 = \dots$
67	HEAT LOSS DUE TO H <sub>2</sub> O FROM COMB. OF H <sub>2</sub> = $9\text{H}_2 \times [(\text{ENTHALPY OF VAPOR AT 1 PSIA \& T GAS LVG}) - (\text{ENTHALPY OF LIQUID AT T AIR})] = 9 \times \frac{\text{ITEM 44}}{100} \times [(\text{ENTHALPY OF VAPOR AT 1 PSIA \& T ITEM 13}) - (\text{ENTHALPY OF LIQUID AT T ITEM 11})] = \dots$		$\frac{67}{41} \times 100 = \dots$
68	HEAT LOSS DUE TO COMBUSTIBLE IN REFUSE = $\text{ITEM 22} \times \text{ITEM 23} = \dots \times \dots = \dots$		$\frac{68}{41} \times 100 = \dots$
69	HEAT LOSS DUE TO RADIATION* = $\frac{\text{TOTAL BTU RADIATION LOSS PER HR}}{\text{LB AS FIRED FUEL}} = \frac{\text{ITEM 28}}{\dots} = \dots$		$\frac{69}{41} \times 100 = \dots$
70	UNMEASURED LOSSES **		$\frac{70}{41} \times 100 = \dots$
71	TOTAL		.....
72	EFFICIENCY = (100 - ITEM 71)		.....

† For rigorous determination of excess air see Appendix 9.2 - PTC 4.1-1964  
 \* If losses are not measured, use ABMA Standard Radiation Loss Chart, Fig. 8, PTC 4.1-1964  
 \*\* Unmeasured losses listed in PTC 4.1 but not tabulated above may be provided for by assigning a mutually agreed upon value for Item 70.

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## APPENDIX E

### DATA RECORDING FORMATS

#### E.1 DOCUMENTATION OF RESULTS

##### E.1.1 Field Measurements

During testing, two sets of measurements are recorded: (1) control room data which indicate the operating condition of the device and (2) mobile laboratory data that were the readouts of the individual analyzers. Figure E-1 is a copy of a typical data sheet used to record the control room data and Figure E-2 is the data sheet for the mobile laboratory data.

While the measurements are made, the console operator in the laboratory fills in the mobile laboratory data sheet. Normally the tests will be conducted with the combustion device control in the manual mode in order to stabilize operating conditions and accelerate the test program.

Concentrations of the following species are measured or calculated and recorded:

Species name	Symbol used
1. Total Nitrogen Oxides	NO <sub>x</sub>
2. Nitric Oxide	NO
3. Nitrogen Dioxide	NO <sub>2</sub>
4. Carbon Dioxide	CO <sub>2</sub>
5. Carbon Monoxide	CO
6. Total Hydrocarbon	HC
7. Sulfur Trioxide	SO <sub>3</sub>
8. Sulfur Dioxide	SO <sub>2</sub>
9. Oxygen	O <sub>2</sub>
10. Solid Particulates	Sld. Part.
11. Condensible Particulates	Con. Part.
12. Particulate Size	Part. Size
13. Smoke Spot	Smoke
14. Opacity	Opac.

The concentration of all gaseous species are measured and displayed continuously by analyzers and strip chart recorders located in the instrumentation trailer. The strip chart recorder tapes will be retained for future reference. The sulfur oxides, smoke, and particulates will be measured at the sampling port and the measurements recorded in data sheets.

A number of data sheets have been developed for use in field measurements of emissions. They are listed below together with their purpose.

Figure No.	Sheet Title	Purpose
E-3	SO <sub>x</sub> Data Sheet	Record measurements taken
E-4	Sulfur Oxides Calculations	Change units, normalize to a standard excess oxygen
E-5	Plume Opacity Observation Record	Record plume opacity readings
E-6	Velocity Traverse	Record temperature and velocity profiles of flue
E-7	Method 5 Control Console Readings	Record volumes, temperatures and pressures of Method 5 unit
E-8	Particulate Calculation Sheet	Calculate weight of solid particulate catch
E-9	Particulate Emission Calculations	Calculate particulate emissions
E-10	Brink Cascade Impactor Data Sheet	Measured weights on stages of cascade impactor
E-11	Andersen Cascade Impactor Data	Measured weights on stages of cascade impactor
E-12	Gaseous Fuel Analysis	Calculation of combustion parameters from gas analysis
E-13	Trace Species and Organics Sampling Data	SASS train operational data

Figure E-1

UNIT OPERATING DATA

Test No. \_\_\_\_\_

Test No. \_\_\_\_\_ Date \_\_\_\_\_ Location \_\_\_\_\_ Engr. \_\_\_\_\_

Unit No. \_\_\_\_\_ Fuel \_\_\_\_\_ Capacity \_\_\_\_\_

Unit Type \_\_\_\_\_ Burner Type \_\_\_\_\_

1. Test Number					
2. Date					
3. Time					
4. Load					
5. Process Rate					
6.					
7.					
8.					
9.					
10.					
11.					
12.					
13.					
14.					
15.					
16.					
17.					
18.					
19.					
20.					
21.					
22.					
23.					
24.					
25.					
26.					
27.					
28.					
29.					
30.					

Figure E-2.

MOBILE LABORATORY DATA

Test No. \_\_\_\_\_

Test No. \_\_\_\_\_ Date \_\_\_\_\_ Location \_\_\_\_\_ Engr. \_\_\_\_\_

Unit No. \_\_\_\_\_ Fuel \_\_\_\_\_ Capacity \_\_\_\_\_

Unit Type \_\_\_\_\_ Burner Type \_\_\_\_\_

1. Test No.									
2. Date									
3. Time									
4. Load									
5. Process Rate									
6. Flue Diam. or Size, ft									
7. Probe Position									
8. Oxygen (%)									
9. NOx (hot) read/3% O <sub>2</sub> (ppm)*									
10. NO (hot) read/3% O <sub>2</sub> (ppm)*									
11. NO <sub>2</sub> (hot) read/3% O <sub>2</sub> (ppm)*									
12. NO (cold) read/3% O <sub>2</sub> (ppm)*									
13. Carbon Dioxide (%)									
14. Carbon Monoxide (ppm) uncor/cor*									
15. Hydrocarbon (ppm) uncor/cor*									
16. Sulfur Dioxide (ppm) uncor/cor*									
17. Smoke Spot (Bacharach)									
18. Atmos. Temp. (°F/°C)									
19. Dew Point Temp. (°F/°C)									
20. Atmos. Pressure (in. Hg)									
21. Relative Humidity (%)									
22.									
23.									
24.									
25.									
26.									
27.									
28.									
29.									
30.									

\*Correction to 3% O<sub>2</sub> should not be performed if the value is measured on a wet basis.



Figure E-4.

Test \_\_\_\_\_

Date \_\_\_\_\_

Sulfur Oxides Calculation

Nomenclature:

- S= % by weight of sulfur in fuel= \_\_\_\_\_
- HV= Fuel Heating Value (BTU/lb)= \_\_\_\_\_
- hi= (moles of species i)/lb fuel
- h<sub>fg</sub>= # of moles of dry flue gas/lb fuel
- Q̇= Fuel flow rate = \_\_\_\_\_
- SO<sub>2</sub> (  $\frac{\text{lb}}{\text{MBTU}}$  ) =  $2 \times 10^4 \left( \frac{S}{HV} \right)$  = \_\_\_\_\_
- SO<sub>2</sub> (  $\frac{\text{lb}}{\text{lb fuel in}}$  ) =  $2 \times 10^{-2} (S)$  = \_\_\_\_\_
- SO<sub>2</sub> (  $\frac{\text{lb}}{\text{hr}}$  ) =  $2 \times 10^{-2} (S \cdot \dot{Q})$  = \_\_\_\_\_
- % carbon in fuel (value assumed) = \_\_\_\_\_
- % sulfur in fuel ( " " ) = \_\_\_\_\_
- % hydrogen in fuel ( " " ) = \_\_\_\_\_
- % O<sub>2</sub> in fuel ( " " ) = \_\_\_\_\_
- % O<sub>2</sub> in stack gas = \_\_\_\_\_
- h<sub>C</sub> =  $\frac{\%C}{1200}$  = \_\_\_\_\_
- h<sub>S</sub> =  $\frac{\%S}{3200}$  = \_\_\_\_\_
- h<sub>H</sub> =  $\frac{\%H}{100}$  = \_\_\_\_\_
- h<sub>O<sub>2</sub></sub> =  $\frac{\% O_2 \text{ fuel}}{3200}$  = \_\_\_\_\_
- h<sub>FG</sub> =  $\frac{4.762 (N_C + N_S) + .9405 h_H - 3.762 h_{O_2} \text{ fuel}}{1 - 4.762 \frac{\%O_2}{100} \text{ stack}}$
- SO<sub>2</sub> (ppm) =  $\frac{h_S}{h_{FG}} \times 10^6 =$  \_\_\_\_\_ (assumed)
- SO<sub>3</sub> (ppm) = (0.1) SO<sub>2</sub> = \_\_\_\_\_ (assumed)







Figure E-8.

PARTICULATE CALCULATION SHEET

Test Crew \_\_\_\_\_

Test No. \_\_\_\_\_ Date \_\_\_\_\_ Location \_\_\_\_\_  
 Box No. \_\_\_\_\_ Sample Probe Position \_\_\_\_\_  
 Test Description \_\_\_\_\_

Dry Gas Meter Vol. (ft <sup>3</sup> )		Impinger Water Vol (ml)					Filter No.	Blank No.		
Final _____	Initial _____	Total _____	Final _____	Initial _____	Δ Vol _____	1			2	3
Beaker No. _____										
Date Weighed _____										
Tare	1									
Wt.	2									
	3									
	4									
	5									
	6									
	Avg									
Bottle No. _____										
Content	Impinger (Water)	Probe (Acetone)	Probe (Water)	Cyclone (Acetone)	Flask (Dry)					
Rinse (ml) _____										
Date Weighed or 250 Bake _____										
Final	1									
Wt. 250	2									
	3									
	4									
	5									
	6									
	Avg									
Residue wt _____										
Final 250-Tare _____										
Date Weighed or 650 Bake _____										
Final	1									
Wt. 650	2									
	3									
	4									
	5									
	6									
	Avg									
Residue Wt _____										
Final 650-Tare _____										

Comments:

Data Sheet 6002-3

Figure E-9.

PARTICULATE EMISSION CALCULATIONS

Test No. \_\_\_\_\_

Test No. \_\_\_\_\_ Date \_\_\_\_\_ Location \_\_\_\_\_ Engr. \_\_\_\_\_

Unit No. \_\_\_\_\_ Fuel \_\_\_\_\_ Load \_\_\_\_\_

Pitot Factor,  $F_s$  \_\_\_\_\_ Barometric Pressure,  $P_{bar}$  \_\_\_\_\_ in. Hg

Tot. Liquid Collected,  $V_{lc}$  \_\_\_\_\_ ml Total Particulate,  $M_n$  \_\_\_\_\_ m gm

Velocity Head,  $\Delta P$  \_\_\_\_\_ iwg Stack Temp.,  $T_s$  \_\_\_\_\_ °R Stack Area,  $A_s$  \_\_\_\_\_ ft<sup>2</sup>

Sample Volume,  $V_m$  \_\_\_\_\_ ft<sup>3</sup> Stack Press.,  $P_{sg}$  \_\_\_\_\_ iwg Excess O<sub>2</sub>,  $XO_2$  % \_\_\_\_\_ %

Orifice Press. Diff.,  $H$  \_\_\_\_\_ iwg Stack Gas Sp. Gravity,  $G_s$  \_\_\_\_\_ n.d.

Sample Time,  $\theta$  \_\_\_\_\_ min Nozzle Diameter,  $D_n$  \_\_\_\_\_ in.

1. Sample Gas Volume  $V_{m_{std}} = 0.0334 V_m (P_{bar} + H/13.6)$  \_\_\_\_\_ SCF
2. Water Vapor  $V_{w_{std}} = 0.0474 V_{lc}$  \_\_\_\_\_ SCF
3. Moisture Content  $B_{w0} = \text{Eq. 2} / (\text{Eq. 1} + \text{Eq. 2})$  \_\_\_\_\_ N.D.
4. Concentration
  - a.  $C = 0.0154 M_n / V_{m_{std}}$  \_\_\_\_\_ grains/DSCF
  - b.  $C = 2.205 \times 10^{-6} M_n / V_{m_{std}}$  \_\_\_\_\_ lb/DSCF
  - c.  $C = \text{Eq. 4b} \times 16.018 \times 10^3$  \_\_\_\_\_ grams/DSCM
5. Abs. Stack Press.  $P_s = P_{bar} \times 13.6 + P_{sg}$  \_\_\_\_\_ in. w abs.
6. Stack Gas Speed  $V_s = 174 P_s \sqrt{\Delta P T_s} \sqrt{\frac{407}{P_s} \times \frac{1.00}{G_s}}$  \_\_\_\_\_ ft/min
7. Stack Gas Flow
  - a.  $Q_{sw} = \text{Eq. 6} \times A_s \times \frac{530}{T_s} \times \frac{P_s}{407}$  \_\_\_\_\_ WSCF/min
  - b.  $Q_{sd} = \text{Eq. 7a} \times (1. - \text{Eq. 3})$  \_\_\_\_\_ DSCF/min
8. Material Flow  $M_s = \text{Eq. 7b} \times \text{Eq. 4b} \times 60$  \_\_\_\_\_ lb/hr
9. XO<sub>2</sub> factor  $XO_{2f} = 2090 / (20.9 - XO_2 \%)$  \_\_\_\_\_ N.D.
10. Emission
  - a.  $E = \text{Eq. 4b} \times F_e \times \text{Eq. 9}$  \_\_\_\_\_ lb/MMBtu
  - b.  $E = \text{Eq. 4c} \times F_m \times \text{Eq. 9} \times 1000$  \_\_\_\_\_ ng/joule
11. % Isokinetic  $I = \frac{14077 \times T_s (V_{m_{std}} + V_{w_{std}})}{\theta \times V_s \times P_s \times D_n^2}$  \_\_\_\_\_ %

	Oil	Gas	Coal
Fe SC Feet/10 <sup>4</sup> Btu	92.2	87.4	98.2
Fm SC Meters/10 <sup>4</sup> joules	0.002475	0.002346	0.002636

Data Sheet 6002-4

BRINK CASCADE IMPACTOR DATA SHEET

TEST RUN NO. \_\_\_\_\_ LOCATION \_\_\_\_\_ DATE \_\_\_\_\_  
 IMPACTOR NO. \_\_\_\_\_ CYCLONE NO. \_\_\_\_\_ OPERATOR \_\_\_\_\_  
 SAMPLE POINT LOCATION \_\_\_\_\_  
 SUBSTRATE COATING \_\_\_\_\_ FUEL \_\_\_\_\_ TEST LOAD \_\_\_\_\_ klb/hr  
 IMPACTOR ORIENTATION \_\_\_\_\_ FLOW THRU IMPACTOR \_\_\_\_\_ CFM  
 FLUE STATIC PRESSURE \_\_\_\_\_ inH<sub>2</sub>O, VELOCITY \_\_\_\_\_  
 NOZZLE DIA. \_\_\_\_\_ mm IMPACTOR PRESSURE DROP \_\_\_\_\_ END TIME \_\_\_\_\_  
 GAS METER END \_\_\_\_\_ CF START TIME \_\_\_\_\_  
 GAS METER START \_\_\_\_\_ CF DURATION \_\_\_\_\_  
 GAS VOLUME \_\_\_\_\_ CF FLOW RATE \_\_\_\_\_ CFM  
 AMBIENT TEMPERATURE \_\_\_\_\_ °F PRESSURE \_\_\_\_\_ IN Hg. HUMIDITY \_\_\_\_\_ %  
 FLUE GAS MOLECULAR WT. \_\_\_\_\_, TEMP. \_\_\_\_\_ °F, DENSITY \_\_\_\_\_ g/cc, VISCOSITY \_\_\_\_\_ POISE

	Stage Number					Stage Blank
	1	2	3	4	5	
Foil + Sample, g						
Unused Foil, g						
Sample, g						
Correction for Blank, g						
Final Sample, g						

FILTER NO.	Sample	Blank
FILTER + SAMPLE, g		
FILTER TARE, g		
SAMPLE, g		
CORRECTION FOR BLANK, g		
FINAL SAMPLE, g		

FULL CONTAINER, g \_\_\_\_\_  
 EMPTY CONTAINER, g \_\_\_\_\_  
 CYCLONE CATCH, g \_\_\_\_\_

Figure E-11.

ANDERSEN CASCADE IMPACTOR DATA

Test No. \_\_\_\_\_ Location \_\_\_\_\_ Owner \_\_\_\_\_  
 Impactor No. \_\_\_\_\_ Nozzle Size \_\_\_\_\_ Filter No. \_\_\_\_\_  
 Stack Temperature \_\_\_\_\_ °F Impactor Flow Rate \_\_\_\_\_ CFM

Plate	Tare (g)	Final (g)	Net (g)	%	Cum. %	ECD (μ)
1						
2						
3						
4						
5						
6						
7						
8						
Back Up Filter						

445

Figure E-12.

**GASEOUS FUEL ANALYSIS** Test No \_\_\_\_\_

Test No \_\_\_\_\_ Date \_\_\_\_\_ Location \_\_\_\_\_ Engr \_\_\_\_\_

Unit No. \_\_\_\_\_ Fuel \_\_\_\_\_ Fuel Sample No \_\_\_\_\_

Fuel Sample Point \_\_\_\_\_ Fuel Analysis by \_\_\_\_\_

Gas	Volume	% CF air / CF fuel	Btu(HHV) / CF fuel	CF CO <sub>2</sub> / CF fuel	CF H <sub>2</sub> O / CF fuel	CF Prod / CF fuel	lb Fuel / CF fuel
CH <sub>4</sub> Methane	x 0.0955	9.94	0.01	0.02	0.1055	0.000416	
C <sub>2</sub> H <sub>6</sub> Ethane	x 0.1671	17.51	0.02	0.03	0.1821	0.000786	
C <sub>3</sub> H <sub>8</sub> Propane	x 0.2387	25.19	0.03	0.04	0.2587	0.001171	
C <sub>4</sub> H <sub>10</sub> Butane	x 0.3103	33.21	0.04	0.05	0.3353	0.001548	
C <sub>5</sub> H <sub>12</sub> Pentane	x 0.3819	41.11	0.05	0.06	0.4119	0.001864	
C <sub>2</sub> H <sub>4</sub> Ethylene	x 0.1432	15.80	0.02	0.02	0.1532	0.000726	
C <sub>3</sub> H <sub>6</sub> Propylene	x 0.2148	23.33	0.03	0.03	0.2298	0.001087	
C <sub>4</sub> H <sub>8</sub> Butylene	x 0.2869	31.23	0.04	0.04	0.3068	0.001449	
C <sub>5</sub> H <sub>10</sub> Pentylene	x 0.3580	39.16	0.05	0.05	0.3830	0.001813	
C <sub>2</sub> H <sub>2</sub> Acetylene	x 0.1193	14.57	0.02	0.01	0.1343	0.000682	
C <sub>6</sub> H <sub>6</sub> Benzene	x 0.3580	38.48	0.06	0.03	0.3730	0.002017	
O <sub>2</sub> Oxygen	x -0.0477				-0.0377	0.000828	
N <sub>2</sub> Nitrogen					0.01	0.000728	
CO <sub>2</sub> Carb. Diox			0.01		0.01	0.001145	
CO Carb. Monox	x 0.0239	3.15	0.01		0.0289	0.000724	
H <sub>2</sub> Hydrogen	x 0.0239	3.18		0.01	0.0289	0.000522	
<b>Total</b>							

**Theoretical Air:**

$$\frac{\text{SCF air}}{10^6 \text{ Btu}} = \frac{\text{CF air}}{\text{CF fuel}} \times 10^6 / \frac{\text{Btu(HHV)}}{\text{CF fuel}} = \text{SCF air}/10^6 \text{ Btu @ } 70^\circ\text{F, } 29.92 \text{ in. Hg.}$$

$$\frac{\text{WSCF Prod}}{10^6 \text{ Btu}} = \frac{\text{CF Prod}}{\text{CF fuel}} \times 10^6 / \frac{\text{Btu(HHV)}}{\text{CF fuel}} = \text{Wet SCF Prod}/10^6 \text{ Btu}$$

$$\% \text{ Moisture} = \frac{\text{CF H}_2\text{O}}{\text{CF fuel}} \times 100 / \frac{\text{CF Prod}}{\text{CF fuel}} = \% \text{ H}_2\text{O}$$

$$\frac{\text{DSCF Prod}}{10^6 \text{ Btu}} = \frac{\text{WSCF Prod}}{10^6 \text{ Btu}} \times \frac{(100 - \% \text{ Moisture})}{100} = \text{Dry SCF}/10^6 \text{ Btu}$$

$$\% \text{ CO}_2, \text{ dry} = \frac{\text{CF CO}_2}{\text{CF fuel}} \times 100 / \left( \frac{\text{CF Prod}}{\text{CF fuel}} - \frac{\text{CF H}_2\text{O}}{\text{CF fuel}} \right) = \% \text{ CO}_2, \text{ dry}$$

$$K = \frac{331.5 \times 10^6}{\text{MW} \times (\text{DSCF}/10^6 \text{ Btu})}$$

$$K' = K/430$$

$$\text{lb}/10^6 \text{ Btu} = (\text{ppm @ } 3\% \text{ O}_2)/K$$

$$\text{ng}/\text{J} = (\text{ppm @ } 3\% \text{ O}_2)/K'$$

MW	K for lb/10 <sup>6</sup> Btu	K' for ng/J
NOx 46	_____	_____
CO 28	_____	_____
HC 16	_____	_____
SOx 64	_____	_____

Data Sheet 6002-6 (Rev. 2)



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APPENDIX F

TRACE SPECIES AND ORGANIC EMISSIONS DATA

Contents

<u>Location Number</u>	<u>Device</u>	<u>Fuel</u>	<u>Test</u>	<u>Page</u>
9	Cement Kiln	Natural Gas	9-3 ESP inlet	452
			9-4 ESP inlet	458
			9-5 ESP outlet	461
			9-6 ESP outlet	464
			9 Overall average	470
10	Black Liquor Recovery Boiler	Black Liquor	10/2-10 ESP inlet	471
			10/2-12 ESP inlet	477
			10/2-14 ESP outlet	480
			10/2-16 ESP outlet	483
12	Petroleum Process Heater	Refinery Gas	12/2-3 Stack	490
			12/2-6 Stack	493
13	Wood/Bark Boiler	Wood and coal	13-18 Dust Coll. Outlet	500
			13-24 Dust Coll. Outlet	507
14	Steel Open Hearth Furnace	No. 6 Fuel Oil + Natural Gas	14-2 ESP inlet	510
15	Diesel Engine	No. 2 Diesel Oil	15-10 Stack	517
			15-11 Stack	523

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TABLE F-1. GENERAL NOTES FOR TRACE SPECIES AND ORGANICS DATA TABULATIONS

- 
1. All sample data are rounded to two significant digits and corrected for blanks.
  2. Single number indicates all sample concentrations were above detection limits.
  3. Single number preceded by "<" indicates all samples were less than detection limits. Value shown is maximum undetected amount.
  4. For two numbers separated by "<", the number on the left of < indicates the detected amount, and the number on the right indicates the maximum potential amount including amounts from samples with positive detection and amounts based on the detection limit for samples that were reported as below the detection limit.
  5. < DL, concentration below detection limits  
=B, sample value equals blank, net value assumed zero  
< B, sample value less than blank, net value assumed zero  
MC, major component, exceeds maximum measurable quantity (about 1000 µg/g for spark source mass spectrometry)  
NES, not enough sample for adequate analysis  
NR, not reported, results uncertain because of complex sample matrix composition
  6. Species for which either the emission rate or input (or both) were below detection limits have mass balance values indicated as follows:
    - < DL, both emission and input below detection limit
    - > value, input value is below detection limit or emission value is above detection limit
    - < value, emission value is less than detection limit.
-

TABLE F-2. TRACE SPECIES AND ORGANIC EMISSIONS, SASS SOLIDS SECTION COLLECTION  
TEST 9-3, CEMENT KILN

Sample Type	Nozzle, Probe, 10 µm Cyclone Solids		3 µm Cyclone Solids		1 µm Cyclone Solids		Filters		Solid Section Wash	
	Sample Number	384	386	393	273	9-3 G				
Sample Weight/Vol.	20.2857 g	23.5244 g	15.6894 g	4.2785 g	1381 ml					
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Antimony	< 50	< 350	< 50	< 400	< 50	< 270	< 50	< 73	0	0
Arsenic	2.0	14	1.6	13	3.0	16	4.0	5.8	< B	0
Barium	< 20	< 140	< 20	< 160	< 20	< 110	< 20	< 29	< B	0
Beryllium	< 0.5	< 3.5	0.6	4.8	1.2	6.4	2.9	4.2	< 0.005	< 2.4
Cadmium	4.4	30	4.6	37	4.7	25	5.1	7.4	0	0
Calcium	310,000	2,100,000	420,000	3,400,000	250,000	1,300,000	250,000	360,000	560	260,000
Chromium	31	210	20	160	31	170	80	120	< B	0
Cobalt	38	260	24	192	30	160	55	80	< 0.08	38
Copper	11	76	11	88	13	69	17	25	0.02	9.4
Iron	12,000	83,000	13,000	100,000	18,000	96,000	22,000	32,000	19	8900
Lead	< 200	< 1400	< 200	< 1600	< 200	< 1100	< 200	< 290	0.16	75
Manganese	82	570	83	660	70	370	140	200	0.18	85
Mercury	< 0.2	< 1.4	< 0.2	< 160	< 0.2	< 1.1	< 0.2	< 2.9	< 0.005	< 2.4
Nickel	24	170	30	240	30	160	39	57	0.09	42
Selenium	< 4	< 28	< 4	< 32	< 4	< 21	< 4	< 5.8	< 0.04	< 19
Tellurium	< 50	< 350	< 50	< 400	< 50	< 270	< 50	< 73	< 2	< 940
Tin	< 50	< 350	< 50	< 400	< 50	< 270	< 50	< 73	< 1	< 470
Titanium	1,900	13,000	2,100	17,000	2,700	14,000	3,000	4,400	0.85	400
Vanadium	30	210	30	240	55	290	90	130	< 0.1	< 47
Zinc	40	280	42	340	40	210	45	65	0.01	4.7
Chloride	709	4,900	1,210	9,700	2,810	15,000	21,000	31,000	11	5,200
Fluoride	150	1,000	290	2,300	256	1,400	420	610	3.8	1,800
Nitrates	8.7	60	8.1	65	13.0	69	28	41	< 0.2	< 94
Sulfates	< 50	< 350	< 50	< 400	< 50	< 270	52,000	76,000	< 6	< 2,800
Total POM	0.1	0.69	0.1	0.80	0.1	0.53	< 1	< 1.5	0.010	4.7
Total PCB	< 1	< 6.9	< 1	< 8.0	< 1	< 5.3	< 1	< 1.5	< 0.001	< 0.47

See notes on Table F-1

452

TABLE F-3. TRACE SPECIES AND ORGANIC EMISSIONS, SASS ORGANIC AND LIQUIDS SECTION COLLECTION TEST 9-3, CEMENT KILN

Sample Type	MAD-2 Resin		Organic Module Rinse		Condensate		Impinger No. 1		Impinger No. 2		Impinger No. 3	
	Sample Number	Sample Weight/Vol.	Units	Units	Units	Units	Units	Units	Units	Units	Units	Units
	296	150 g	$\mu\text{g/g}$	$\mu\text{g/m}^3$	$\mu\text{g/ml}$	$\mu\text{g/m}^3$	$\mu\text{g/ml}$	$\mu\text{g/m}^3$	$\mu\text{g/ml}$	$\mu\text{g/m}^3$	$\mu\text{g/ml}$	$\mu\text{g/m}^3$
	9-3 H	823 ml										
	9-3 I	1089 ml										
	437	1465 ml										
	9-3 J	1585 ml										
	None											
Antimony	< 50	< 2,600	< B	0	< 0.1	< 37	0.14	68	0	0		
Arsenic	< 0.5	< 26	< B	0	< 0.02	< 7.4	< B	0	< 0.020	< 11		
Barium	< 20	< 1,000	< B	0	< 0.1	< 37	< 0.059	< 29	< 0.10	< 54		
Beryllium	0.8	41	< 0.005	< 1.4	< 0.005	< 1.9	< 0.005	< 2.5	< 0.005	< 2.7		
Cadmium	0.8	41	= B	0	< 0.01	< 3.7	0.0082	4.1	< 0.005	< 3.1		
Calcium	24,000	1,200,000	23	6,400	6.3	2,300	< B	0	0	0		
Chromium	3	150	< B	0	< 0.02	< 7.4	< B	0	0.13	68		
Cobalt	15	770	0.02	5.6	< 0.02	< 7.4	< 0.003	< 1.5	0	0		
Copper	15	770	0.06	17	0.01	3.7	0.020	9.9	0.011	6.1		
Iron	59	3,000	3.0	840	0.68	250	0.057	2.9	0	0		
Lead	< 190	< 9,700	< B	0	< 0.02	< 7.4	0.016	7.8	0	0		
Manganese	9	460	0.061	17	0.038	14	0.014	6.8	0	0		
Mercury	< 0.2	< 100	< 0.005	< 1.4	< 0.005	< 1.9	< 0.005	< 2.5	< 0.005	< 2.7		
Nickel	3.5	180	0.05	14	< 0.02	< 7.4	< 0.005	< 2.7	0.054	29		
Selenium	< 4	< 200	< 0.04	< 11	< 0.04	< 15	< 0.040	< 20	< 0.040	< 21		
Tellurium	< 50	< 2,600	< 2	< 560	< 2	< 740	< 2.0	< 990	< 2.0	< 1,100		
Tin	< 50	< 2,600	< 1	< 280	< 1	< 370	< 1.0	< 510	< 1.0	< 540		
Titanium	60	3,100	< 0.5	< 140	< 0.5	< 190	< 0.39	< 190	< 0.26	< 140		
Vanadium	< 10	< 510	< 0.1	< 28	< 0.1	< 37	< 0.10	< 51	< 0.10	< 54		
Zinc	14	720	0.14	39	0.06	22	0.017	8.5	0	0		
Chloride	36	1,800	9.5	2,700	2.1	780	< 0.040	< 200	180	95,000		
Fluoride	61	3,100	0.26	73	0.34	130	< 0.20	< 99	< 0.020	< 110		
Nitrates	< B	0	0.44	120	0.50	190	1.4	680	--	--		
Sulfates	54	2,800	2	560	10	3,700	< 6.0	< 3,000	--	--		
Total POM	< 1	< 51	0.256	72	0.017	6.3	< 0.010	< 5.1	0.063	34		
Total PCB	< 1	< 51	< 0.001	< 2.8	< 0.001	3.7	< 0.001	< 0.051	< 0.001	< 0.54		

453

See notes on Table F-1

TABLE F-4. TRACE SPECIES AND ORGANICS EMISSIONS, PROCESS SAMPLES AND MASS BALANCES  
TEST 9-3, CEMENT KILN

Sample Type	Emission in Partic. < 3 µm	Total Emission Concen.	Total Emission Rate	Kiln Feed Slurry		Kiln Discharge Clinker		Kiln Emission by Process Flows	Kiln Emission Ratio	Kiln Mass Balance
Sample Number	393 + 275	SASS	Kiln exit by SASS	1016		1017		Feed-Clinker	SASS (Feed-Clinker)	(SASS + Clinker) Feed
Sample Weight/Vol.	19.967 g	2.937 m <sup>3</sup>	20.12 m <sup>3</sup> /s	26000 g/s		10200 g/s				
Units	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s	µg/g	µg/s	µg/g	µg/s	µg/s	--	--
Antimony	< 340	< 3700	< 75000	< 25	< 650000	< 50	< 510000	< DL	< DL	< DL
Arsenic	22	48 < 92	960 < 1800	1.7	440000	1.7	17000	27000	0.04 < 0.07	0.04
Barium	< 130	< 1600	< 32000	< 15	< 390000	< 20	< 200000	< DL	< DL	< DL
Beryllium	11	61 < 72	1200 < 1400	0.3	7800	1.4	14000	0	< DL	1.9 < 2.0
Cadmium	32	146 < 153	2900 < 3100	1.7	44000	5.4	55000	0	< DL	1.3
Calcium	1400000	8800000	178000000	240000	6.2x10 <sup>9</sup>	450000	4.6x10 <sup>9</sup>	1.6x10 <sup>9</sup>	0.11	0.77
Chromium	290	890	18000	10	260000	31	320000	0	< DL	1.3
Cobalt	240	1500	31000	10	260000	26	270000	0	< DL	1.2
Copper	94	1100	22000	14	360000	18	180000	180000	0.12	0.56
Iron	128	220000	4500000	13000	340x10 <sup>6</sup>	25000	260x10 <sup>6</sup>	80x10 <sup>6</sup>	0.056	0.78
Lead	< 1400	83 < 14000	1700 < 290000	< 100	< 2600000	< 200	< 2000000	< DL	< DL	< DL
Manganese	570	2300	49000	50	1300000	140	1400000	0	< DL	1.1
Mercury	< 4.0	5.1 < 26	103 < 510	< 0.1	< 2600	< 0.2	< 2000	< DL	< DL	< DL
Nickel	220	920	18000	10	260000	23	230000	30000	0.60	0.095
Selenium	< 27	11 < 370	230 < 7500	< 4	< 100000	< 4	< 41000	< DL	< DL	< DL
Tellurium	< 340	< 7800	< 160000	< 25	< 650000	< 50	< 510000	< DL	< DL	< DL
Tin	< 340	1600 < 5800	32000 < 120000	< 25	< 650000	< 50	< 510000	< DL	< DL	< DL
Titanium	18000	51000	1000000	1100	2.9x10 <sup>6</sup>	2400	24x10 <sup>6</sup>	5000000	0.20	0.86
Vanadium	420	890 < 1600	18000 < 32000	27	700000	65	660000	40000	0.45 < 0.80	0.97 < 0.99
Zinc	280	950	19000	11	290000	35	360000	0	< DL	1.3
Chloride	46000	170000	3400000	93.1	2400000	12.0	120000	2300000	1.5	1.5
Fluoride	2000	11000	210000 < 220000	66.7	1700000	54.0	560000	1100000	0.19 < 0.20	0.45 < 0.46
Nitrates	110	1200 < 1300	25000 < 27000	< 1	< 26000	< 1.2	< 12000	< DL	< DL	< DL
Sulfates	76000	82000 < 89000	1600000 < 1800000	41.7	1100000	< 40	< 410000	0.69x10 <sup>6</sup> < 1.1x10 <sup>6</sup>	2.3	1.8 < 2.0
Total POM	0.53 < 0.68	85 < 180	1700 < 3600	0.5	13000	< 0.1	< 1000	12000 < 13000	0.14	0.13 < 0.35
Total PCB	< 6.8	< 85	< 1700	< 1	< 26000	< 1	< 10000	< DL	< DL	< DL

454

See notes on Table F-1

TABLE F-5. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY  
TEST 9-3, CEMENT KILN

Sample Type	Combined Solids		XAD-2 Resin		Combined Liquids		Total Emission Concn.	Total Emission Rate
	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.
	9-3 A	63,7780 g	9-3 B	150 g	9-3 C	4,692 ml	SASS 2.937 m <sup>3</sup>	20.12 m <sup>3</sup> /s
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s
Antimony	< 0.8	< 51	< 0.5	< 26	0.020	34	34 < 111	680 < 2200
Arsenic	22	1400	< 2.1	< 110	< B	0	1400 < 1510	28000 < 30000
Barium	200	13000	3	150	< B	0	13000	260000
Beryllium	0.3	19	< 0.5	< 26	< B	0	19 < 45	380 < 900
Cadmium	< 0.4	< 26	< 0.9	< 46	< 0.004	< 6.8	< 79	< 1600
Calcium	MC	MC	24	1200	MC	MC	1200 < MC	24000 < MC
Chromium	36	2300	< B	0	0.060	100	2400	12000
Cobalt	6	380	< 0.1	< 5.1	0.0038	6.5	390	7800 < 7900
Copper	10	640	1.0	51	0.013	21	710	14000
Iron	MC	MC	= B	0	0.58	990	990 < MC	20000 < MC
Lead	30	190	< 2	< 100	0.032	54	240 < 340	4900 < 6900
Manganese	40	2600	0.5	26	0.032	54	2700	54000
Mercury	NR	--	NR	--	NR	--	NR	--
Nickel	10	640	1.1	56	0.042	72	770	15000
Selenium	1	64	< 2	< 100	< 0.1	< 170	64 < 330	1300 < 6700
Tellurium	< 0.2	< 13	< 0.5	< 26	< 0.004	< 6.8	< 46	< 920
Tin	0.7	45	< 0.5	< 26	< B	0	45 < 71	910 < 1400
Titanium	930	59000	8.0	410	< 0.095	< 160	5900 < 60000	1200000
Vanadium	40	2600	0.19	9.7	0.0058	9.9	2600	53000
Zinc	30	190	= B	0	0.38	650	740	15000
Chlorine	900	57000	= B	0	2.6	4400	61000	1200000
Fluorine	560	36000	< B	0	MC	MC	3600 < MC	720000 < MC

See notes on Table F-1

TABLE F-6. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY (Continued)  
TEST 9-3, CEMENT KILN

Sample Type	Combined Solids		KAD-2 Resin		Combined Liquids		Total Emission Concen.	Total Emission Rate
Sample Number	9-3A		9-3 B		9-3 C		SASS	
Sample Weight/Vol.	63,7780 g		150 g		4692 ml		2.937 m <sup>3</sup>	20.12 m <sup>3</sup> /s
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s
Aluminum	MC	MC	6.0	310	0.44	750	1100 < MC	21000 < MC
Bismuth	0.5	32	< 0.5	< 26	< 0.008	< 14	32 < 72	640 < 1400
Boron	6	380	2.0	100	< B	0	480	9700
Bromine	20	1300	< 7.0	< 360	0.028	48	1300 < 1700	27000 < 34000
Cerium	28	1800	< 0.5	< 26	0.016	26	1800 < 1900	37000
Cesium	35	2200	1.0	51	0.0099	17	2300	46000
Dysprosium	1	64	< 0.5	< 26	< 0.004	< 6.8	64 < 97	1300 < 1900
Erbium	0.5	32	< 0.5	< 26	< 0.004	< 6.8	32 < 65	640 < 1300
Europium	0.5	32	< 0.5	< 26	< 0.004	< 6.8	32 < 65	640 < 1300
Gadolinium	0.9	57	< 0.5	< 26	< 0.004	< 6.8	57 < 90	1100 < 1800
Gallium	8	510	< 0.4	< 20	< B	0	510 < 530	10000 < 11000
Germanium	0.5	32	< 0.5	< 26	< B	0	32 < 58	640 < 1200
Gold	< 0.2	< 13	< 0.5	< 26	< 0.004	< 6.8	< 46	< 920
Hafnium	1	64	< 0.5	< 26	< 0.004	< 6.8	64 < 97	1300 < 1900
Holmium	0.7	45	< 0.5	< 26	< 0.004	< 6.8	45 < 78	910 < 1600
Iodine	22	1400	< 3.5	< 180	0.2	330	1700 < 1900	35000 < 38000
Iridium	< 0.2	< 13	< 0.5	< 26	< 0.004	< 6.8	< 46	< 920
Lanthanum	25	1600	< 0.5	< 26	< 0.026	44	1600 < 1700	33000 < 54000
Lithium	13	830	0.8	41	= B	0	870	18000
Lutetium	0.2	13	< 0.5	< 26	< 0.004	< 6.8	13 < 46	260 < 920
Magnesium	MC	MC	56	2900	< B	0	2900 < MC	58000 < MC
Molybdenum	1	64	< B	0	0.0022	3.7	68	2000
Neodymium	3	190	< 0.5	< 26	0.02	34	220 < 250	4500 < 5000
Niobium	8	510	< 0.5	< 26	< 0.004	< 6.8	510 < 540	10000 < 11000
Osmium	< 0.2	< 13	< 0.5	< 26	< 0.004	< 6.8	< 46	< 920

See note on Table F-1

TABLE F-7. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY (Continued)  
TEST 9-3, CEMENT KILN

Sample Type	Combined Solids		XAD-2 Resin		Combined Liquids		Total Emission Concen.	Total Emission Rate
Sample Number	9-3 A		9-3 B		9-3 C		SASS	
Sample Weight/Vol.	63,7780 g		150 g		4692 ml		2.937 m <sup>3</sup>	20.12 m <sup>3</sup> /s
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s
Palladium	< 0.2	< 13	< 0.5	< 26	< 0.004	< 6.8	< 46	< 920
Platinum	< 0.2	< 13	< 0.5	< 26	< 0.004	< 6.8	< 46	< 920
Phosphorus	820	52000	< B	0	0.016	27	52000	1000000
Potassium	MC	MC	550	28000	MC	MC	28000 < MC	560000 < MC
Praseodymium	1	64	< 0.5	< 26	< 0.02	< 34	64 < 120	1300 < 2500
Rhenium	< 0.2	< 13	< 0.5	< 26	< 0.004	< 6.8	< 46	< 920
Rhodium	< 0.2	< 13	< 0.5	< 26	< 0.004	< 6.8	< 46	< 920
Rubidium	140	8900	0.3	15	0.095	160	9100	180000
Ruthenium	< 0.2	< 13	< 0.5	< 26	< 0.004	< 6.8	< 46	< 920
Samarium	2	130	< 0.5	< 26	< 0.004	< 6.8	130 < 160	2600 < 3300
Scandium	5	320	0.4	20	< 0.005	< 8.4	340 < 350	6800 < 7000
Silicon	MC	MC	360	18000	< B	0	18000 < MC	360000 < MC
Silver	0.4	26	< 0.5	< 26	MC	MC	26 < MC	520 < MC
Sodium	MC	MC	90	4600	MC	MC	46000 < MC	93000 < MC
Sulfur	MC	MC	B	0	MC	MC	MC	MC
Strontium	100	6400	0.4	20	< B	0	6400	130000
Tantalum	< 0.2	< 13	< 0.5	< 26	< 0.2	< 340	< 380	< 7600
Thallium	3	190	< 0.5	< 26	< 0.004	< 6.8	190 < 220	3800 < 4500
Terbium	0.2	13	< 0.5	< 26	< 0.004	< 6.8	< 46	< 920
Thorium	4	260	< 0.5	< 26	< 0.004	< 6.8	260 < 290	5300 < 5900
Thulium	0.2	13	< 0.5	< 26	< 0.004	< 6.8	13 < 46	260 < 290
Tungsten	< 1	< 64	< 0.5	< 26	< 0.004	< 6.8	< 97	< 1900
Uranium	4	260	< 0.5	< 26	< 0.004	< 6.8	260 < 290	5300 < 5900
Ytterbium	1	64	< 0.5	< 26	< 0.004	< 6.8	64 < 97	1300 < 1900
Yttrium	8	510	< 0.5	< 26	< B	0	510 < 540	10900 < 11000
Zirconium	34	2200	< B	0	< B	0	2200	44000

See note on Table F-1

TABLE F-8. TRACE SPECIES AND ORGANIC EMISSIONS, SASS SOLIDS SECTION COLLECTION  
TEST 9-4, CEMENT KILN

Sample Type	Nozzle, Probe, 10 µm Cyclone Solids		3 µm Cyclone Solids		1 µm Cyclone Solids		Filters		Solid Section Wash	
	Sample Number	394	410	407	274	9-4 A				
Sample Weight/Vol.	17.6210 g		19.4157 g		12.6696 g		4.4659 g		1625 ml	
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Antimony	< 50	< 300	< 50	< 340	< 50	< 220	< 50	< 77	0.1	56
Arsenic	< 0.5	< 3.0	2.5	17	1.0	4.4	1.0	1.5	= B	0
Barium	< 20	< 120	< 20	< 130	< 20	< 87	< 20	< 31	< B	0
Beryllium	1.7	10	2.0	13	1.5	6.6	2.3	3.5	< 0.005	< 2.8
Cadmium	4.5	27	3.0	20	3.7	16	3.6	55	0.005	2.8
Calcium	480000	2900000	260000	1700000	290000	1300000	210000	320000	299	170000
Chromium	21	130	18	120	32	140	42	65	< B	0
Cobalt	36	220	31	210	34	150	34	52	0.03	17
Copper	14	85	12	80	14	61	17	26	0.01	5.6
Iron	10000	61000	10000	67000	17000	74000	22000	34000	8.1	4500
Lead	< 200	< 1200	< 200	< 1300	< 200	< 870	< 200	< 310	0.07	39
Manganese	90	550	48	320	65	280	100	150	0.09	50
Mercury	< 0.2	< 1.2	< 0.2	< 1.3	< 0.2	< 0.87	< 0.2	< 0.31	< 0.005	< 2.8
Nickel	29	180	22	150	29	130	31	48	0.01	5.6
Selenium	< 4	< 24	< 4	< 27	< 4	< 17	< 4	< 6.2	< 0.04	< 22
Tellurium	< 50	< 300	< 50	< 340	< 50	< 220	< 50	< 77	< 2	< 1100
Tin	< 50	< 300	< 50	< 340	< 50	< 220	< 50	< 77	< 1	< 560
Titanium	1900	12000	2000	13000	2600	11000	3000	4600	< 0.45	< 250
Vanadium	40	240	50	340	70	310	80	120	< 0.1	< 56
Zinc	40	240	35	230	41	180	42	65	= B	0
Chloride	990	6000	1400	9400	3200	14000	24000	37000	1.1	620
Fluoride	140	850	160	1100	320	960	330	510	0.48	270
Nitrates	6.6	40	7.3	49	8.4	37	16	25	< 0.2	< 110
Sulfates	50	300	< 50	< 340	170	740	32000	49000	6	3400
Total POM	NR	--	NR	--	NR	--	NR	--	NR	--
Total PCB	NR	--	NR	--	NR	--	NR	--	NR	--

See notes on Table F-1

TABLE F-9. TRACE SPECIES AND ORGANIC EMISSIONS, SASS ORGANIC AND LIQUIDS SECTION COLLECTION TEST 9-4, CEMENT KILN

Sample Type	XAD-2 Resin		Organic Module Rinse		Condensate		Impinger No. 1		Impinger No. 2		Impinger No. 3	
Sample Number	299		221		9-4 B		838		9-4 C		None	
Sample Weight/Vol.	148.3 g		307 ml		1703 ml		829 ml		1214 ml			
Units	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Antimony	< 50	< 2600	< B	0	< 0.1	< 59	< B	0	0.12	48		
Arsenic	< 0.5	< 26	< B	0	< 0.02	< 12	< B	0	< 0.012	< 5.2		
Barium	< 20	< 1000	< B	0	< 0.1	< 59	< 0.095	< 27	< 0.0066	< 28		
Beryllium	= B	0	< 0.005	< 0.53	< 0.005	< 2.9	< 0.0049	< 1.4	< 0.005	< 2.1		
Cadmium	< 0.5	< 26	= B	0	0.015	8.8	< 0.0098	< 2.8	0.004	1.7		
Calcium	< B	0	0.6	64	1.8	1100	< B	0	< B	0		
Chromium	< 1	< 51	< B	0	< 0.02	< 12	< B	0	< B	0		
Cobalt	< 5	< 260	< 0.02	< 2.1	< 0.02	< 12	< 0.001	< 0.3	< B	0		
Copper	4	200	= B	0	< 0.01	< 5.9	0.030	8.6	< B	0		
Iron	< B	0	0.29	31	0.16	94	0.22	62	< B	0		
Lead	< 190	< 9700	= B	0	< 0.02	< 12	0.030	8.6	< B	0		
Manganese	< B	0	0.020	2.1	0.010	5.9	< 0.0007	< 0.2	< B	0		
Mercury	0.5	26	< 0.005	< 0.53	< 0.005	< 2.9	< 0.0049	< 1.4	< 0.005	< 2.1		
Nickel	< 1.5	< 77	0.02	2.1	< 0.02	< 12	< 0.002	< 0.7	< B	0		
Selenium	< 4	< 200	< 0.04	< 4.2	< 0.04	< 24	< 0.040	< 11	< 0.040	< 17		
Tellurium	< 50	< 2600	< 2	< 210	< 2	< 1200	< 2.1	< 590	< 2.0	< 830		
Tin	< 50	< 2600	< 1	< 110	< 1	< 590	< 1.0	< 290	< 0.99	< 410		
Titanium	< 60	< 3100	< 0.45	< 48	< 0.5	< 290	< 0.48	< 140	< 0.099	< 41		
Vanadium	< 10	< 510	< 0.1	< 11	< 0.1	< 59	< 0.10	< 29	< 0.099	< 41		
Zinc	< B	0	= B	0	0.05	29	0.012	3.5	< B	0		
Chloride	< 4	< 200	1.1	120	0.42	250	< 0.40	< 110	< B	0		
Fluoride	31	1600	< 0.4	< 42	0.34	200	< 0.21	< 59	< 0.20	< 83		
Nitrates	< B	0	< 0.2	< 21	0.26	150	0.11	31	--	--		
Sulfates	53	2700	6	640	< 6	< 3500	6.0	1700 (SO <sub>2</sub> )	--	--		
Total POM	NR	--	NR	--	NR	--	NR	--	NR	--		
Total PCB	NR	--	NR	--	NR	--	NR	--	NR	--		

459

See notes on Table F-1

TABLE F-10. TRACE SPECIES AND ORGANICS EMISSIONS, PROCESS SAMPLES AND MASS BALANCES  
TEST 9-4, CEMENT KILN

Sample Type	Emission in Partic. < 3 µm	Total Emission Concen.	Total Emission Rate	Kiln Feed Slurry		Kiln Discharge Clinker		Kiln Emission by Process Flows	Kiln Emission Ratio	Kiln Mass Balance	Electrostatic Precipitator Catch		Collection Ratio
Sample Number	407 + 274	SASS		1018		1019		Feed-Clinker	<u>SASS</u> (Feed - Clinker)	(SASS + Clinker) Feed	1020		<u>SASS</u> ESP
Sample Weight/Vol.	17.1355	2.897 m <sup>3</sup>	19.01 m <sup>3</sup> /s	24000 g/s		9400 g/s					470 g/s		
Units	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s	µg/g	µg/s	µg/g	µg/s	--	--	--	µg/g	µg/s	--
Antimony	< 300	100 < 3800	1900 < 72000	<30	<720000	<50	<470000	< DL	< DL	< DL	<50	<24000	< DL
Arsenic	5.9	23 < 69	440 < 1300	2.2	53000	1.5	14000	39000	0.01<0.03	0.27<0.29	1.5	700	0.62 < 1.9
Barium	< 120	< 1600	< 30000	<15	<360000	<20	<190000	< DL	< DL	< DL	<20	< 9400	< DL
Beryllium	10	34 < 45	650 < 860	0.4	9600	2.0	19000	0	< DL	2.0 < 2.1	1.8	850	0.76 < 1.0
Cadmium	71	83 < 110	1600 < 2100	0.7	17000	4.0	38000	0	< DL	2.3 < 2.4	4.1	1900	0.84 < 1.1
Calcium	1600000	6600000	1.3x10 <sup>8</sup>	90000	2.2x10 <sup>9</sup>	520000	4.8x10 <sup>9</sup>	0	< DL	2.2	300000	140x10 <sup>6</sup>	0.93
Chromium	210	450 < 520	8600 < 9900	6	140000	27	250000	0	< DL	1.8 < 1.9	20	9400	0.91 < 1.1
Cobalt	200	660 < 930	13000 < 18000	17	410000	39	370000	40000	0.33<0.45	0.93<0.95	31	15000	0.87 < 1.2
Copper	87	480	9100	4	96000	14	130000	0	< DL	1.4	10	4700	1.9
Iron	110000	240000	4600000	7100	170x10 <sup>6</sup>	20000	190x10 <sup>6</sup>	0	< DL	1.1	11000	5200000	0.88
Lead	< 1200	48 < 13000	910 < 25000	< 120	<3000000	< 200	<1900000	< DL	< DL	< DL	<200	<94000	< DL
Manganese	430	1400	27000	< 0.1	< 2400	< 0.2	< 1900	< DL	< DL	< DL	< 0.2	< 94	< DL
Mercury	< 1.2	29 < 38	550 < 720	12	290000	29	270000	20000	0.50<0.60	0.97	22	10000	0.99 < 1.2
Nickel	180	520 < 620	9900<12000	< 4	< 96000	< 4	< 38000	< DL	< DL	< DL	< 4	< 1900	< DL
Selenium	6.2 < 23	< 350	< 6700	< 30	< 720000	< 50	<470000	< DL	< DL	< DL	< 50	<24000	< DL
Tellurium	< 300	< 7200	<140000	< 30	< 720000	< 50	< 470000	< DL	< DL	< DL	< 50	<24000	< DL
Tin	< 300	< 5600	<110000	< 30	< 720000	< 50	< 470000	< DL	< DL	< DL	< 50	<24000	< DL
Titanium	16000	41000<45000	780000<860000	1100	26x10 <sup>6</sup>	2200	21x10 <sup>6</sup>	500000	0.16<0.17	0.84	2100	1000000	0.78<0.86
Vanadium	430	1100 < 1700	21000 < 32000	17	410000	50	470000	0	< DL	1.2	40	19000	1.1 < 1.7
Zinc	250	760	14000	15	360000	31	290000	290000	0.2	0.84	30	14000	1.0
Chloride	51000	66000	1300000	73	1.8x10 <sup>6</sup>	43.2	410000	1.4x10 <sup>6</sup>	0.93	0.95	2950	1.4x10 <sup>6</sup>	0.93
Fluoride	1500	5200<5500	99000 < 100000	41.5	2.0x10 <sup>6</sup>	79.6	750000	1.3x10 <sup>6</sup>	0.076<0.077	0.42	115	54000	1.8 < 1.9
Nitrates	62	330 < 480	6300 < 9100	< 1.5	< 36000	< 1.5	< 14000	< DL	< DL	< DL	8.97	4200	1.5 < 2.2
Sulfates	50000	55000<62000	1000000<1200000	73.6	1.8x10 <sup>6</sup>	< 45	<420000	1.4x10 <sup>6</sup> <1.8x10 <sup>6</sup>	0.71	0.56< 0.67	<45	<21000	< DL

See notes on Table F-1

450

TABLE F-11. TRACE SPECIES AND ORGANIC EMISSIONS, SASS SOLIDS SECTION COLLECTION  
TEST 9-5, CEMENT KILN

Sample Type	Nozzle, Probe, 10 µm Cyclone Solids		3 µm Cyclone Wash		1 µm Cyclone Solids		Filters		Filter Wash	
Sample Number	9-5 E		455		9-5 F		275		365	
Sample Weight/Vol.	324 ml		271 ml		148 ml		0.1859 g		15 ml	
Units	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Antimony	< 0.1	< 3.5	< B	0	< 0.1	< 1.6	< 500	< 9.9	NES	--
Arsenic	< 0.003	< 0.10	< B	0	< 0.003	< 0.047	25	0.50	NES	--
Barium	< 0.5	< 17	< 0.35	< 10	< 0.5	< 7.9	< 40	< 0.79	NES	--
Beryllium	< 0.005	< 0.17	< 0.005	< 0.14	< 0.005	< 0.079	8	0.16	< 0.005	< 0.008
Cadmium	< 0.01	< 0.35	= B	0	< 0.01	< 0.16	20	0.40	NES	--
Calcium	110	3800	370	11000	840	13000	440000	8700	3.0	4.8
Chromium	0.10	3.5	0.15	4.3	0.45	7.1	420	8.3	NES	--
Cobalt	< 0.02	< 0.69	0.04	1.2	0.06	0.95	250	5.0	NES	--
Copper	< 0.02	< 0.69	= B	0	0.06	0.95	50	0.99	NES	--
Iron	4.3	150	13	380	42	660	14000	280	NES	--
Lead	< 0.1	< 3.5	< 0.08	< 2.3	< 0.1	< 1.6	< 2000	< 40	< 0.1	< 0.16
Manganese	0.15	5.2	0.15	4.3	0.42	6.6	350	6.9	NES	--
Mercury	< 0.003	< 0.10	< 0.008	< 2.3	< 0.003	< 0.047	< 2.0	< 0.040	< 0.003	< 0.005
Nickel	0.07	2.4	0.13	3.8	0.30	4.7	220	4.4	NES	--
Selenium	< 0.005	< 0.17	< 0.005	< 0.14	< 0.005	< 0.079	< 4	< 0.079	NES	--
Tellurium	< 0.5	<17	< 0.5	< 14	< 0.5	< 7.9	< 500	< 9.9	NES	--
Tin	< 0.5	<17	< 0.5	< 14	< 0.5	< 7.9	< 500	< 9.9	NES	--
Titanium	0.5	17	2.4	69	7.3	120	3500	69	NES	--
Vanadium	< 0.02	< 0.69	0.2	5.8	0.2	3.2	< 100	< 2.0	NES	--
Zinc	0.02	0.69	< B	0	0.17	2.7	110	2.2	NES	--
Chloride	2.1	73	0.64	19	1.1	17	43000	850	NES	--
Fluoride	0.84	29	2.0	58	2.6	41	--	--	NES	--
Nitrates	0.38	13	0.86	25	1.9	30	7900	160	NES	--
Sulfates	< 8	<280	< 8	<230	18	280	--	--	NES	--
Total POM	NR	--	NR	--	NR	--	NR	--	NR	--
Total PCB	NR	--	NR	--	NR	--	NR	--	NR	--

See notes on Table F-1

TABLE F-12. TRACE SPECIES AND ORGANIC EMISSIONS, SASS ORGANIC AND LIQUIDS SECTION COLLECTION TEST 9-5, CEMENT KILN

Sample Type	XAD-2 Resin		Organic Module Rinse		Condensate		Impinger No. 1		Impinger No. 2		Impinger No. 3	
Sample Number	300		323		9-5 A		9-5 B		1026		9-5 C	
Sample Weight/Vol.	158 g		376 ml		2275		4363		1843 ml		1121 ml	
Units	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Antimony	< 50	< 840	< B	0	< 0.1	< 24	< 0.023	< 11	0.97	110	< B	0
Arsenic	< 0.5	< 8.4	< B	0	< 0.02	< 4.8	< 0.013	< 6.2	< 0.022	< 2.5	< 0.005	< 0.64
Barium	30	510	< B	0	< 0.1	< 24	< 0.094	< 44	< 0.11	< 12	< 0.025	< 3.0
Beryllium	= B	0	< 0.005	< 0.20	< 0.005	< 1.2	< 0.005	< 2.3	< 0.009	< 0.98	< 0.005	< 0.60
Cadmium	1.0	17	= B	0	< 0.01	< 2.4	< 0.010	< 4.6	0.002	0.17	< B	0
Calcium	23000	390000	0.1	4.0	0.63	150	0.76	350	0.82	90	< B	0
Chromium	3	51	0.12	4.8	< 0.02	< 4.9	0.0048	2.2	0.44	48	0.20	23
Cobalt	15	250	0.03	1.2	< 0.02	< 4.9	0.055	26	0.12	13	< B	0
Copper	4	67	= B	0	0.01	2.4	0.010	4.7	0.007	0.75	< B	0
Iron	170	2900	0.9	36	0.14	34	0.17	78	1.2	130	< B	0
Lead	< 190	< 3200	= B	0	< 0.02	< 4.8	0.050	23	0.013	1.4	= B	0
Manganese	2	34	0.22	8.8	0.080	19	0.044	20	0.082	9.0	0.011	1.3
Mercury	< 0.2	< 3.4	< 0.005	< 0.20	< 0.005	< 1.2	< 0.004	< 2.3	< 0.009	< 0.98	< 0.005	< 0.60
Nickel	6.5	110	0.09	3.6	0.02	4.9	< 0.016	< 7.4	0.20	22	0.033	3.9
Selenium	< 4	< 67	< 0.04	< 1.6	< 0.04	< 9.7	< 0.039	< 18	< 0.072	< 7.9	< 0.040	< 4.8
Tellurium	< 50	< 840	< 2	< 80	< 2	< 490	< 1.8	< 860	< 3.6	< 390	< 2.0	< 230
Tin	< 50	< 840	< 1	< 40	< 1	< 240	< 0.94	< 440	< 1.8	< 190	< 0.98	< 120
Titanium	110	1900	< 0.45	< 18	0.7	170	< 0.48	< 220	< 0.36	< 39	< B	0
Vanadium	< 10	< 170	< 0.1	< 4.0	< 0.1	< 24	< 0.094	< 44	< 0.18	< 19	< 0.098	< 12
Zinc	3.5	59	0.06	2.4	0.05	12	0.037	17	0.029	3.2	< B	0
Chloride	37	620	0.22	8.8	< 0.5	< 1.2	< 0.48	< 220	9.2	10000	3.5	420
Fluoride	21	350	< 0.2	< 8.0	< 0.2	< 49	< 0.20	< 93	< 0.36	< 39	< 0.20	< 23
Nitrates	63	110	2.2	8.8	1.4	340	0.94	440	--	--	--	--
Sulfates	300	5100	10	400	< 6	< 1500	< 5.5	< 2600 (SO <sub>2</sub> )	--	--	--	--
Total PCM	NR	--	NR	--	NR	--	NR	--	NR	--	NR	--
Total PCB	NR	--	NR	--	NR	--	NR	--	NR	--	NR	--

462

See notes on Table F-1

TABLE F-13. TRACE SPECIES AND ORGANICS EMISSIONS, PROCESS SAMPLES AND MASS BALANCES  
TEST 9-5, CEMENT KILN

Sample Type	Emission in Partic. < 3 µm	Total Emission Concen.	Total Emission Rate	Kiln Feed Slurry		Kiln Discharge Clinker		Electrostatic Precipitator (ESP) Catch		Kiln Emission by Process Flows	Stack Emission Ratio	Overall Mass Balance	ESP Collection Efficiency
				1021	1022	1023	Feed - Clinker - ESP	SASS (Kiln Emissions)	(SASS + Clinker + ESP) Feed				
Sample Number	9-5 F + 275 + 365	SASS		24000 g/s		9200 g/s		490 g/s					
Sample Weight/Vol.		0.375 m <sup>3</sup>	21.1 m <sup>3</sup> /s										
Units	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s	µg/g	µg/s	µg/g	µg/s	µg/g	µg/s	µg/s	--	--	--
Antimony	< 12	110 < 990	2300 < 21000	< 3.5	<84000	<50	<460000	<50	<25000	< DL	< DL	< DL	< DL
Arsenic	0.50<0.55	0.5 < 23	10 < 490	1.6	38000	2.5	23000	2.0	980	14000	0.0007<0.035	0.63<0.64	0.9899>0.6667
Barium	< 8.7	530 < 620	11000 <13000	< 15	<360000	<20	<180000	<20	< 9800	< DL	< DL	< DL	< DL
Beryllium	0.16 <1.7	0.16 <5.9	3.4 < 120	1.3	31000	1.0	9200	1.8	860	21000	0.0002<0.0057	0.33	0.9959>0.8800
Cadmium	0.40<0.56	18 < 25	380 < 530	1.0	24000	5.4	50000	4.3	2100	0	< DL	2.2	0.8418>0.7984
Calcium	22000	420000	8900000	77000	1.8x10 <sup>9</sup>	520000	4.8x10 <sup>9</sup>	280000	1.40x10 <sup>6</sup>	0	< DL	3.4	0.9402
Chromium	15	150 < 160	3200 < 3400	8	190000	31	290000	14	6900	0	< DL	1.6	0.6216<0.6106
Cobalt	6.0	300 < 310	6300 < 6500	22	530000	28	260000	36	18000	250000	0.025<0.026	0.54	0.7407<0.7347
Copper	1.9	76 < 78	1600	6	140000	15	140000	12	5900	0	< DL	1.1	0.7867
Iron	940	4700	99000	7700	180x10 <sup>6</sup>	23000	210x10 <sup>6</sup>	11000	5400000	0	< DL	1.5	0.9820
Lead	< 42	24 < 3300	510 < 70000	< 150	<3600000	<200	<180000	<200	< 98000	< DL	< DL	< DL	< DL
Manganese	14	120	25000	58	1400000	110	1000000	80	39000	360000	0.0069	0.74	0.9398
Mercury	< 0.092	< 9.1	< 190	< 0.2	< 4800	< 0.2	< 1800	< 0.2	< 98	< DL	< DL	< DL	< DL
Nickel	9.1	160 < 170	3400 < 3600	16	380000	24	220000	24	12000	150000	0.023<0.024	0.62	0.7792>0.7692
Selenium	< 0.16	< 110	< 2300	< 4	< 96000	< 4	< 37000	< 4	< 2000	< DL	< DL	< DL	< DL
Tellurium	< 8.8	< 29000	< 610000	< 40	<960000	< 50	<460000	< 50	< 35000	< DL	< DL	< DL	< DL
Tin	< 8.8	< 1900	< 40000	< 40	<960000	< 50	<460000	< 50	< 25000	< DL	< DL	< DL	< DL
Titanium	190	2300 < 2600	49000<55000	1300	31x10 <sup>6</sup>	2400	22x10 <sup>6</sup>	2000	990000	8000000	0.0061<0.0069	0.74	0.9528<0.9474
Vanadium	3.2 < 5.2	11 < 290	230 < 6100	20	480000	70	640000	40	20000	0	< DL	1.4	0.9886<0.7663
Zinc	4.9	98	2100	20	480000	22	200000	55	27000	250000	0.0084	0.48	0.9278
Chloride	870	12000<13000	25000<270000	79.6	1900000	2.85	26000	2100	1000000	870000	0.29 < 0.31	0.67<0.68	0.8000>0.7874
Fluoride	41	480 < 690	12000 <15000	40.6	970000	62.0	570000	163	80000	320000	0.038< 0.047	0.68<0.69	0.8696>0.8421
Nitrates	190	2100	44000	4.01	96000	< 1.4	< 13000	8.22	4000	79000 < 92000	0.56 > 0.48	0.50<0.64	0.0833
Sulfates	280	5800 < 7800	120000<160000	28.6	690000	<45	<410000	< 45	<22000	60000<690000	2	0.17<0.86	< DL

463

See notes on Table F-1

TABLE F-14. TRACE SPECIES AND ORGANIC EMISSIONS, SASS SOLIDS SECTION COLLECTION TEST 9-6, CEMENT KILN

Sample Type	Nozzle, Probe, 10 µm Cyclone Solids		3 µm Cyclone Solids		1 µm Cyclone Solids		Filters		Solid Section Wash	
	Sample Number	Sample Weight/Vol.	Units	Units	Units	Units	Units	Units	Units	Units
Sample Number	409	0.0122 g			408	0.5775 g	276	0.2042	None	
Sample Weight/Vol.										
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Antimony	< 0.8	< 0.001			< 26	< 1.6	< 500	< 11		
Arsenic	20	0.026			0.65	0.040	10	0.22		
Barium	120	0.16			< 65	< 4.0	< 20	< 0.44		
Beryllium	0.5	0.00065			< 0.7	< 0.043	16	0.35		
Cadmium	< 0.7	< 0.00091			< 1.3	< 0.080	16	0.35		
Calcium	MC	--			260000	16000	440000	9600		
Chromium	66	0.086			100	6.2	240	5.2		
Cobalt	3	0.0039			26.0	1.6	230	5.0		
Copper	15	0.020			21.0	1.3	70	1.5		
Iron	MC	--			8800	540	17000	370		
Lead	26	0.034			< 13	< 0.80	< 2000	< 44		
Manganese	490	0.64			100	6.2	320	7.0		
Mercury	--	--			< 0.02	< 0.012	< 2	< 0.044		
Nickel	14	0.018			65	4.0	140	3.0		
Selenium	2	0.0026			< 0.5	< 0.031	< 4	< 0.087		
Tellurium	--	--			< 65	< 4.0	< 500	< 11		
Tin	< 0.9	< 0.0012			< 65	< 4.0	< 500	< 11		
Titanium	MC	--			3600	220	4000	87		
Vanadium	44	0.057			81	5.0	100	2.2		
Zinc	63	0.082			36	2.2	230	5.0		
Chloride	MC	--			--	--	61000	1300		
Fluoride	MC	--			--	--	--	--		
Nitrates	--	--			--	--	5850	130		
Sulfates	MC	--			--	--	--	--		
Total POM										
Total PCB										

See notes on Table F-1

TABLE F-15. TRACE SPECIES AND ORGANIC EMISSIONS, SASS ORGANIC AND LIQUIDS SECTION COLLECTION TEST 9-6, CEMENT KILN

Sample Type	XAD-2 Resin		Organic Module Rinse		Condensate		Impinger No. 1		Impinger No. 2		Impinger No. 3	
Sample Number	295		475		9-6 K		1027		9-6 L		None	
Sample Weight/Vol.	161 g		417 ml		2863 ml		3764 ml		2220 ml			
Units	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Antimony	< 50	< 860	< B	0	0.2	61	0.10	42	0.99	230		
Arsenic	< 0.5	< 8.6	< B	0	< 0.02	< 6.1	< 0.012	< 4.7	< 0.014	< 3.2		
Barium	< 20	< 340	0.35	16	< 0.1	< 31	< 0.090	< 36	0.17	39		
Beryllium	= B	0	< 0.005	< 0.22	< 0.005	< 1.5	< 0.005	< 2.0	< 0.005	< 1.2		
Cadmium	< 0.5	< 8.6	0.14	6.2	< 0.01	< 3.1	< 0.010	< 3.8	0.018	4.4		
Calcium	30000	520000	= B	0	1.4	430	1.4	550	< B	0		
Chromium	1	17	B	0	0.03	9.2	0.021	8.5	0.17	39		
Cobalt	< 3	< 52	< 0.02	< 0.89	0.02	6.1	0.014	5.8	0.12	29		
Copper	1	17	0.04	1.8	0.02	6.1	0.020	8.0	0.18	44		
Iron	23	390	0.30	13	0.08	24	0.14	55	< B	0		
Lead	< 190	< 3300	0.03	1.3	< 0.02	< 6.1	0.029	12	0.015	3.5		
Manganese	< B	0	0.025	1.1	0.015	4.6	0.017	6.9	0.038	9.0		
Mercury	< 2	< 34	< 0.005	< 0.22	< 0.005	< 1.5	< 0.005	< 2.0	< 0.005	< 1.2		
Nickel	< 1.5	< 26	0.02	0.89	0.04	12	0.035	14	0.13	30		
Selenium	< 4	< 69	< 0.04	< 1.8	< 0.04	< 12	< 0.040	< 16	< 0.040	< 9.5		
Tellurium	< 50	< 860	< 2	< 89	< 2	< 610	< 2.0	< 800	< 1.4	< 320		
Tin	< 50	< 860	< 1	< 44	< 1	< 310	< 1.0	< 410	< 0.99	< 230		
Titanium	< 60	< 1000	= B	0	< 0.5	< 150	< 0.48	< 190	< 0.24	< 58		
Vanadium	< 10	< 170	< 0.1	< 4.4	< 0.1	< 31	< 0.10	< 41	< 0.099	< 23		
Zinc	< B	0	= B	0	0.05	15	0.048	19	0.014	3.2		
Chloride	19	330	3.6	160	1.3	400	0.043	170	68	16000		
Fluoride	30	520	< 0.4	< 1.8	< 0.2	< 61	< 0.020	< 80	< 0.20	< 47		
Nitrates	41	700	1.0	44	0.44	130	0.64	260	--	--		
Sulfates	< 58	< 1000	< 6	< 270	< 6	< 1800	< 6.1	< 2500 (SO <sub>2</sub> )	--	--		
Total POM	0.00091	0.016	0.000018	0.00081	NR	NR	NR	NR	NR	NR		
Total PCB	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR		

465

See notes on Table F-1

TABLE F-16. TRACE SPECIES AND ORGANICS EMISSIONS, PROCESS SAMPLES AND MASS BALANCES  
TEST 9-6, CEMENT KILN

Sample Type	Emission in Partic. < 3 µm	Total Emission Concen.	Total Emission Rate	Kiln Feed Slurry		Kiln Discharge Clinker		Electrostatic Precipitator (ESP) Catch		Kiln Emission by Process Flows	Stack Emission Ratios	Overall Mass Balance	ESP Collection Efficiency
Sample Number	408 + 276	SASS		1028		1029		1030		Feed - Clinker - ESP	SASS (Kiln Emission)	(SASS + Clinker + ESP) Feed	ESP Catch (SASS + ESP Catch)
Sample Weight/Vol.	0.7817 g	9.375 m <sup>3</sup>	21.7 m <sup>3</sup> /s	24000 g/s		11000 g/s		490 g/s					
Units	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s	µg/g	µg/s	µg/g	µg/s	µg/g	µg/s	µg/s	--	--	--
Antimony	< 2.7	340<1200	7400<26000	< 22	<530000	< 50	<550000	< 50	<25000	< DL	< DL	< DL	< DL
Arsenic	0.22	0.28 <23	6.1 < 500	1.8	43000	2.0	22000	2.5	1200	20000	0.00031<0.025	0.54<0.55	0.9949>0.7059
Barium	< 4.4	55 < 470	1200<10000	< 10	<240000	< 20	<220000	< 20	< 9800	< DL	< DL	< DL	< DL
Beryllium	0.35<0.39	0.35<5.3	7.6 < 120	0.5	12000	0.9	9900	0.9	440	1700	0.0045 < 0.7	0.86<0.87	0.9830>0.7857
Cadmium	0.35<0.43	11 < 27	240 < 590	0.5	12000	3.0	33000	3.8	1900	0	< DL	2.9 < 3.0	0.8879>0.7631
Calcium	26000	530000	12x10 <sup>6</sup>	130000	3.1x10 <sup>9</sup>	250	2800000	210	100000	3000000	4.0	0.013	0.008264
Chromium	11	86	1900	7	170000	22	240000	23	11000	0	< DL	1.5	0.8527
Cobalt	6.6	47 < 100	1000<2200	10	240000	25	280000	23	11000	0	< DL	1.2	0.9167>0.8333
Copper	2.8	80	1800	5	120000	12	130000	9	4400	0	< DL	1.1	0.7097
Iron	910	1000	22000	9500	230x10 <sup>6</sup>	23000	250x10 <sup>6</sup>	11000	5400000	0	< DL	1.1	0.9959
Lead	< 45	16 < 48	350 < 1000	< 90	<2200000	<200	<2200000	<200	< 98000	< DL	< DL	< DL	< DL
Manganese	13	35	760	50	1200000	140	1500000	72	35000	0	< DL	1.3	0.9787
Mercury	< 0.056	< 39	< 850	< 0.1	< 2400	< 0.2	< 2200	< 0.2	< 98	< DL	< DL	< DL	< DL
Nickel	7.0	64 < 90	1400<2000	12	290000	22	240000	20	9800	40000	0.035<0.05	0.86<0.87	0.8750<0.8305
Selenium	< 0.12	0.003<110	0.065<2400	< 4	< 96000	< 4	< 44000	< 4	< 2000	< DL	< DL	< DL	< DL
Tellurium	<15	< 2800	< 61000	< 25	<600000	< 50	< 550000	< 50	< 25000	< DL	< DL	< DL	< DL
Tin	<15	< 1800	< 39000	< 25	<600000	< 50	< 550000	< 50	< 25000	< DL	< DL	< DL	< DL
Titanium	310	310<1700	6700<37000	1100	31x10 <sup>6</sup>	2300	25x10 <sup>6</sup>	2100	1000000	5000000	0.0013<0.0074	0.84	0.9933>0.9643
Vanadium	7.2	7.3 <280	160 < 6100	26	620000	60	660000	45	22000	0	< DL	1.1	0.9927>0.7829
Zinc	7.2	48	1000	10	240000	42	460000	41	20000	0	< DL	2.0	0.9523
Chloride	1300	18000	390000	72.1	1700000	15.8	1700000	3550	1800000	0	< DL	1.4	0.8219
Fluoride	--	530 <730	11000<16000	46.5	1100000	74.5	820000	181	89000	190000	0.058<0.084	0.84	0.8900<0.8476
Nitrates	1300	1300	28000	< 1.4	< 34000	< 1.2	< 13000	7.74	3800	< DL	< DL	< DL	< DL
Sulfates	--	<3100	< 67000	41.9	1000000	34.1	380000	52.8	26000	590000	< 1.1	0.41<0.47	> 0.2796
Total POM	NR	0.017	0.36	NR	NR	NR	NR	NR	NR	--	--	--	--
Total FCB	NR	NR	NR	NR	NR	NR	NR	NR	NR	--	--	--	--

466

See notes on Table F-1

TABLE F-17. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY  
TEST 9-6, CEMENT KILN

Sample Type	Combined Solids		XAD-2 Resin		Combined Liquids		Total Emission Concen.	Total Emission Rate
	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s
Sample Number	409 + 408 + 276		9-6 B		9-6 C		SASS	
Sample Weight/Vol.	0.7939 g		161 g		8847 ml		9.375 m <sup>3</sup>	21.7 m <sup>3</sup> /s
Antimony	< 0.63	< 0.067	< 1	< 17	0.066	62	62 < 79	1300 < 1700
Arsenic	26	2.8	< B	0	< B	0	2.8	61
Barium	92	9.8	1	17	0.044	42	69	1500
Beryllium	0.57	0.060	< 0.5	< 9	< 0.0037	< 3.5	0.060 < 13	1.3 < 270
Cadmium	< 0.63	< 0.067	< 0.5	< 9	< 0.004	< 3.8	< 13	< 280
Calcium	MC	MC	180	3100	MC	MC	3100 < MC	67000 < MC
Chromium	120	13	< B	0	0.029	27	40	870
Cobalt	8.6	0.91	< 0.1	< 1.7	0.0079	7.5	8.4 < 10	180 < 220
Copper	9.9	1.1	= B	0	0.034	32	33	720
Iron	MC	MC	5	90	0.24	220	310 < MC	6700 < MC
Lead	6.4	0.68	< 2	34	0.015	14	49	1100
Manganese	150	16	< B	0	0.011	10	26	560
Mercury	NR	--	NR	--	NR	--	NR	--
Nickel	53	5.7	< B	0	0.49	460	470	10000
Selenium	2.4	0.25	< 1	< 17	< 0.1	< 94	0.25 < 110	5.4 < 2400
Tellurium	< 0.33	< 0.036	< 0.5	< 9	< 0.004	< 3.8	< 13	< 280
Tin	1.2 < 1.3	0.12 < 0.14	1	17	< B	0	17	370
Titanium	150 < MC	16 < MC	< 11	< 190	< 0.097	< 91	16 < MC	350 < MC
Vanadium	99	10	0.4	6.9	0.018	17	34	740
Zinc	29	3.0	< B	0	0.17	160	160	3500
Chlorine	MC	MC	8	140	0.076	71	310 < MC	6700 < MC
Fluorine	100 < MC	8.7 < MC	< B	0	< B	0	8.7 < MC	190 < MC

See notes on Table F-1

TABLE F-18. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY (Continued)  
TEST 9-6, CEMENT KILN

Sample Type	Combined Solids		XAD-2 Resin		Combined Liquids		Total Emission Concen.	Total Emission Rate
Sample Number	409 + 408 + 276		9-6 B		9-6 C		SASS	
Sample Weight/Vol.	0.7939 g		161 g		8847 ml		9.375 m <sup>3</sup>	21.7 m <sup>3</sup> /s
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s
Aluminum	MC	MC	110	1900	0.17	160	2100 < MC	45000 < MC
Bismuth	< 0.42	< 0.036	< 0.5	< 8.6	< 0.004	< 3.8	< 12	< 270
Boron	30	2.5	< B	0	< B	0	2.5	54
Bromine	88	7.4	2	34	0.20	190	230	5000
Cerium	20	1.7	< 0.5	< 8.6	0.0065	6.2	7.9 < 17	170 < 360
Cesium	38	3.2	< 0.2	< 3.4	0.0018	1.7	4.9 < 8.3	110 < 180
Dysprosium	< 0.42	< 0.036	< 0.5	< 8.6	< 0.004	< 3.8	< 12	< 270
Erbium	< 0.42	< 0.036	< 0.5	< 8.6	< 0.004	< 3.8	< 12	< 270
Europium	0.69	0.059	< 0.5	< 8.6	< 0.004	< 3.8	0.059 < 12	1.3 < 270
Gadolinium	1.7	0.14	< 0.5	< 8.6	< 0.004	< 3.8	0.14 < 13	3.0 < 270
Gallium	12	1.0	< 0.4	< 6.9	< B	0	1.0 < 7.9	22 < 170
Germanium	2.3	0.19	< 0.5	< 8.6	< B	0	0.19 < 8.8	4.1 < 190
Gold	< 0.42	< 0.036	< 0.5	< 8.6	< 0.004	< 3.8	< 12	< 270
Hafnium	< 0.42	< 0.036	< 0.5	< 8.6	< 0.004	< 3.8	< 12	< 270
Holmium	< 0.42	< 0.036	< 0.5	< 8.6	< 0.004	< 3.8	< 12	< 270
Iodine	22	1.8	< 0.7	< 12	0.40	380	380 < 390	8300 < 8500
Iridium	< 0.42	< 0.036	< 0.5	< 8.6	< 0.004	< 3.8	< 12	< 270
Lanthanum	20	1.7	< 0.5	< 8.6	< 0.027	< 26	1.7 < 36	37 < 790
Lithium	20	1.7	= B	0	0.0021	2.0	3.7	80
Lutetium	< 0.42	< 0.036	< 0.5	< 8.6	< 0.004	< 3.8	< 12	< 270
Magnesium	MC	MC	100	1700	< B	0	1700 < MC	37000 < MC
Molybdenum	8.0	0.68	< B	0	0.010	9.5	10	220
Neodymium	6.7	0.56	< 0.5	< 8.6	< 0.004	< 3.8	0.56 < 13	12 < 280
Niobium	6.7	0.57	< 0.5	< 8.6	< 0.006	< 5.7	0.57 < 15	12 < 320
Osmium	< 0.42	< 0.036	< 0.5	< 8.6	< 0.004	< 3.8	< 12	< 270

See note on Table F-1

TABLE F-19. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY (Continued)  
TEST 9-6, CEMENT KILN

Sample Type	Combined Solids		MAD-2 Resin		Combined Liquids		Total Emission Concen.	Total Emission Rate
	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.
	409 + 408 + 276	0.7939 g	9-6 B	161 g	9-6 C	8847 ml	SASS	9.375 m <sup>3</sup>
								21.7 m <sup>3</sup> /B
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s
Palladium	< 0.42	< 0.036	< 0.5	< 8.6	< 0.004	< 3.8	< 12	< 270
Platinum	< 0.42	< 0.036	< 0.5	< 8.6	< 0.004	< 3.8	< 12	< 270
Phosphorus	250 < MC	21 < MC	33	570	1.6	1500	2100 < MC	45000 < MC
Potassium	MC	MC	52	890	< B	0	890 < MC	19000 < MC
Praseodymium	5.2	0.44	< 0.5	< 8.6	< 0.02	< 19	0.44 < 28	9.5 < 610
Rhenium	< 0.42	< 0.036	< 0.5	< 8.6	< 0.004	< 3.8	< 12	< 270
Rhodium	< 0.42	< 0.036	< 0.5	< 8.6	< 0.004	< 3.8	< 12	< 270
Rubidium	240	20	< B	0	0.0055	5.2	25	550
Ruthenium	< 0.42	< 0.036	< 0.5	< 8.6	< 0.004	< 3.8	< 12	< 270
Samarium	3.5	0.29	< 0.5	< 8.6	< 0.004	< 3.8	0.29 < 13	6.3 < 280
Scandium	6.4	0.54	< 0.3	< 5.2	< 0.005	< 4.7	0.54 < 10	12 < 230
Silicon	MC	MC	MC	MC	0.69	650	650 < MC	14000 < MC
Silver	0.86	0.072 < 0.073	< 0.5	< 8.6	MC	MC	0.072 < MC	1.6 < MC
Sodium	62 < MC	5.2 < MC	130	2200	MC	MC	2200 < MC	48000 < MC
Sulfur	MC	MC	1	17	MC	MC	17 < MC	370 < MC
Strontium	150	13	0.2	3.4	0.0073	6.9	23	510
Tantalum	< 0.42	< 0.036	< 0.5	< 8.6	< 0.004	< 3.8	< 12	< 270
Thallium	0.031 < 0.65	0.0026 < 0.055	< 0.5	< 8.6	< 0.004	< 3.8	0.0026 < 12	0.056 < 270
Terbium	0.42	0.036	< 0.5	< 8.6	< 0.004	< 3.8	< 12	< 270
Thorium	7.6 < 7.7	0.64 < 0.65	< 4	< 69	< 0.004	< 3.8	0.64 < 73	14 < 1600
Thulium	< 0.42	< 0.036	< 0.5	< 8.6	< 0.004	< 3.8	< 12	< 270
Tungsten	< 0.42	< 0.036	< 0.5	< 8.6	< 0.004	< 3.8	< 12	< 270
Uranium	4.2	0.35 < 0.36	< 4	< 69	< 0.04	< 3.8	0.35 < 110	7.6 < 2300
Ytterbium	< 0.42	< 0.036	< 0.5	< 8.6	< 0.004	< 3.8	< 12	< 270
Yttrium	6.9	0.59	< 0.5	< 8.6	< B	0	0.59 < 9.2	13 < 200
Zirconium	60	5.1	< B	0	< B	0	5.1	110

See note on Table F-1

TABLE F-20. POM COMPOUNDS BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY  
LOCATION 9, CEMENT KILN

POM Component	Kiln Exit, Test 9-3				ESP Exit, Test 9-6			
	XAD-2 Resin (296)		Module Wash (9-3H)		XAD-2 Resin (295)		Module Wash (475)	
	ng/g	ng/m <sup>3</sup>	ng/ml	ng/m <sup>3</sup>	ng/g	ng/m <sup>3</sup>	ng/ml	ng/m <sup>3</sup>
Anthracene	0.37	19	0.028	7.8	0.35	6.0	0.0022	0.097
Phenanthrene	--	--	--	--	0.02	0.35	--	--
Methyl Anthracenes	0.01	0.51	0.0080	2.2	0.15	2.5	--	--
Fluoranthene	0.26	13	0.016	4.5	0.27	4.6	0.0013	0.059
Pyrene	0.044	2.2	0.0080	2.2	0.11	1.8	0.015	0.65
*Benzo(c)phenanthrene	--	--	--	--	--	--	--	--
Chrysene	0.02	1.1	--	--	0.013	0.23	--	--
Benz(a)anthracene	--	--	--	--	0.0009	0.016	--	--
Methyl Chrysenes	--	--	--	--	0.0011	0.019	--	--
*7,12-Dimethylbenz(a) anthracene	--	--	--	--	--	--	--	--
Benzo Fluoranthenes	--	--	0.012	3.4	0.0037	0.063	--	--
*Benz(a)pyrene	--	--	0.012	3.4	0.0022	0.038	--	--
Benz(e)pyrene	--	--	--	--	0.002	0.035	--	--
Perylene	--	--	--	--	0.0018	0.031	--	--
*3-Methylcholanthrene	--	--	--	--	--	--	--	--
Indeno(1,2,3-cd)pyrene	--	--	--	--	--	--	--	--
Benzo(ghi)perylene	--	--	--	--	--	--	--	--
*Dibenzo(a,h)anthracene	--	--	--	--	--	--	--	--
*Dibenzo(c,g)carbazole	--	--	--	--	--	--	--	--
*Dibenz(ai and ah)pyrenes	--	--	--	--	--	--	--	--
Total	0.71	36	0.084	24	0.91	16	0.018	0.81

\* Compounds required to be identified for this contract

Note: Values in this table are expressed in nonograms (ng), (1 ng = 10<sup>-9</sup> g).  
Values in other trace species and organics tables in this report are  
expressed in micrograms (µg), (1 µg = 10<sup>-6</sup> g).

TABLE F-21. TRACE SPECIES AND ORGANIC EMISSIONS, SASS SOLIDS SECTION COLLECTION  
TEST 10/2-10, BLACK LIQUOR RECOVERY BOILER

Sample Type	Nozzle, Probe, 10 µm Cyclone Solids		3 µm Cyclone Solids		1 µm Cyclone Solids		Filters		Solid Section Wash	
	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.
	389	3.5376 g	380	0.8531 g	391	3.9293 g	287 + 288	9.4446 g	10/2-10 F	643 ml
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Antimony	< 20	< 43	< 40	< 21	< 20	< 48	< 20	< 120	< 0.5	< 200
Arsenic	< 1	< 2	2	1.0	5	12	5	29	< 0.02	< 7.9
Barium	70	150	30	16	40	96	20	120	< 0.1	< 39
Beryllium	0.2	0.43	< 0.2	< 0.1	< 0.1	< 0.24	< 0.1	< 0.58	< 0.003	< 1.2
Cadmium	14	30	18	9.4	10	24	7	40	0.01	3.9
Calcium	200	430	110	57	29	70	28	160	1.3	510
Chromium	27	58	36	19	8	19	3.4	20	0.14	55
Cobalt	8	17	6	3.1	8	19	10	58	< 0.02	< 7.9
Copper	3.6	7.8	3.6	1.9	2.0	4.8	2.1	12	0.03	12
Iron	210	450	240	130	110	260	41	240	1.3	510
Lead	16	35	20	10	18	43	16	92	< 0.1	< 39
Manganese	75	160	54	28	31	74	28	160	0.11	43
Mercury	< 0.5	< 1	< 1.0	< 5.2	< 0.5	< 1.2	< 0.5	< 2.9	< 0.005	< 2.0
Nickel	19	41	20	10	17	41	8	46	0.12	47
Selenium	< 1	< 2	< 2	< 1.0	< 1	< 2.4	< 1	< 5.8	< 0.02	< 7.9
Tellurium	< 100	< 220	< 200	< 100	< 100	< 240	< 100	< 580	< 2	< 790
Tin	< 50	< 110	< 100	< 520	< 50	< 120	< 50	< 290	< 3	< 1200
Titanium	15	32	56	29	< 15	< 36	< 15	< 87	< 1	< 390
Vanadium	3	6	< 6	< 3.1	< 3	< 7.2	< 3	< 17	< 0.1	< 39
Zinc	41	89	58	30	56	130	52	300	0.13	51
Chloride	48000	104000	49000	26000	47000	110000	52000	300000	110	43000
Fluoride	75	160	(4600)	2400	110	260	130	750	< 0.2	< 79
Nitrates	< 3.5	< 7.6	< 3.5	< 1.8	< 2.5	< 6.0	< 2.5	< 14	< 0.10	< 39
Sulfates	710000	1500000	630000	330000	650000	1600000	750000	4300000	810	320000
Total PCM	< 500	< 1100	NES	NES	< 200	< 480	210	1200	< 0.0003	< 0.12
Total PCB	< 1000	< 2100	NES	NES	< 500	< 1200	< 200	< 1200	< 0.001	< 0.39

See notes on Table F-1

471

TABLE F-22. TRACE SPECIES AND ORGANIC EMISSIONS, SASS ORGANIC AND LIQUIDS SECTION COLLECTION TEST 10/2-10, BLACK LIQUOR RECOVERY BOILER

Sample Type	XAD-2 Resin		Organic Module Rinse		Condensate		Impinger No. 1		Impinger No. 2		Impinger No. 3	
	Sample Number	Sample Weight/Vol.	Units	Units	Units	Units	Units	Units	Units	Units	Units	Units
	292	164 g	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
	243	92 ml	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
	205	353 ml	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
	10/2-10 G	1191 ml	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
	10/2-10 H	1301 ml	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
	304	983 ml	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Antimony	37	3700	< 0.5	< 28	< 0.5	< 110	< 0.50	< 370	< B	0	< 8	0
Arsenic	< 1	< 100	< 0.02	< 1.1	< 0.020	< 4.3	< 0.020	< 15	< 0.020	< 16	< 0.020	12
Barium	140	14000	NES	--	< 0.1	< 22	< 0.10	< 73	< 0.10	< 79	< 0.10	< 60
Beryllium	< 0.1	< 10	< 0.003	< 0.17	< 0.003	< 6.5	< 0.0030	< 2.2	< 0.0030	< 2.4	< 0.030	< 1.8
Cadmium	< 1	< 100	NES	--	< 0.01	< 2.2	< 0.010	< 7.3	0.0085	6.7	0.024	15
Calcium	< B	0	NES	--	1.3	280	0.21	150	0.71	570	8.6	5200
Chromium	1.7	170	NES	--	0.08	17	0.077	56	0.20	160	0.29	180
Cobalt	< 1	< 100	NES	--	< 0.02	< 4.3	0.025	18	0.073	58	0.54	320
Copper	< B	0	NES	--	< 0.01	< 2.2	0.013	9.2	0.043	34	0.040	24
Iron	< B	0	NES	--	4.3	930	0.60	430	1.2	980	2.1	1300
Lead	< B	0	< 0.1	< 5.6	< 0.1	< 22	< 0.10	< 73	< 0.059	< 47	< 0.046	< 20
Manganese	< B	0	NES	--	1.2	260	0.38	280	0.12	98	0.078	47
Mercury	< 0.5	< 50	< 0.005	< 0.28	< 0.05	< 11	< 0.0050	3.7	< 0.0050	< 4.0	< 0.0050	< 3.0
Nickel	< B	0	NES	--	0.32	69	0.092	67	0.13	100	0.31	180
Selenium	< 1	< 100	< 0.1	< 5.6	< 0.03	< 6.5	< 0.20	150	< 0.20	< 160	< 0.20	< 120
Tellurium	< 100	< 10000	NES	--	< 2	< 430	< 2.0	< 1500	< 2.0	< 1600	< 2.0	< 1200
Tin	< 50	< 5000	NES	--	< 3	< 650	< 3.0	< 2200	< 3.0	< 2400	< 3.0	< 1800
Titanium	< 15	< 1500	NES	--	< 1	< 220	< 1.0	< 730	< 1.0	< 790	< 1.0	< 600
Vanadium	< 3	< 300	NES	--	< 0.1	< 22	< 0.10	< 73	< 0.1	< 79	< 0.1	< 60
Zinc	< B	0	NES	--	< 0.05	< 11	< B	0	< B	0	0.92	550
Chloride	< 13	< 1300	< 2	< 110	50	11000	< B	0	210	170000	91	54000
Fluoride	96	9600	< 2	< 110	< 0.2	< 43	< 0.40	< 290	< 0.10	79	< 0.20	< 120
Nitrates	< 1	< 100	1.7	96	< 0.1	< 22	< B	0	--	--	--	--
Sulfates	< B	0	120	6700	680	150000	76	56000	--	--	--	--
Total POM	780	78000	0.380	21	< 0.001	< 0.22	< 0.00040	< 0.29	< 0.00020	0.16	< 0.00020	< 0.12
Total PCB	< 25	< 2500	< 0.050	< 2.8	< 0.005	< 1.1	< 0.0020	< 1.5	< 0.00050	0.40	< 0.00050	< 0.30

472

See notes on Table F-1

TABLE F-23. TRACE SPECIES AND ORGANICS EMISSIONS, PROCESS SAMPLES AND MASS BALANCES  
TEST 10/2-10, BLACK LIQUOR RECOVERY BOILER

Sample Type	Emission In. Partic. < 3 µm	Total Emission Concen.	Total Emission Rate	Fuel Input, Black Liquor		Smelt Output		Furnace Emission	Furnace Emission Ratio	Mass Balance
Sample Number	391,287,288	SASS		297		1000		Liquor -	SASS	(Smelt + SASS)
Sample Weight/Vol.	13.3739 g	1.636 m <sup>3</sup>	54.6 m <sup>3</sup> /s	15185 g/s		6536 g/s		Smelt	(Liq-Smelt)	Liquor
Units	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s	µg/s	µg/s	µg/g	µg/s	µg/s		
Antimony	< 170	3700 < 4600	200000 < 250000	< 20	< 300000	< 20	< 130000	< 170000	> 1.18	1.1
Arsenic	41	42 < 200	2300 < 1100	< 1	< 15000	< 1	< 6500	< 8500	> 0.27	0.6
Barium	220	15000	820000	25	380000	30	200000	180000	4.6	2.7
Beryllium	< 0.82	0.43 < 19	23 < 1000	< 0.1	< 1520	0.2	1300	220	0.1	0.9
Cadmium	64	130 < 240	7100 < 13000	1.8	27000	3	20000	7000	1.01	1.0
Calcium	230	7300	400000	28	430000	600	3.9x10 <sup>6</sup>	-3.5x10 <sup>6</sup>	- 0.11	10.0
Chromium	39	750	41000	< 0.3	< 4600	18	120000	- 120000	- 0.34	>35.0
Cobalt	77	560 < 610	27000 < 33000	3.2	49000	11	72000	- 23000	- 1.2	2.02
Copper	17	100	5500	1.0	15000	4.3	28000	- 13000	- 0.42	2.23
Iron	500	5200	280000	44	670000	110	720000	- 50000	- 5.6	1.5
Lead	140	180 < 390	9800 < 21000	7	110000	3	20000	90000	0.11	0.27
Manganese	230	1200	66000	28	430000	96	630000	- 200000	- 0.33	1.6
Mercury	< 4.1	< 80	< 4400	< 0.3	< 4600	< 0.5	< 3300	< 1300	3.4	< 1.7
Nickel	87	540	29000	4	61000	10	65000	- 4000	- 7.3	1.54
Selenium	< 8.2	< 560	< 31000	< 1	< 15000	< 1	< 6500	8500	- 3.7	< 2.50
Tellurium	< 820	< 11000	< 600000	< 75	< 1.1x10 <sup>6</sup>	< 100	< 650000	< 450000	1.33	1.14
Tin	< 410	< 13000	< 710000	< 50	< 760000	< 50	< 330000	< 430000	1.65	1.4
Titanium	< 120	61 < 3900	3300 < 210000	< 9	< 140000	25	160000	- 20000	1.65	1.2
Vanadium	< 24	6.7 < 610	370 < 33000	< 1	< 15000	4	26000	- 11000	- 0.03	1.8
Zinc	430	1200	66000	4	61000	7.3	48000	13000	5.1	1.9
Chloride	310000	790000	4.3x10 <sup>6</sup>	7300	110x10 <sup>6</sup>	15300	100x10 <sup>6</sup>	10x10 <sup>6</sup>	0.43	0.95
Fluoride	1000	13000 < 14000	710000 < 760000	46	700000	107	700000	0	--	2.0
Nitrates	< 20	200 < 290	11000 < 16000	NR	--	< 0.5	< 3300	--	--	--
Sulfates	5.9x10 <sup>6</sup>	7.9x10 <sup>6</sup>	430x10 <sup>6</sup>	NR	--	601000	3.9x10 <sup>9</sup>	--	--	--
Total POM	1200	790000	4.3x10 <sup>6</sup>	209	3.2x10 <sup>6</sup>	< 5	< 33000	3.2x10 <sup>6</sup>	1.36	1.36
Total PCB	< 1200	< 7300	< 400000	< 50	< 760000	< 10	< 65000	< 700000	< 0.6	< 0.66

See notes on Table F-1

TABLE F-24. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY  
TEST 10/2-10, BLACK LIQUOR RECOVERY BOILER

Sample Type	Combined Solids		XAD-2 Resin		Combined Liquids		Total Emission Concen.	Total Emission Rate
Sample Number	10/2-10 A		10/2-10 B		10/2-10 C		SASS	
Sample Weight/Vol.	17.7646 g		164 g		3299 ml		1.636 m <sup>3</sup>	54.6 m <sup>3</sup> /s
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s
Antimony	< 0.8	< 8.7	< 2	< 200	0.0091	18	18 < 230	980 < 12000
Arsenic	2	22	< 2	< 200	< B	0	22 < 220	1200 < 12000
Barium	8	87	9	900	0.048	98	1100	60060
Beryllium	< 0.8	< 8.7	< 2	< 200	< 0.0021	< 4.2	< 210	< 11000
Cadmium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Calcium	510	5500	MC	MC	MC	MC	5500 < MC	300000 < MC
Chromium	7	76	2	200	< B	0	280	15000
Cobalt	0.6	6.5	< 2	< 200	0.1	200	210 < 410	11000 < 22000
Copper	5	54	5	500	< B	< B	550	30000
Iron	49	530	38	3800	MC	MC	4300 < MC	230000 < MC
Lead	< 0.8	< 8.7	< 9	< 900	0.056	110	110 < 1000	6000 < 55000
Manganese	20	220	0.6	60	0.0037	760	1000	55000
Mercury	NR	--	NR	--	NR	--	NR	--
Nickel	36	390	7.3	730	0.16	330	1500	82000
Selenium	< 1	< 11	< 2	< 200	0.04	81	81 < 290	4400 < 16000
Tellurium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Tin	< 0.8	< 8.7	< 2	< 200	< B	0	< 210	< 11000
Titanium	< 24	< 260	2.3	2300	0.65	1300	3600 < 3900	200000 < 210000
Vanadium	0.7	7.6	0.8	800	0.00013	0.26	810	44000
Zinc	6	65	5	500	MC	MC	570 < MC	31000 < MC
Chlorine	MC	MC	2	200	< B	0	200 < MC	11000 < MC
Fluorine	130	1400	12	1200	MC	MC	2600 < MC	140000 < MC

See notes on Table F-1

TABLE F-25. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY (Continued)  
 TEST 10/2-10, BLACK LIQUOR RECOVERY BOILER

Sample Type	Combined Solids		MAD-2 Resin		Combined Liquids		Total Emission Concen.	Total Emission Rate
Sample Number	10/2-10 A		10/2-10 B		10/2-10 C		SASS	
Sample Weight/Vol.	17.7646 g		164 g		3299 ml		1.636	54.6 m <sup>3</sup> /u
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s
Aluminum	10	110	9	900	0.31	620	1600	87000
Bismuth	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Boron	9	98	< B	0	< B	0	98	5300
Bromine	31	340	< 2	< 200	< B	0	340 < 540	18000 < 29000
Cerium	< 0.8	< 8.7	< 2	< 200	< B	0	< 210	< 11000
Cesium	< 0.8	< 8.7	< 1	< 100	< 0.0025	< 5.1	< 110	< 6000
Dysprosium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Erbium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Europium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Gadolinium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Gallium	< 0.7	< 7.6	< 2	< 200	< B	0	< 210	< 11000
Germanium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Gold	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Hafnium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Holmium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Iodine	9	98	< 2	< 200	< B	0	98 < 300	5400 < 16000
Iridium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Lanthanum	< 0.8	< 8.7	< 2	< 200	< B	0	< 210	< 11000
Lithium	85	920	0.5	50	0.0045	9.0	980	54000
Lutetium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Magnesium	330	3600	170	1700	0.51	1000	6300	340000
Molybdenum	< 0.8	< 8.7	< B	0	< B	0	< 8.7	< 500
Neodymium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Niobium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Osmium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000

See note on Table F-1

TABLE F-26. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY (Continued)  
TEST 10/2-10, BLACK LIQUOR RECOVERY BOILER

Sample Type	Combined Solids		XAD-2 Resin		Combined Liquids		Total Emission Concen.	Total Emission Rate
Sample Number	10/2-10 A		10/2-10 B		10/2-10 C		SASS	
Sample Weight/Vol.	17.7646 g		164 g		3299 ml		1.636	54.6 m <sup>3</sup> /s
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s
Palladium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Platinum	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Phosphorus	120	1300	24	2400	< B	0	3700	200000
Potassium	MC	MC	8	800	MC	MC	800 < MC	44000 < MC
Praseodymium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Rhenium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Rhodium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Rubidium	63	680	0.8	80	< B	0	760	41000
Ruthenium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Samarium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Scandium	< 1	< 11	< 0.3	< 30	< 0.002	< 4.0	< 45	< 2400
Silicon	210	2300	120	12000	MC	MC	14000 < MC	760000 < MC
Silver	< 0.8	< 8.7	< 2	< 200	MC	MC	MC	MC
Sodium	MC	MC	240	24000	MC	MC	24000 < MC	MC
Sulfur	MC	MC	22	2200	MC	MC	2200 < MC	120000 < MC
Strontium	4	43	3	300	< B	0	340	18000
Tantalum	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Thallium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Terbium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Thorium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Thulium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Tungsten	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Uranium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Ytterbium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Yttrium	< 0.8	< 8.7	< 2	< 200	< 0.003	< 6.0	< 210	< 11000
Zirconium	1	11	< B	0	< B	0	11	600

See note on Table F-1

TABLE F-27. TRACE SPECIES AND ORGANIC EMISSIONS, SASS SOLIDS SECTION COLLECTION  
TEST 10/2-12, BLACK LIQUOR RECOVERY BOILER

Sample Type	Nozzle, Probe, 10 µm Cyclone Solids		3 µm Cyclone Solids		1 µm Cyclone Solids		Filters		Solid Section Wash	
	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.
	383	0.6481 g	388	0.1911 g	397	1.4589 g	285 + 286	6.1269 g	10/2-12 I	955 ml
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Antimony	< 20	< 9.7	< 100	< 14	< 20	< 22	< 20	< 92	< 0.5	< 360
Arsenic	< 2	< 0.97	< 50	< 7.2	< 1	< 1.1	< 1	< 4.6	< 0.020	< 14
Barium	30	15	20	2.9	20	22	32	150	< 0.1	< 72
Beryllium	< 0.2	< 0.097	< 1	< 0.14	< 0.1	< 0.11	< 0.1	< 0.46	< 0.003	< 2.2
Cadmium	15	7.3	31	4.5	10	11	10	46	0.02	14
Calcium	200	97	300	43	36	39	23	110	1.5	1100
Chromium	58	28	41	59	18	20	6.2	29	0.27	190
Cobalt	12	5.8	< 10	< 1.4	6	6.6	7	32	0.07	50
Copper	4.0	1.9	< 2	< 0.29	2.5	2.7	2.2	10	0.04	29
Iron	370	180	250	36	130	140	4.1	19	1.1	790
Lead	25	12	< 20	2.9	20	22	28	130	< 0.1	< 72
Manganese	74	36	44	6.3	2.8	3.1	20	92	0.066	47
Mercury	< 1	< 0.49	< 10	< 1.4	< 1	< 1.1	< 0.5	< 2.3	< 0.005	< 3.6
Nickel	38	19	< 10	< 1.4	20	22	6	28	0.10	72
Selenium	< 2	< 0.97	50	7.2	< 1	< 1.1	< 1	< 4.6	< 0.2	< 140
Tellurium	< 200	< 97	< 1000	< 140	< 100	< 110	< 100	< 460	< 2	< 1400
Tin	< 100	< 49	< 500	< 72	< 50	< 55	< 50	< 230	< 3	< 2200
Titanium	30	15	< 150	< 22	< 15	< 16	< 15	< 69	< 1	< 720
Vanadium	< 6	< 2.9	< 30	< 4.3	< 3	< 3.3	< 3	< 14	< 0.1	< 72
Zinc	52	25	73	10	39	43	33	150	0.09	65
Chloride	31000	15000	50000	7200	30000	33000	35000	160000	54	39000
Fluoride	(4200)	2000	780	110	< 1000	< 1100	40.0	180	0.36	258
Nitrates	< 8	< 3.9	< 60	< 8.6	19	21	28	130	< 0.10	< 72
Sulfates	64000	31000	690000	99000	590000	650000	670000	3100000	420	300000
Total POM							0.29	1.3	< 0.0002	< 0.14
Total PCB							< 100	< 460	< 0.0005	< 0.36

See notes on Table F-1

477

TABLE F-28. TRACE SPECIES AND ORGANIC EMISSIONS, SASS ORGANIC AND LIQUIDS SECTION COLLECTION TEST 10/2-12, BLACK LIQUOR RECOVERY BOILER

Sample Type	XAD-2 Resin		Organic Module Rinse		Condensate		Impinger No. 1		Impinger No. 2		Impinger No. 3	
Sample Number	291		235		206		314		315		316	
Sample Weight/Vol.	153 g		168 g		246		985 ml		948 ml		924 ml	
Units	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Antimony	< 20	< 2300	< 1	< 130	< 0.5	< 92	< 0.50	< 370	< B	0	< B	0
Arsenic	< 1	< 120	< 0.02	< 2.5	< 0.020	< 3.7	< 0.020	< 15	< 0.020	< 14	< 0.019	< 14
Barium	10	1200	< 0.05	< 6.3	< 0.1	< 18	< 0.10	< 7.4	< 0.10	< 71	< 0.10	< 69
Beryllium	< 0.1	< 12	< 0.005	< 0.63	< 0.003	< 0.55	< 0.0030	< 2.3	< 0.0030	< 2.1	< 0.0030	< 2.1
Cadmium	< 1	< 120	< 0.01	< 1.3	0.04	7.4	< 0.010	< 0.74	0.034	24	0.024	17
Calcium	< B	0	0.66	83	1.6	300	< B	0	< B	0	0.097	68
Chromium	7.2	830	0.36	45	0.31	57	0.088	65	0.24	170	0.29	200
Cobalt	< 1	< 120	< 0.02	< 2.5	0.04	7.4	< 0.017	< 13	0.040	26	0.036	25
Copper	< B	0	< 0.01	< 1.3	< 0.01	< 1.8	< B	0	0.011	7.5	0.030	21
Iron	< B	0	4.2	530	4.4	810	0.68	500	1.3	900	2.1	1400
Lead	< B	0	< 0.02	< 2.5	< 0.1	< 18	< 0.10	< 7.4	< 0.044	< 32	< 0.042	< 29
Manganese	< B	0	0.40	51	0.38	70	0.035	26	0.076	54	0.068	47
Mercury	< 0.5	< 58	< 0.005	< 0.63	< 0.005	< 0.92	< 0.0050	< 3.7	< 0.0050	< 3.5	< 0.0050	< 3.5
Nickel	< B	0	0.40	51	0.49	91	< 0.037	< 27	0.11	75	0.19	140
Selenium	10	1200	< 0.02	< 2.5	< 0.05	< 9.2	< 0.050	< 37	< 0.20	< 140	< 0.19	< 140
Tellurium	< 100	< 1200	< 3	< 380	< 2	< 370	< 2.0	< 1500	< 2.0	< 1400	< 1.9	< 1400
Tin	< 50	< 5800	< 1	< 130	< 3	< 550	< 3.0	< 2300	< 3.0	< 2100	< 3.0	< 2100
Titanium	< 15	< 1700	< 0.5	< 63	< 1	< 180	< 1.0	< 74	< 1.0	< 710	< 1.0	< 690
Vanadium	< 3	< 350	< 0.1	< 38	< 0.1	< 18	< 0.10	< 7.4	< 0.1	< 71	< 0.1	< 69
Zinc	< B	0	0.11	14	0.15	28	< B	0	0.11	7.5	0.31	220
Chloride	97	11000	9.9	1300	12	2200	< B	0	5000	3500000	410	290000
Fluoride	32	3700	1.1	140	0.54	100	< 0.40	< 293	< 0.20	< 140	< 0.19	< 140
Nitrates	< 1	< 120	0.40	51	0.58	110	9.1	6800	--	--	--	--
Sulfates	< B	0	40.0	6100	340	63000	250	190000	--	--	--	--
Total PCM	50	5800			< 0.001	< 0.18	< 0.00020	< 0.15	0.0013	0.90	< 0.00040	< 0.28
Total PCB	< 25	< 2900			< 0.005	< 0.92	< 0.00050	< 0.37	< 0.00010	< 0.071	< 0.0010	< 0.69

478

See notes on Table F-1

TABLE F-29. TRACE SPECIES AND ORGANICS EMISSIONS, PROCESS SAMPLES AND MASS BALANCES  
TEST 10/2-12, BLACK LIQUOR RECOVERY BOILER

Sample Type	Emission In. Partic. < 3 µm	Total Emission Concn.	Total Emission Rate	Fuel Input, Black Liquor		Smelt Output		Furnace Emission	Furnace Emission Ratio	Mass Balance
Sample Number	397,285,286	SASS		1003		1002		Liquor-	SASS	(Smelt + SASS)
Sample Weight/Vol.	7.5858	1.330	44.3 m <sup>3</sup> /s	9964 g/s		4289 g/s		Smelt	Liq.-Smelt	Liquor
Units	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s	µg/g	µg/s	µg/g	µg/s	µg/s		
Antimony	< 110	< 3400	< 150000	< 20	< 200000	< 20	< 86000	< 110000	< 1.3	< 1.18
Arsenic	< 5.7	< 200	< 8900	< 1	< 10000	< 1	< 4300	< 5700	< 1.6	< 1.32
Barium	170	1400 < 1600	62000 < 71000	42	420000	40	170000	250000	0.25	0.55
Beryllium	< 0.57	< 23	< 1000	< 0.1	< 1000	< 0.1	< 430	< 570	< 1.8	< 1.43
Cadmium	57	130 < 250	5700 < 11000	1.7	17000	2	8600	8400	0.68	0.84
Calcium	150	2000	89000	47	470000	950	4x10 <sup>6</sup>	- 3.5x10 <sup>6</sup>	- 0.03	8.7
Chromium	50	1700	75000	< 0.6	< 6000	17	73000	- 67000	- 1.1	25
Cobalt	38	160 < 290	7100 < 13000	2.4	24000	12	51000	- 27000	- 0.26	2.4
Copper	13	71 < 75	3100 < 3100	1.0	10000	8.3	36000	- 26000	- 0.12	3.9
Iron	160	5600	250000	39	390000	150	640000	- 250000	- 1.0	2.3
Lead	150	170 < 390	7500 < 17000	8	80000	8	34000	46000	0.16	0.51
Manganese	95	430	19000	32	320000	110	470000	- 150000	- 0.13	1.53
Mercury	< 3.4	< 80	< 3500	< 0.5	< 5000	< 0.5	< 2100	< 2900	< 1.2	1.12
Nickel	50	500 < 530	22000 < 23000	3.4	34000	10	43000	- 9000	- 2.4	1.9
Selenium	< 5.7	1100 < 1600	49000 < 71000	< 1	< 10000	< 1	< 4300	< 5700	< 8.6	< 5.3
Tellurium	< 570	< 1900	< 84000	< 100	< 1x10 <sup>6</sup>	< 100	< 430000	< 570000	< 0.15	< 0.5
Tin	< 780	< 16000	< 710000	< 50	< 500000	< 50	< 210000	< 290000	< 2.4	< 1.8
Titanium	< 85	23 < 4900	1000 < 220000	< 11	< 110000	20	86000	< 24000	< 0.04	< 0.8
Vanadium	< 17	< 620	< 27000	< 2	< 20000	< 3	< 13000	< 7000	< 3.9	< 2.0
Zinc	190	560	25000	6.9	69000	10	43000	26000	0.96	0.99
Chloride	190000	4.1x10 <sup>6</sup>	180x10 <sup>6</sup>	7280	73x10 <sup>6</sup>	37800	162x10 <sup>6</sup>	-89x10 <sup>6</sup>	- 2.0	4.7
Fluoride	180 < 1300	6500 < 8300	290000 < 370000	74	740000	95	410000	330000	0.88	0.95
Nitrates	150	7100 < 7300	310000 < 320000	NR	--	< 0.5	< 2100	--	--	--
Sulfates	3.8x10 <sup>6</sup>	4.2x10 <sup>6</sup>	186x10 <sup>6</sup>	NR	--	641000	2.7x10 <sup>9</sup>	--	--	--
Total POM	1.3	5800	260000	117	1.2x10 <sup>6</sup>	< 10	< 43000	1.2x10 <sup>6</sup>	0.22	0.25
Total PCB	< 460	< 3300	< 150000	< 50	< 500000	< 50	< 210000	< 290000	< 0.5	< 0.72

See notes on Table F-1

TABLE F-30. TRACE SPECIES AND ORGANIC EMISSIONS, SASS SOLIDS SECTION COLLECTION  
TEST 10/2-14, BLACK LIQUOR RECOVERY BOILER, LOCATION 10

Sample Type	Nozzle, Probe, 10 µm Cyclone Solids		3 µm Cyclone Solids		1 µm Cyclone Solids		Filters		Solid Section Wash	
	Sample Number	Sample Weight/Vol.	NONE		396		279		10/2-14 J	
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Antimony	< 200	< 0.96			< 200	< 1.6	< 20	< 0.45	< 0.5	< 33
Arsenic	< 10	< 0.048			< 10	< 0.080	< 1	< 0.022	< 0.02	< 1.3
Barium	10	0.048			20	0.16	130	2.9	< 0.1	< 6.5
Beryllium	< 2	< 0.0096			< 1	< 0.0080	0.36	0.0081	< 0.003	< 0.20
Cadmium	< 20	< 0.096			< 10	< 0.080	5	0.11	< 0.01	< 0.65
Calcium	160	0.77			140	1.1	37000	830	1.0	65
Chromium	76	0.36			88	0.71	20	0.45	0.08	5.2
Cobalt	< 20	< 0.096			< 11	< 0.089	10	0.22	0.05	3.3
Copper	14	0.067			6.6	0.053	9.5	0.21	0.03	2.0
Iron	1100	5.3			660	5.3	1100	25	0.42	27
Lead	< 80	< 0.38			< 30	< 0.24	25	0.56	< 0.1	< 6.5
Manganese	44	0.21			41	0.33	36	0.81	0.018	1.2
Mercury	< 10	< 0.048			< 5	< 0.040	< 0.5	< 0.011	< 0.005	< 0.33
Nickel	< 20	< 0.096			33	0.27	11	0.25	< 0.05	< 3.3
Selenium	200	0.96			10	0.080	40	0.90	< 0.001	< 0.065
Tellurium	< 2000	< 9.6			< 1000	< 8.0	< 100	< 2.2	< 2	< 130
Tin	< 1000	< 4.8			< 500	< 4.0	< 50	< 1.1	< 3	< 200
Titanium	400	1.9			300	2.4	140	3.1	< 1	< 65
Vanadium	< 60	< 0.29			< 33	< 0.27	4	0.090	< 0.1	< 6.5
Zinc	120	0.57			87	0.70	37	0.83	0.05	3.3
Chloride	65000	310			130000	1000	88000	2000	30	2000
Fluoride	(29000)	140			(46000)	370	(3090)	69	< 0.2	< 13
Nitrates	< 350	< 1.7			< 800	< 6.4	< 90	< 2.0	< 0.1	< 6.5
Sulfates	570000	2700			720000	5800	590000	13000	48	3100
Total POM									0.00037	0.024
Total PCB									<0.0005	< 0.033

See notes on Table F-1

TABLE F-31. TRACE SPECIES AND ORGANIC EMISSIONS, SASS ORGANIC AND LIQUIDS SECTION COLLECTION TEST 10/2-14, BLACK LIQUOR RECOVERY BOILER, LOCATION 10

Sample Type	XAD-2 Resin		Organic Module Rinse		Condensate		Impinger No. 1		Impinger No. 2		Impinger No. 3	
	Sample Number	Sample Weight/Vol.	Units	Units	Units	Units	Units	Units	Units	Units	Units	Units
	293	158.6 g										
			$\mu\text{g/g}$	$\mu\text{g/m}^3$	$\mu\text{g/ml}$	$\mu\text{g/m}^3$	$\mu\text{g/ml}$	$\mu\text{g/m}^3$	$\mu\text{g/ml}$	$\mu\text{g/m}^3$	$\mu\text{g/ml}$	$\mu\text{g/m}^3$
Antimony	< 20	< 230	< 0.5	< 7.7	< 0.5	< 120	< 0.51	< 86	< 0.026	< 3.6	< 0.0055	< 0.72
Arsenic	< 1	< 11	< 0.02	< 0.31	< 0.020	< 4.8	< 0.020	< 3.4	< 0.020	< 2.7	< 0.020	< 2.6
Barium	10	110	< 0.1	< 1.5	< 0.1	< 24	< 0.10	< 17	< 0.10	< 14	< 0.099	< 13
Beryllium	< 0.1	< 1.1	< 0.003	< 0.046	< 0.003	< 7.2	< 0.0030	< 0.51	< 0.0030	< 0.41	< 0.0030	< 0.39
Cadmium	2	23	0.01	0.031	0.01	2.4	< 0.010	< 1.7	0.0021	0.29	0.032	4.1
Calcium	< B	0	1.9	29	0.8	190	0.55	93	< B	0	< B	0
Chromium	3.2	36	0.26	4.0	< 0.02	< 4.8	0.13	21	0.24	33	0.88	110
Cobalt	< 1	< 11	< 0.02	< 0.31	< 0.02	< 4.8	< 0.017	< 2.9	0.022	2.9	0.093	12
Copper	< B	0	0.02	0.31	< 0.01	< 2.4	0.021	3.6	0.0037	0.50	0.0038	0.50
Iron	< B	0	2.1	32	0.08	19	0.84	140	1.6	220	6.0	790
Lead	< B	0	< 0.1	< 1.5	< 0.1	< 24	< 0.10	< 17	< 0.074	< 10	< 0.071	< 9.3
Manganese	< B	0	0.085	1.3	0.020	4.8	0.036	6.1	0.069	9.3	0.14	19
Mercury	< 0.5	< 5.7	< 0.005	< 0.077	< 0.005	< 1.2	< 0.0051	< 0.86	< 0.0050	< 0.68	< 0.0050	< 0.65
Nickel	< B	0	0.19	2.9	< 0.05	< 12	< 0.040	< 6.7	0.085	11	0.060	79
Selenium	< 1	< 11	< 0.1	< 1.5	< 0.02	< 4.8	< 0.020	< 3.4	< 0.18	< 24	< 0.18	< 24
Tellurium	< 100	< 1100	< 2	< 31	< 2	< 480	< 2.0	< 340	< 2.0	< 270	< 2.0	< 260
Tin	< 50	< 570	< 3	< 46	< 3	< 720	< 3.0	< 510	< 3.0	< 410	< 3.0	< 390
Titanium	< 15	< 170	< 1	< 15	< 1	< 240	< 1.0	< 170	< 1.0	< 140	< 1.0	< 130
Vanadium	< 3	< 34	< 0.1	< 1.5	< 0.1	< 240	< 0.1	< 17	< 0.1	< 14	< 0.1	< 1.3
Zinc	< B	0	0.48	7.4	0.02	4.8	0.037	6.2	< B	0	< B	0
Chloride	< 20	< 230	14	220	< 2	< 480	< B	0	1100	140000	660	86000
Fluoride	77	870	0.56	8.6	< 0.2	< 48	< 0.30	< 51	0.26	35	0.42	55
Nitrates	< 1	< 11	1.1	17	< 0.10	< 24	27	4600	--	--	--	--
Sulfates	< B	0	6.0	92	60.0	14000	260	44000	--	--	--	--
Total POM	4900	56000	0.61	9.4	< 0.0002	< 0.048	< 0.0020	< 0.34	0.012	1.6	0.042	5.5
Total PCB	< 25	< 280	< 0.005	< 0.077	< 0.0005	< 0.0005	< 0.00051	< 0.086	< 0.0010	< 0.14	< 0.00010	< 0.013

431

See notes on Table F-1

TABLE F-32. TRACE SPECIES AND ORGANICS EMISSIONS, PROCESS SAMPLES AND MASS BALANCES  
TEST 10/2-14, BLACK LIQUOR RECOVERY BOILER

Sample Type	Emission In. Partic. < 3 µm	Total Emission Concen.	Total Emission Rate	Fuel Input, Black Liquor		Smelt Output		Furnace Emission	Furnace Emission Ratio	Mass Balance
Sample Number	396 + 279	SASS		1009, 1010		1007, 1008		Liquor -	SASS	(Smelt + SASS)
Sample Weight/Vol.	0.4259	13.977 m <sup>3</sup>	66.8 m <sup>3</sup> /s	14528 g/s		5244 g/s		Smelt	Liq-Smelt	Liquor
Units	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s	µg/s	µg/s	µg/g	µg/s	µg/s		
Antimony	2.1	< 490	< 33000	< 20	< 290000	< 20	< 100000	< 190000	< 0.18	0.48
Arsenic	0.10	< 15	< 1000	< 1	< 14000	< 1	< 5200	< 9300	< 0.11	0.43
Barium	3.1	120 < 190	8000 < 13000	26	380000	35	180000	190000	0.04	0.51
Beryllium	0.0081 < 0.016	0.008 < 3.4	0.5 < 220	< 0.1	< 1400	0.2	1000	< 400	0.0012 < 0.55	0.7 < 0.87
Cadmium	0.11 < 0.19	30 < 33	2000 < 2200	1.2	17000	3	16000	1700	1.18	1.02
Calcium	830	1200	80000	49	710000	800	4.2x10 <sup>6</sup>	-3.5x10 <sup>6</sup>	- 0.02	6.0
Chromium	1.2	220	15000	< 0.7	< 10000	17	89000	- 79000	- 0.19	10.2
Cobalt	0.22 < 0.31	48 < 68	3200 < 4500	2.6	38000	13	68000	- 30000	- 0.11	1.9
Copper	0.26	7.9 < 10	520 < 670	1.6	23000	4	21000	2300	0.23	0.92
Iron	30	1400	93000	24	350000	115	600000	- 250000	- 0.37	2.0
Lead	0.56 < 0.80	2.1 < 69	140 < 4600	6	87000	7	37000	50000	0.003 < 0.09	0.42 < 0.47
Manganese	1.0	51	3400	30	440000	98	510000	- 78000	- 0.04	1.18
Mercury	< 0.051	< 9.3	< 620	< 0.5	< 7300	< 0.5	< 2600	< 4600	< 0.13	< 0.44
Nickel	0.52	93 < 120	6200 < 8000	2.0	29000	10	52000	- 23000	- 0.3	2.0
Selenium	0.98	1.9 < 72	130 < 4800	< 2	< 29000	< 1	< 5200	24000	0.006 < 0.2	0.19 < 0.3
Tellurium	< 10	< 2600	< 170000	< 150	< 2x10 <sup>6</sup>	< 100	< 520000	< 1.6x10 <sup>6</sup>	< 0.1	< 0.3
Tin	< 5.1	< 2900	< 190000	< 50	< 730000	< 50	< 260000	< 460000	< 0.4	< 0.6
Titanium	5.5	7.5 < 950	500 < 62000	< 11	< 160000	< 15	< 79000	< 81000	0.006 < 0.8	0.5 < 0.9
Vanadium	0.090 < 0.36	0.09 < 110	6 < 7300	< 2	< 29000	3	16000	< 13000	0.0005 < 0.5	0.5 < 0.8
Zinc	1.5	2.4	160	8	120000	11	58000	59000	0.003	0.50
Chloride	3000	160000	11x10 <sup>6</sup>	6750	9.8x10 <sup>6</sup>	29000	152x10 <sup>6</sup>	- 54x10 <sup>6</sup>	-0.2	1.7
Fluoride	440	2400	160000	100	1.4x10 <sup>6</sup>	150	790000	670000	0.24	0.65
Nitrates	< 8.4	4600	300000	--	--	< 0.5	2600	--	--	--
Sulfates	19000	39000	2.6x10 <sup>6</sup>	--	--	480000	2.5x10 <sup>9</sup>	--	--	--
Total POM	--	56000	3.7x10 <sup>6</sup>	73	1x10 <sup>6</sup>	< 10	< 52000	1x10 <sup>6</sup>	3.7	3.5
Total PCB	--	< 290	< 19000	< 50	< 730000	< 50	< 260000	< 460000	< 0.04	< 0.4

See notes on Table F-1

TABLE F-33. TRACE SPECIES AND ORGANIC EMISSIONS, SASS SOLIDS SECTION COLLECTION  
TEST 10/2-16, BLACK LIQUOR RECOVERY BOILER

Sample Type	Nozzle, Probe, 10 µm Cyclone Solids		3 µm Cyclone Solids		1 µm Cyclone Solids		Filters		Solid Section Wash	
	Sample Number	Sample Weight/Vol.	Units	Units	Units	Units	Units	Units	Units	Units
Sample Number	381	0.1076 g	NONE		382		280		10/2-16 A	
Sample Weight/Vol.	0.1076 g				0.0755 g		0.2503 g		840 µl	
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Antimony	< 200	< 1.5			< 200	< 1.1	< 20	< 0.35	< 0.5	< 30
Arsenic	< 10	< 0.076			< 10	< 0.053	< 1	< 0.018	< 0.02	< 1.2
Barium	NES	--			NES	--	NES	--	NES	--
Beryllium	< 2	< 0.015			< 1	< 0.0053	< 1	< 0.018	< 0.003	< 0.18
Cadmium	NES	--			NES	--	NES	--	< 0.01	< 0.59
Calcium	NES	--			NES	--	NES	--	1.3	77
Chromium	NES	--			NES	--	NES	--	0.15	8.9
Cobalt	NES	--			NES	--	NES	--	< 0.02	< 1.2
Copper	NES	--			NES	--	NES	--	< 0.01	< 0.59
Iron	NES	--			NES	--	NES	--	0.41	24
Lead	< 100	< 0.76			< 50	< 0.27	25	0.44	< 0.1	< 5.9
Manganese	NES	--			NES	--	NES	--	0.024	1.4
Mercury	< 10	< 0.076			< 5	< 0.027	< 5	< 0.088	< 0.005	< 0.30
Nickel	NES	--			NES	--	NES	--	< 0.05	< 3.0
Selenium	200	1.5			5	0.027	20	0.35	0.01	0.59
Tellurium	NES	--			NES	--	NES	--	< 2	<120
Tin	NES	--			NES	--	NES	--	< 3	<180
Titanium	NES	--			NES	--	NES	--	< 1	< 59
Vanadium	NES	--			NES	--	NES	--	< 0.1	< 5.9
Zinc	NES	--			NES	--	NES	--	0.06	3.5
Chloride	69000	520			68000	360	48000	850	23	1400
Fluoride	(1400)	11			(1600)	8.5	(2400)	42	0.58	34
Nitrates	< 55	< 0.42			< 90	< 0.48	< 270	< 4.8	< 0.20	< 12
Sulfates	590000	4500			550000	2900	51000	900	86	5100
Total POM									0.0018	0.11
Total PCB									< 0.0001	< 0.0059

See notes on Table F-1

483

TABLE F-34. TRACE SPECIES AND ORGANIC EMISSIONS, SASS ORGANIC AND LIQUIDS SECTION COLLECTION TEST 10/2-16, BLACK LIQUOR RECOVERY BOILER

Sample Type	XAD-2 Resin		Organic Module Rinse		Condensate		Impinger No. 1		Impinger No. 2		Impinger No. 3	
	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.
Units	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Antimony	< 50	< 630	< 1	< 14	< 0.5	< 160	< 0.50	< 46	< 0.011	< 1.4	< B	0
Arsenic	< 0.1	< 1.3	< 0.02	< 0.28	< 0.020	< 6.5	< 0.020	< 1.8	< 0.020	< 2.6	< 0.020	< 2.0
Barium	12	150	< 0.05	< 0.70	--	--	--	--	--	--	--	--
Beryllium	0.4	5.1	< 0.005	< 0.070	< 0.003	< 0.97	< 0.0030	< 0.27	< 0.0030	< 0.39	< 0.0030	< 0.30
Cadmium	1.0	13	< 0.01	< 0.14	< 0.01	< 3.2	< 0.010	< 0.91	< 0.0016	< 0.21	0.0098	0.99
Calcium	< B	0	0.5	7.0	0.9	290	< B	0	0.13	17	< B	0
Chromium	1.5	19	0.23	3.2	0.05	16	0.25	23	0.30	39	0.43	43
Cobalt	20	250	< 0.02	< 0.28	< 0.02	< 6.5	< 0.016	< 1.5	0.04	5.6	0.46	46
Copper	< B	0	< 0.01	< 0.14	< 0.01	< 3.2	0.015	1.3	0.015	2.0	= B	0
Iron	100	1300	1.4	20	0.04	13	0.19	18	1.6	211	2.0	200
Lead	5	63	< 0.02	< 0.28	< 0.1	< 32	< 0.10	< 9.1	< 0.092	< 12	< 0.091	< 9.1
Manganese	= B	0	0.05	0.70	0.035	11	0.021	1.9	0.076	9.9	0.070	7.0
Mercury	< 0.5	< 6.3	< 0.005	< 0.070	< 0.005	< 1.6	< 0.0050	< 0.46	< 0.0050	< 0.65	< 0.0050	< 0.50
Nickel	2.5	32	0.11	1.5	< 0.05	< 16	< 0.031	< 2.8	0.14	18	0.18	18
Selenium	< 5	< 63	< 0.02	< 0.28	< 0.01	< 3.2	< 0.010	< 0.91	< 0.097	< 13	< 0.20	< 20
Tellurium	< 100	< 1300	< 3	< 42	< 2	< 650	< 2.0	< 180	< 2.0	< 260	< 2.0	< 200
Tin	< 50	< 630	< 1	< 14	< 3	< 970	< 3.0	< 270	< 3.0	< 390	< 3.0	< 300
Titanium	150	1900	< 0.5	< 7.0	< 1	< 320	< 1.0	< 91	< 1.0	< 130	< 0.98	< 98
Vanadium	< 5	< 63	< 0.1	< 1.4	< 0.1	< 32	< 0.10	< 9.1	< 0.1	< 13	< 9.8	< 980
Zinc	2.6	33	0.37	5.2	0.13	42	< B	0	< B	0	< B	0
Chloride	11	140	13	180	4.3	1400	< B	0	28	3600	39	3900
Fluoride	12	150	< 0.4	< 5.6	< 0.2	< 65	< 0.30	< 27	< 0.20	< 26	0.77	77
Nitrates	0.70	8.9	< 0.2	< 2.8	< 0.20	< 65	< B	0	--	--	--	--
Sulfates	< B	0	15	210	100	32000	51	4600	--	--	--	--
Total POM	380	4800	9.8	140	0.00026	0.084	0.00053	0.048	< 0.00040	< 0.052	< 0.00040	< 0.040
Total PCB	< 10	< 130	< 0.005	< 0.070	< 0.0005	< 0.16	< 0.00050	< 0.046	< 0.000010	< 0.013	< 0.000098	< 0.0099

See notes on Table F-1

484

TABLE F-35. TRACE SPECIES AND ORGANICS EMISSIONS, PROCESS SAMPLES AND MASS BALANCES  
TEST 10/2-16, BLACK LIQUOR RECOVERY BOILER

Sample Type	Emission In. Partic. < 3 µm	Total Emission Concen.	Total Emission Rate	Fuel Input, Black Liquor		Smelt Output		Furnace Emission	Furnace Emission Ratio	Mass Balance
Sample Number	382 + 280	SASS		1014		1013		Liquor - Smelt	SASS	(Smelt + SASS)
Sample Weight/Vol.	0.3258 g	14.213 m <sup>3</sup>	60.7 m <sup>3</sup> /h	13263 g/s		4787 g/s			Liq-Smelt	Liquor
Units	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s	µg/s	µg/s	µg/g	µg/s	µg/s		
Antimony	< 1.5	< 160	< 9700	< 20	< 270000	< 50	< 240000	< 26000	< 0.04	< 0.93
Arsenic	< 0.071	< 16	< 970	< 1	< 13000	< 0.2	< 960	< 12000	< 0.08	< 0.15
Barium	NES	150	9100	30	400000	22	100000	300000	0.03	0.29
Beryllium	< 0.023	5.1 < 8.4	300 < 510	< 0.1	< 1300	0.5	2400	- 1000	- 0.3	2.0
Cadmium	NES	18 < 19	1100 < 1200	0.9	12000	0.5	2400	9500	0.11	0.3
Calcium	NES	440	27000	30	400000	220	1x10 <sup>6</sup>	660000	- 0.04	2.7
Chromium	NES	150	9100	< 0.5	< 6600	1.5	7200	< - 550	< -17	> 2.5
Cobalt	NES	300 < 320	18000 < 19000	2.6	34000	12	57000	23000	- 0.8	2.2
Copper	NES	3.3 < 7	200 < 420	1.4	19000	2.5	12000	6600	0.03	0.7
Iron	NES	1700	100000	14	190000	90	430000	- 250000	- 0.4	2.9
Lead	0.44 < 0.71	63 < 130	3800 < 7900	7	93000	5	24000	69000	0.06	0.3
Manganese	NES	32	1900	32	420000	100	480000	- 54000	- 0.04	1.1
Mercury	< 0.11	< 10	< 600	< 1	< 13000	< 0.5	< 2400	< 11000	< 0.06	0.22
Nickel	NES	69 < 91	4200 < 5500	< 1	< 13000	3	14000	- 1100	- 3.8	1.4
Selenium	0.062	1.9 < 110	110 < 6700	< 1	< 13000	< 5	< 24000	- 11000	- 0.01	1.8
Tellurium	NES	< 2700	< 160000	< 150	< 2x10 <sup>6</sup>	< 100	< 480000	< 1.5x10 <sup>6</sup>	< 0.1	< 0.3
Tin	NES	< 2800	< 170000	< 100	< 1.3x10 <sup>6</sup>	< 50	< 240000	< 1x10 <sup>6</sup>	< 0.16	< 0.3
Titanium	NES	1900 < 2600	110000 < 160000	< 15	< 200000	100	480000	> - 280000	> -0.4	> 3.0
Vanadium	NES	< 130	< 7900	< 3	< 40000	< 5	< 20000	< 16000	< 0.5	< 0.8
Zinc	NES	84	5100	5.4	< 72000	11	53000	< 19000	> 0.3	> 0.8
Chloride	1200	13000	790000	6900	91x10 <sup>6</sup>	125000	598x10 <sup>6</sup>	- 500x10 <sup>6</sup>	- 0.002	6.5
Fluoride	51	330 < 460	20000 < 28000	47.5	630000	86	410000	220000	0.09	0.7
Nitrates	< 5.3	9.1 < 91	550 < 5500	--	--	< 0.5	< 2400	--	--	--
Sulfates	3800	46000	2.8x10 <sup>6</sup>	--	--	600000	2.9x10 <sup>9</sup>	--	--	--
Total POM	NR	5000	300000	< 20	< 270000	< 20	< 96000	< 170000	1.8	1.5
Total PCB	NR	< 130	< 7900	< 50	< 660000	< 50	< 240000	< 420000	< 0.02	< 0.37

See notes on Table F-1

TABLE F-36. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY  
TEST 10/2-16, BLACK LIQUOR RECOVERY BOILER

Sample Type	Solid Section Wash		XAD-2 Resin		Combined Liquids		Total Emission Concen.	Total Emission Rate
Sample Number	10/2-16 A		10/2-16 B		10/2-16 C		SASS	
Sample Weight/Vol.	540 ml		180 g		9313 ml		14.213 m <sup>3</sup>	60.7 m <sup>3</sup> /s
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s
Antimony	< 0.008	< 0.48	< 0.5	< 6.3	0.068	44	44 < 51	2700 < 3100
Arsenic	< 0.004	< 0.24	< 0.3	< 3.8	< B	0	4.0	< 240
Barium	0.04	2.4	2	25	< B	0	< 27	1600
Beryllium	< 0.008	< 0.48	< 0.5	< 6.3	< 0.0067	< 4.4	< 11	< 670
Cadmium	< 0.008	< 0.48	< 0.5	< 6.3	< 0.01	< 6.6	< 13	< 780
Calcium	MC	MC	240	3000	MC	MC	3000 < MC	MC
Chromium	0.39	23	< B	0	0.27	180	200	12000
Cobalt	0.007	0.41	0.1	1.3	0.0058	3.8	5.5	330
Copper	0.02	1.2	1	13	0.056	37	50	3000
Iron	0.41	24	5	63	0.59	390	480	29000
Lead	0.05	3.0	< 2	< 25	0.025	16	19 < 44	1100 < 2700
Manganese	0.097	5.7	= B	0	0.070	46	52	3100
Mercury	NR	--	NR	--	NR	--	NR	--
Nickel	0.06	3.5	1.3	16	0.079	52	72	4400
Selenium	< 0.02	< 1.2	< 0.5	< 6.3	0.4	260	260 < 270	1600
Tellurium	< 0.008	< 4.8	< 0.5	< 6.3	< 0.007	< 4.6	< 16	< 970
Tin	< 0.008	< 4.8	< 1	< 13	0.18	120	120 < 140	7300
Titanium	0.04	2.4	1	13	< 0.14	< 93	15 < 110	910 < 6700
Vanadium	< 0.002	< 0.12	0.1	1.3	0.018	12	13	790
Zinc	0.06	3.5	< B	0	0.48	320	320	19000
Chlorine	1.4	83	32	410	0.82	540	1000	61000
Fluorine	0.4	24	3	38	MC	MC	62 < MC	MC

See notes on Table F-1

TABLE F-37. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY (Continued)  
TEST 10/2-16, BLACK LIQUOR RECOVERY BOILER

Sample Type	Solid Section Wash		XAD-2 Resin		Combined Liquids		Total Emission Concen.	Total Emission Rate
Sample Number	10/2-16 A		10/2-16 B		10/2-16 C		SASS	
Sample Weight/Vol.	840 ml		180 g		9313		14.213 m <sup>3</sup>	60.7 m <sup>3</sup> /s
Units	µg/ml	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s
Aluminum	0.6	3.5	64	810	0.039	26	840	51000
Bismuth	< 0.02	< 1.2	< 0.5	< 6.3	< 0.007	< 4.6	< 12	< 730
Boron	0.15	0.89	< B	0	0.16	100	100	6000
Bromine	0.04	2.4	< 2	< 25	0.44	29	31 < 56	1900
Cerium	< 0.008	< 0.48	< 0.5	< 6.3	0.0061	4.0	4.0 < 11	240 < 670
Cesium	0.003	0.18	< 0.5	< 6.3	0.0035	2.3	2.5 < 8.8	150 < 530
Dysprosium	< 0.008	< 0.48	< 0.5	< 6.3	< 0.007	< 4.6	< 11	< 670
Erbium	< 0.008	< 0.48	< 0.5	< 6.3	< 0.007	< 4.6	< 11	< 670
Europium	< 0.008	< 0.48	< 0.5	< 6.3	< 0.007	< 4.6	< 11	< 670
Gadolinium	< 0.008	< 0.48	< 0.5	< 6.3	< 0.007	< 4.6	< 11	< 670
Gallium	< 0.007	< 0.41	< 0.4	< 5.1	< B	0	< 5.5	< 330
Germanium	< 0.005	< 0.30	< 0.5	< 6.3	< B	0	< 6.6	< 400
Gold	< 0.008	< 0.48	< 0.5	< 6.3	< 0.007	< 4.6	< 11	< 670
Hafnium	< 0.008	< 0.48	< 0.5	< 6.3	< 0.007	< 4.6	< 11	< 670
Holmium	< 0.008	< 0.48	< 0.5	< 6.3	< 0.007	< 4.6	< 11	< 670
Iodine	< 0.01	< 0.59	< 0.5	< 6.3	< B	0	< 6.9	< 420
Iridium	< 0.008	< 0.48	< 0.5	< 6.3	< 0.007	< 4.6	< 11	< 670
Lanthanum	< 0.008	< 0.48	< 0.5	< 6.3	0.035	23	23 < 30	1400
Lithium	0.015	0.89	0.1	1.3	0.037	24	26	1600
Lutetium	< 0.008	< 0.48	< 0.5	< 6.3	< 0.007	< 4.6	< 11	< 670
Magnesium	2.7	160	37	470	1.4	910	1500	91000
Molybdenum	0.07	4.1	< B	0	0.019	12	16	970
Neodymium	< 0.008	< 0.48	< 0.5	< 6.3	< 0.007	< 4.6	< 11	< 670
Niobium	< 0.008	< 0.48	< 0.5	< 6.3	0.03	20	20 < 27	1200
Osmium	< 0.008	< 0.48	< 0.5	< 6.3	< 0.007	< 4.6	< 11	< 670

See note on Table F-1

TABLE F-38. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY (Continued)  
TEST 10/2-16, BLACK LIQUOR RECOVERY BOILER

Sample Type	Solid Section Wash		XAD-2 Resin		Combined Liquids		Total Emission Concen.	Total Emission Rate
Sample Number	10/2-16 A		10/2-16 B		10/2-16 C		SASS	
Sample Weight/Vol.	840 ml		180 g		9313 ml		14.213 m <sup>3</sup>	60.7 m <sup>3</sup> /a
Units	µg/ml	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s
Palladium	< 0.008	< 0.48	< 0.5	< 6.3	< 0.007	< 4.6	< 11	< 670
Platinum	< 0.008	< 0.48	< 0.5	< 6.3	< 0.007	< 4.6	< 11	< 670
Phosphorus	0.4	2.4	< B	0	2.5	1600	1600	97000
Potassium	MC	MC	< B	0	MC	MC	MC	MC
Praseodymium	< 0.008	< 0.48	< 0.5	< 6.3	0.01	6.6	616 < 13	400 < 790
Rhenium	< 0.008	< 0.48	< 0.5	< 6.3	< 0.007	< 4.6	< 11	< 670
Rhodium	< 0.008	< 0.48	< 0.5	< 6.3	< 0.007	< 4.6	< 11	< 670
Rubidium	0.02	1.2	0.2	2.5	< B	0	3.7	220
Ruthenium	< 0.008	< 0.48	< 0.5	< 6.3	< 0.007	< 4.6	< 11	< 670
Samarium	< 0.008	< 0.48	< 0.5	< 6.3	< 0.007	< 4.6	< 11	< 670
Scandium	< 0.01	< 0.59	< 0.1	< 1.3	< 0.009	< 5.9	7.8	470
Silicon	1.8	110	42	530	MC	MC	640 < MC	MC
Silver	< 0.01	< 0.59	< 0.5	< 6.3	MC	MC	MC	MC
Sodium	MC	MC	< B	0	MC	MC	MC	MC
Sulfur	MC	MC	14	180	MC	MC	180 < MC	MC
Strontium	0.03	1.8	0.4	5.1	0.086	56	63	3800
Tantalum	< 0.008	< 0.48	< 0.5	< 6.3	< 0.007	< 4.6	< 11	< 670
Thallium	< 0.008	< 0.48	< 0.5	< 6.3	< 0.007	< 4.6	< 11	< 670
Terbium	< 0.008	< 0.48	< 0.5	< 6.3	< 0.007	< 4.6	< 11	< 670
Thorium	< 0.008	< 0.48	< 0.5	< 6.3	< 0.007	< 4.6	< 11	< 670
Thulium	< 0.008	< 0.48	< 0.5	< 6.3	< 0.007	< 4.6	< 11	< 670
Tungsten	< 0.008	< 0.48	< 0.5	< 6.3	< 0.007	< 4.6	< 11	< 670
Uranium	< 0.06	< 3.5	< 0.5	< 6.3	< 0.007	< 4.6	< 11	< 670
Ytterbium	< 0.008	< 0.48	< 0.5	< 6.3	< 0.007	< 4.6	< 11	< 670
Yttrium	< 0.008	< 0.48	< 0.5	< 6.3	< 0.0012	< 0.77	< 7.6	
Zirconium	0.03	1.8	< B	0	< B	0	1.8	

See note on Table F-1

TABLE F-39. POM COMPOUNDS BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY  
LOCATION 10/2, BLACK LIQUOR RECOVERY BOILER

POM Component	Furnace Outlet, 10/2-10				ESP Outlet, 10/2-16			
	XAD-2 Resin 293		Module Wash 243		XAD-2 Resin 294		Module Wash 267	
	ng/g	ng/m <sup>3</sup>	ng/ml	ng/m <sup>3</sup>	ng/g	ng/m <sup>3</sup>	ng/ml	ng/m <sup>3</sup>
Anthracene	81	8100	0.057	3.2	130	14000	40	550
Phenanthrene	--	--	--	--	--	--	--	--
Methyl Anthracenes	0.93	93	--	--	6.6	730	--	--
Fluoranthene	7.7	770	0.2	11	19	2100	17	240
Pyrene	2.5	250	0.15	8.4	11	1200	0.14	2
*Benzo(c)phenanthrene	--	--	--	--	0.08	8.8	0.026	0.36
Chrysene	0.42	42	1.6	88	3.8	420	3.6	51
Benz(a)anthracene	--	--	0.06	3.4	--	--	0.47	6.6
Methyl Chrysenes	--	--	--	--	0.08	8.8	0.044	0.61
*7,12-Dimethylbenz(a) anthracene	--	--	--	--	--	--	--	--
Benzo Fluoranthenes	0.11	11	0.95	53	3	330	2.0	28
*Benz(a)pyrene	0.06	6	0.22	12	1.6	180	0.33	4.6
Benz(e)pyrene	--	--	0.23	13	--	--	0.34	4.8
Perylene	--	--	--	--	--	--	0.084	1.2
*3-Methylcholanthrene	--	--	--	--	--	--	--	--
Indeno(1,2,3-cd)pyrene	--	--	--	--	0.42	46	0.086	1.2
Benzo(ghi)perylene	--	--	--	--	0.14	15	0.14	2.0
*Dibenzo(a,h)anthracene	--	--	--	--	0.15	17	--	--
*Dibenzo(c,g)carbazole	--	--	--	--	--	--	--	--
*Dibenz(ai and ah)pyrenes	--	--	--	--	--	--	--	--
<b>Total</b>	<b>93</b>	<b>9300</b>	<b>3.4</b>	<b>193</b>	<b>170</b>	<b>19000</b>	<b>68.6</b>	<b>960</b>

\* Compounds required to be identified for this contract

Note: Values in this table are expressed in nonograms (ng), (1 ng = 10<sup>-9</sup> g).  
Values in other trace species and organics tables in this report are  
expressed in micrograms (µg), (1 µg = 10<sup>-6</sup> g).

TABLE F-40. TRACE SPECIES AND ORGANIC EMISSIONS, SASS SOLIDS SECTION COLLECTION  
TEST 12/2-3, PETROLEUM PROCESS HEATER

Sample Type	Nozzle, Probe, 10 µm Cyclone Solids		3 µm Cyclone Solids		1 µm Cyclone Solids		Filters		Solid Section Wash	
	None		None		None		277 ~ 0.1 g		12/2-3 A 691 ml	
Sample Number										
Sample Weight/Vol.										
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Antimony							NES	--	< 0.5	< 30
Arsenic							NES	--	< 0.01	< 0.5
Barium							NES	--	< 0.05	< 3
Beryllium							NES	--	< 0.005	< 0.3
Cadmium							NES	--	< 0.01	< 0.5
Calcium							NES	--	< 8	0
Chromium							NES	--	0.17	8.6
Cobalt							NES	--	0.08	4
Copper							NES	--	0.08	4
Iron							NES	--	16.0	810
Lead							NES	--	< 0.03	< 1.5
Manganese							NES	--	3.2	160
Mercury							< 0.2	0	< 0.005	< 0.3
Nickel							NES	--	1.5	76
Selenium							NES	--	< 0.01	< 0.5
Tellurium							NES	--	< 5	< 300
Tin							NES	--	< 1	< 50
Titanium							NES	--	< 1	< 50
Vanadium							NES	--	< 0.1	< 5
Zinc							NES	--	0.15	7.6
Chloride							520	3.8	1.0	50
Fluoride							NES	--	0.40	20
Nitrates							< 200	< 1.5	0.08	4
Sulfates							780000	5700	24.0	1200
Total POM							NES	--	NR	--
Total PCB							NES	--	NR	--

See notes on Table F-1

TABLE F-41. TRACE SPECIES AND ORGANIC EMISSIONS, SASS ORGANIC  
AND LIQUIDS SECTION COLLECTION  
TEST 12/2-3, PETROLEUM PROCESS HEATER

Sample Type	XAD-2 Resin		Organic Module Rinse		Condensate		Impinger No. 1		Impinger No. 2		Impinger No. 3	
Sample Number	298		12/2-3 B		12/2-3 C		Combined with		Combined with		Combined with	
Sample Weight/Vol.	158 g		617 ml		5326 ml		Condensate		Condensate		Condensate	
Units	$\mu\text{g/g}$	$\mu\text{g/m}^3$	$\mu\text{g/ml}$	$\mu\text{g/m}^3$	$\mu\text{g/ml}$	$\mu\text{g/m}^3$	$\mu\text{g/ml}$	$\mu\text{g/m}^3$	$\mu\text{g/ml}$	$\mu\text{g/m}^3$	$\mu\text{g/ml}$	$\mu\text{g/m}^3$
Antimony	< 50	< 600	< 0.5	< 20	< 0.23	< 88						
Arsenic	< 3	< 30	< 0.010	< 0.5	< 0.0058	< 2.3						
Barium	< 2.5	< 29	< 0.05	< 2	< 0.051	< 2.0						
Beryllium	< 0.5	< 6	< 0.05	< 2	< 0.0043	< 1.7						
Cadmium	6400	74000	< 0.01	< 0.5	< 0.0071	< 2.8						
Calcium	< B	0	0.10	5	< B	0						
Chromium	7.0	80	0.15	6.8	0.039	15						
Cobalt	< 25	< 290	< 0.05	< 2	< 0.048	< 19						
Copper	2.0	20	0.02	90	< 0.0071	< 2.8						
Iron	3.0	30	2.3	100	0.69	270						
Lead	< B	0	< 0.03	< 1	< B	0						
Manganese	= B	0	0.31	14	0.043	17						
Mercury	< 0.5	< 6	< 0.005	< 0.2	< 0.051	< 20						
Nickel	< 1.0	< 10	0.15	6.8	< 0.069	< 27						
Selenium	< 5	< 58	< 0.01	< 0.5	< 0.0043	< 1.7						
Tellurium	< 25	< 290	< 5	< 200	< 5.1	< 2000						
Tin	< 250	< 2900	< 1	< 40	< 1.0	< 390						
Titanium	50	600	< 1	< 40	< 1.0	< 390						
Vanadium	< 5	< 60	< 0.1	< 4	< 0.10	< 39						
Zinc	4.5	52	0.072	3.2	0.032	12						
Chloride	2.6	30	1.0	40	18	6800						
Fluoride	36.1	417	0.32	14	0.54	210						
Nitrates	< B	0	= B	0	< B	0						
Sulfates	220	2500	18.0	812	1400(SO <sub>2</sub> )	19000(SO <sub>2</sub> )						
Total POM	< 1	< 12	< 0.01	< 0.5	NR	--						
Total PCB	< 1	< 12	< 0.001	< 0.05	NR	--						

491

See notes on Table F-1

TABLE F-42. TRACE SPECIES AND ORGANICS EMISSIONS, PROCESS SAMPLES AND MASS BALANCES  
TEST 12/2-3, PETROLEUM PROCESS HEATER

Sample Type	Emission in Partic. < 3 µm	Total Emission Concen.	Total Emission Rate
Sample Number			
Sample Weight/Vol.	NES	13.67 m <sup>3</sup>	2.9 m <sup>3</sup> /s
Units	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s
Antimony	--	< 700	< 2000
Arsenic	--	< 40	< 120
Barium	--	< 40	< 120
Beryllium	--	< 10	< 30
Cadmium	--	74000	210000
Calcium	--	5	15
Chromium	--	110	320
Cobalt	--	4 < 300	12 < 900
Copper	--	120	350
Iron	--	1210	3500
Lead	--	< 3	< 9
Manganese	--	190	550
Mercury	0	< 30	< 90
Nickel	--	83 < 120	240 < 350
Selenium	--	< 60	< 170
Tellurium	--	< 2800	< 8100
Tin	--	< 3400	< 9900
Titanium	--	600 < 1100	1700 < 3200
Vanadium	--	< 110	< 320
Zinc	--	75	220
Chloride	3.8	6900	20000
Fluoride	--	660	1900
Nitrates	--	5.5	16
Sulfates	5700	10000	30000
Total POM	--	< 13	< 38
Total PCB	--	< 12	< 35

See notes on Table F-1

TABLE F-43. TRACE SPECIES AND ORGANIC EMISSIONS, SASS SOLIDS SECTION COLLECTION TEST 12/2-6, PETROLEUM PROCESS HEATER

Sample Type	Nozzle, Probe, 10 µm Cyclone Solids		3 µm Cyclone Solids		1 µm Cyclone Solids		Filters		Solid Section Wash	
	None		None		None		278 0.1019 g		12/2-6 D 761 ml	
Sample Number										
Sample Weight/Vol.										
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Antimony							NES	--	< 0.5	< 30
Arsenic							NES	--	< 0.01	< 0.7
Barium							NES	--	< 0.05	< 3
Beryllium							NES	--	< 0.005	< 0.3
Cadmium							NES	--	0.01	0.7
Calcium							NES	--	< B	0
Chromium							NES	--	0.21	14
Cobalt							NES	--	< 0.05	< 3
Copper							NES	--	0.02	1
Iron							NES	--	7.9	530
Lead							NES	--	< 0.03	< 2
Manganese							NES	--	2.1	140
Mercury							< 0.2	< 0.001	< 0.005	< 0.3
Nickel							NES	--	0.85	58
Selenium							NES	--	< 0.01	< 0.7
Tellurium							NES	--	< 5	< 300
Tin							NES	--	< 1	< 70
Titanium							NES	--	< 1	< 70
Vanadium							NES	--	< 0.1	< 7
Zinc							NES	--	0.04	3
Chloride							4800	44	= B	0
Fluoride							NES	--	< 0.2	< 10
Nitrates							360	3.3	0.10	6.8
Sulfates							910000	8200	13	880
Total POM							NES	--	NR	--
Total PCB							NES	--	NR	--

See notes on Table F-1

TABLE F-44. TRACE SPECIES AND ORGANIC EMISSIONS, SASS ORGANIC AND LIQUIDS SECTION COLLECTION TEST 12/2-6, PETROLEUM PROCESS HEATER

Sample Type	XAD-2 Resin		Organic Module Rinse		Condensate		Impinger No. 1		Impinger No. 2		Impinger No. 3	
Sample Number	534		12/2-6 E		12/2-6 F		Combined with		Combined with		Combined with	
Sample Weight/Vol.	160 g		682 ml		4788 ml		Condensate		Condensate		Condensate	
Units	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Antimony	< 50	< 710	< 0.5	< 30	< 0.19	< 80						
Arsenic	< 3	< 43	< 0.01	< 0.6	< 0.0054	< 2.3						
Barium	10	140	< 0.05	< 3	< 0.050	< 2.1						
Beryllium	< 0.5	< 7	< 0.005	< 0.3	< 0.0042	< 1.8						
Cadmium	0.5	7	< 0.01	< 0.6	< 0.0069	< 2.9						
Calcium	20000	280000	0.1	6	< B	0						
Chromium	6.5	93	0.19	12	0.12	50						
Cobalt	< 25	< 360	< 0.05	< 3	< 0.047	< 20						
Copper	2.0	28	< 0.01	< 0.6	< 0.0069	< 2.9						
Iron	110	1600	1.2	73	0.63	270						
Lead	2.0	28	< 0.03	< 2	< B	0						
Manganese	12	170	0.17	10	0.031	13						
Mercury	< 0.5	< 7	< 0.005	< 0.3	< 0.0050	< 2.1						
Nickel	6.0	85	0.15	9.1	0.066	28						
Selenium	< 5	< 70	< 0.01	< 0.6	< 0.0038	< 1.6						
Tellurium	< 25	< 360	< 5	< 300	< 5.0	< 2100						
Tin	< 250	< 3600	< 1	< 60	< 1.0	< 430						
Titanium	190	2700	< 1	< 60	< 1.0	< 430						
Vanadium	< 5	< 70	< 0.1	< 6	< 0.069	< 29						
Zinc	10	140	0.01	0.6	0.0033	1.4						
Chloride	< 2.6	< 37	< B	0	< B	0						
Fluoride	53	750	< 0.2	< 12	0.25	110						
Nitrates	< B	0	< B	0	< B	0						
Sulfates	230	3300	10.0	610	9400 (SO <sub>2</sub> )	110000 (SO <sub>2</sub> )						
Total POM	< 1	< 14	0.01	0.6	NR	--						
Total PCB	< 1	< 14	< 0.001	< 0.06	NR	--						

See notes on Table F-1

TABLE F-45. TRACE SPECIES AND ORGANICS EMISSIONS, PROCESS SAMPLES AND MASS BALANCES  
TEST 12/2-6, PETROLEUM PROCESS HEATER

Sample Type	Emission in Partic. < 3 $\mu\text{m}$	Total Emission Concen.	Total Emission Rate
Sample Number			
Sample Weight/Vol.	NES	11.24 m <sup>3</sup>	3.03 m <sup>3</sup> /s
Units	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{s}$
Antimony		< 850	< 2600
Arsenic		< 47	< 140
Barium		140 < 150	420 < 450
Beryllium		< 10	< 28
Cadmium	*	7.7 < 11	23 < 33
Calcium		280000	850000
Chromium		170	520
Cobalt		< 390	< 1200
Copper		29 < 33	88 < 100
Iron		2500	7600
Lead		28 < 32	85 < 97
Manganese		330	1000
Mercury	< 0.001	< 10	< 29
Nickel		180	550
Selenium		< 73	< 22
Tellurium		< 3100	< 9400
Tin		< 4200	< 13000
Titanium		2700 < 3300	8200 < 10000
Vanadium		112	340
Zinc		150	450
Chloride	44	44 < 81	130 < 250
Fluoride		860 < 880	2600 < 2700
Nitrates	3.3	10.1	31
Sulfates	8200	13000	39000
Total POM		0.6 < 15	1.8 < 45
Total PCB		< 15	< 45

See notes on Table F-1

TABLE F-46. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY  
TEST 12/2-6, PETROLEUM PROCESS HEATER

Sample Type	Combined Solids		XAD-2 Resin		Combined Liquids		Total Emission Concn.	Total Emission Rate
	$\mu\text{g/g}$	$\mu\text{g}/\text{m}^3$	$\mu\text{g/g}$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{ml}$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{s}$
Sample Number	278		534		12/2-6 C		SASS	
Sample Weight/Vol.	0.1019 g		160 g		5470 ml		11.24 $\text{m}^3$	3.03 $\text{m}^3/\text{s}$
Antimony	0.3	0.0027	< 0.4	< 5.7	< B	0	0.0027<5.7	0.0082<17
Arsenic	2	0.018	< 0.2	< 2.8	< B	0	0.018<2.8	0.055<8.5
Barium	35	0.32	10	140	0.00091	0.44	140	420
Beryllium	< 0.01	< 9.1x10 <sup>-5</sup>	< 0.4	< 5.7	< 0.0013	< 0.62	< 6.3	< 19
Cadmium	0.3	0.0027	< 0.6	< 8.5	< 0.0060	< 2.9	0.0027<11	0.0082<35
Calcium	MC	MC	80	1100	< 1.2	< 600	1100< MC	3300 < MC
Chromium	12	0.11	2.5	36	< B	0	36	110
Cobalt	0.8	0.0073	< 0.1	< 14	0.0027	1.3	1.3 < 15	3.9 < 46
Copper	14	0.13	3	43	0.37	180	220	680
Iron	190	1.7	19	270	< B	0	270	820
Lead	6	0.054	< 2	28	< 0.0024	< 1.2	28 < 29	85 < 88
Manganese	8	0.073	0.5	7.1	< B	0	7.2	22
Mercury	NR	--	NR	--	NR	--	NR	--
Nickel	8	0.073	2	28	0.037	18	46	140
Selenium	< 0.2	< 0.0018	< 5.5	< 78	< B	0	< 78	< 240
Tellurium	< 0.3	< 0.0027	< 0.55	< 7.8	< 0.0040	< 2.0	< 9.8	30
Tin	4	0.0036	< 0.75	< 11	< B	0	0.0036<11	0.011 < 33
Titanium	12	0.11	4	57	0.031	15	72	220
Vanadium	1	0.0091	0.2	2.8	< B	0	2.8	8.5
Zinc	35	0.32	5.5	78	0.18	87	170	500
Chlorine	150	1.3	3.4	48	< B	0	49	150
Fluorine	350	3.2	11	160	< B	0	160	490

See notes on Table F-1

TABLE F-47. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY (Continued)  
TEST 12/2-6, PETROLEUM PROCESS HEATER

Sample Type	Combined Solids		XAD-2 Resin		Combined Liquids		Total Emission Concen.	Total Emission Rate
Sample Number	278		534		12/6 C		SASS	
Sample Weight/Vol.	0.1019 g		160 g		5470 ml		11.24 m <sup>3</sup>	3.03 m <sup>3</sup> /s
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s
Aluminum	MC	MC	2.0	0.18	0.018	8.7	8.9 < MC	27 < MC
Bismuth	< 0.1	< 0.00091	< 0.4	< 0.036	< 0.0069	< 3.4	< 3.4	10
Boron	150	1.3	2.5	0.22	< B	0	1.5	4.6
Bromine	0.7	0.0063	< 0.9	< 0.080	< B	0	0.0063 < 0.086	0.019 < 0.26
Cerium	0.5	0.0045	< 0.45	< 0.040	= B	0	0.0045 < 0.045	0.014 < 0.14
Cesium	0.1	0.00091	< 0.25	< 0.022	< B	0	0.0091 < 0.023	0.0028 < 0.069
Dysprosium	< 0.1	< 0.00091	< 0.4	< 0.036	< 0.0040	< 2.0	< 2.0	< 6.2
Erbium	< 0.1	< 0.00091	< 0.4	< 0.036	< 0.0040	< 2.0	< 2.0	< 6.2
Europium	< 0.1	< 0.00091	< 0.4	< 0.036	< 0.0040	< 2.0	< 2.0	< 6.2
Gadolinium	0.1	0.00091	< 0.4	< 0.036	< 0.0040	< 2.0	0.0091 < 2.0	0.0028 < 6.2
Gallium	0.5	0.0045	< 0.3	< 0.027	< B	0	0.0045 < 0.032	0.014 < 0.095
Germanium	< 0.1	< 0.00091	< 0.4	< 0.036	< B	0	< 0.037	< 0.11
Gold	< 0.1	< 0.00091	< 0.4	< 0.036	< 0.0040	< 2.0	< 2.0	< 6.2
Hafnium	0.3	0.0027	< 0.4	< 0.036	< 0.0040	< 2.0	0.0027 < 2.0	0.0082 < 6.2
Holmium	< 0.1	< 0.00091	< 0.4	< 0.036	< 0.0040	< 2.0	< 2.0	< 6.2
Iodine	0.2	0.0018	0.65	0.058	0.0027	1.3	1.4	4.1
Iridium	< 0.1	< 0.00091	< 0.4	< 0.036	< 0.0040	2.0	2.0	6.1
Lanthanum	1	0.0091	< 0.65	< 0.058	0.0033	1.6	1.6 < 1.7	4.8 < 5.1
Lithium	0.1	0.00091	0.10	0.0089	0.00069	0.34	0.35	1.1
Lutetium	< 0.1	< 0.00091	< 0.4	< 0.036	< 0.0040	< 2.0	< 2.0	< 6.2
Magnesium	MC	MC	12	1.1	< B	0	1.1 < MC	3.3 < MC
Molybdenum	0.5	0.0045	7.0	0.62	= B	0	0.62	1.0
Neodymium	0.1	0.00091	< 0.4	< 0.036	< 0.0040	< 2.0	0.00091 < 2.0	0.0028 < 6.2
Niobium	< 0.1	< 0.00091	< 0.4	< 0.036	< 0.0040	< 2.0	< 2.0	< 6.2
Osmium	< 0.1	< 0.00091	< 0.4	< 0.036	< 0.0040	< 2.0	< 2.0	< 6.2

See note on Table F-1

TABLE F-48. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY (Continued)  
TEST 12/2-6, PETROLEUM PROCESS HEATER

Sample Type	Combined Solids		XAD-2 Resin		Combined Liquids		Total Emission Concen.	Total Emission Rate
Sample Number	278		534		12/6 C		SASS	
Sample Weight/Vol.	0.1019 g		160 g		5470 ml		11.24 m <sup>3</sup>	3.03 m <sup>3</sup> /s
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s
Palladium	< 0.1	<0.00091	< 0.4	< 0.036	< 0.004	< 2.0	< 2.0	< 6.1
Platinum	< 0.1	<0.00091	< 0.4	< 0.036	< 0.004	< 2.0	< 2.0	< 6.1
Phosphorus	23	0.21	22	2.0	< B	0	2.2	6.7
Potassium	>500	>4.5	42	3.7	MC	MC	MC	MC
Praseodymium	< 0.1	<0.00091	< 0.4	< 0.036	< 0.004	< 2.0	< 2.0	< 6.1
Rhenium	< 0.1	<0.00091	< 0.4	< 0.036	< 0.004	< 2.0	< 2.0	< 6.1
Rhodium	< 0.1	<0.00091	< 0.4	< 0.036	< 0.004	< 2.0	< 2.0	< 6.1
Rubidium	3	0.027	0.45	0.40	< B	0	0.43	1.3
Ruthenium	< 0.1	<0.00091	< 0.4	< 0.036	< 0.004	< 2.0	< 2.0	< 6.1
Samarium	0.2	0.0018	< 0.4	< 0.036	< 0.004	< 2.0	0.0018<2.0	0.0055<6.1
Scandium	< 0.1	<0.00091	< 0.1	< 0.0089	< 0.004	< 2.0	< 2.0	< 6.1
Silicon	MC	MC	60	5.3	< 0.82	400	400 < MC	1200 < MC
Silver	42	0.38	< 1.2	< 0.11	< 0.004	< 2.0	0.38 < 2.5	1.2 < 7.6
Sodium	MC	MC	69	6.1	MC	MC	6.1 < MC	18 < MC
Sulfur	MC	MC	17	1.5	MC	MC	1.5 < MC	4.5 < MC
Strontium	3	0.027	1.3	0.12	0.0062	3.2	3.3	10
Tantalum	< 0.1	<0.00091	< 0.4	< 0.036	< 0.004	< 2.0	< 2.0	< 6.1
Thallium	0.2	0.0018	< 0.4	< 0.036	< 0.004	< 2.0	0.0018<2.0	0.0055<6.1
Terbium	< 0.1	<0.00091	< 0.4	< 0.036	< 0.004	< 2.0	< 2.0	< 6.1
Thorium	0.8	0.0073	< 0.4	< 0.036	< 0.004	< 2.0	0.0073<2.0	0.022<6.1
Thulium	< 0.1	<0.00091	< 0.4	< 0.036	< 0.004	< 2.0	< 2.0	< 6.1
Tungsten	< 0.3	<0.0027	< 0.4	< 0.036	< 0.004	< 2.0	< 2.0	< 6.1
Uranium	0.6	0.0054	< 3	< 0.027	< 0.004	< 2.0	0.0054<2.0	0.016 < 6.1
Ytterbium	< 0.1	<0.00091	< 0.4	< 0.036	< 0.004	< 2.0	< 2.0	< 6.1
Yttrium	0.6	0.0054	< 0.4	< 0.036	< B	0	0.0054<0.041	0.016<0.12
Zirconium	10	0.091	2	0.18	< B	0	0.27	8.2

See note on Table F-1

TABLE F-49. POM COMPOUNDS BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY  
LOCATION 12/2, PROCESS HEATER

POM Component	XAD-2 Resin 534		Module Wash 12/2-6E	
	ng/g	ng/m <sup>3</sup>	ng/ml	ng/m <sup>3</sup>
Anthracene	0.50	7.1	0.018	1.1
Phenanthrene	--	--	--	--
Methyl Anthracenes	0.11	1.6	--	--
Fluoranthene	0.07	0.93	0.007	0.44
Pyrene	0.04	0.54	0.002	0.11
*Benzo(c)phenanthrene	--	--	--	--
Chrysene	0.0007	0.01	--	--
Benz(a)anthracene	--	--	--	--
Methyl Chrysenes	--	--	--	--
*7,12-Dimethylbenz(a) anthracene	--	--	--	--
Benzo Fluoranthenes	--	--	--	--
*Benz(a)pyrene	--	--	--	--
Benz(e)pyrene	--	--	--	--
Perylene	--	--	--	--
*3-Methylcholanthrene	--	--	--	--
Indeno(1,2,3-cd)pyrene	--	--	--	--
Benzo(ghi)perylene	--	--	--	--
*Dibenzo(a,h)anthracene	--	--	--	--
*Dibenzo(c,g)carbazole	--	--	--	--
*Dibenz(ai and ah)pyrenes	--	--	--	--
<b>Total</b>	<b>0.71</b>	<b>10.1</b>	<b>0.027</b>	<b>1.66</b>

\* Compounds required to be identified for this contract

Note: Values in this table are expressed in nonograms (ng), (1 ng = 10<sup>-9</sup> g).  
Values in other trace species and organics tables in this report are  
expressed in micrograms (µg), (1 µg = 10<sup>-6</sup> g).

TABLE F-50. TRACE SPECIES AND ORGANIC EMISSIONS, SASS SOLIDS SECTION COLLECTION TEST 13-18, WOOD-BARK BOILER

Sample Type	Nozzle, Probe, 10 µm Cyclone Solids		3 µm Cyclone Solids		1 µm Cyclone Solids		Filters		Solid Section Wash	
Sample Number	392		737		740		282		13-18 M	
Sample Weight/Vol.	0.2803		0.2647 g		1.1314 g		1.2379 g		1334 ml	
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Antimony	NES	--	NES	--	NES	--	NES	--	< 0.5	< 59
Arsenic	NES	--	NES	--	1700	170	1800	180	0.04	4.7
Barium	NES	--	NES	--	NES	--	NES	--	< 0.05	< 5.9
Beryllium	NES	--	NES	--	NES	--	NES	--	< 0.005	< 0.59
Cadmium	NES	--	NES	--	NES	--	NES	--	< 0.01	< 1.2
Calcium	NES	--	NES	--	NES	--	NES	--	200	24000
Chromium	NES	--	NES	--	NES	--	NES	--	0.05	5.9
Cobalt	NES	--	NES	--	NES	--	NES	--	< 0.05	< 5.9
Copper	NES	--	NES	--	NES	--	NES	--	0.06	7.1
Iron	NES	--	NES	--	NES	--	NES	--	6.9	820
Lead	NES	--	NES	--	NES	--	NES	--	0.21	25
Manganese	NES	--	NES	--	NES	--	NES	--	1.6	190
Mercury	0.6	0.015	0.5	0.012	0.4	0.040	0.4	0.040	< 0.005	< 0.59
Nickel	NES	--	NES	--	NES	--	NES	--	0.15	18
Selenium	NES	--	NES	--	NES	--	NES	--	< 0.01	< 1.2
Tellurium	NES	--	NES	--	NES	--	NES	--	< 5	< 590
Tin	NES	--	NES	--	NES	--	NES	--	< 1	< 120
Titanium	NES	--	NES	--	NES	--	NES	--	< 1	< 120
Vanadium	NES	--	NES	--	NES	--	NES	--	< 0.1	< 12
Zinc	NES	--	NES	--	NES	--	NES	--	0.60	71
Chloride	NES	--	NES	--	130	13	NES	--	2.1	250
Fluoride	2500	62	NES	--	NES	--	840	84	< 0.2	< 24
Nitrates	NES	--	NES	--	< 5	0.50	NES	--	0.86	100
Sulfates	NES	--	NES	--	80000	8000	NES	--	55	6500
Total POM	NES	--	NES	--	90	0.91	49	5.4	2.5	300
Total PCB	NES	--	NES	--	< 1	< 0.1	< 1	< 0.11	< 0.01	< 1.2

See notes on Table F-1

500

TABLE F-51. TRACE SPECIES AND ORGANIC EMISSIONS, SASS ORGANIC AND LIQUIDS SECTION COLLECTION TEST 13-18, WOOD-BARK BOILER

Sample Type	XAD-2 Resin		Organic Module Rinse		Condensate		Impinger No. 1		Impinger No. 2		Impinger No. 3	
	Sample Number	Sample Weight/Vol.	530	139 g	13-18 N	349 ml	13-18 O	3641 ml	Combined with Condensate	Combined with Condensate	Combined with Condensate	Combined with Condensate
Units	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Antimony	< 50	< 620	< 0.5	< 16	< 0.060	< 20						
Arsenic	< 3	< 37	0.10	3.1	< 0.0012	< 0.38						
Barium	2.5	31	< 0.05	< 1.6	< 0.0060	< 2.0						
Beryllium	< 0.5	< 6.2	< 0.005	< 0.16	< 0.00060	< 0.2						
Cadmium	< 0.5	< 6.2	< 0.01	< 0.31	< 0.0012	< 0.38						
Calcium	< B	0	0.33	10	0.038	12						
Chromium	2.5	31	1.10	34	< 0.0060	< 2.0						
Cobalt	< 2.5	< 310	< 0.05	< 1.6	< 0.0060	< 2.0						
Copper	1.5	19	0.02	0.62	< 0.0012	< 0.38						
Iron	< B	0	11.0	340	< 0.0060	< 2.0						
Lead	< B	0	< B	0	< 0.0036	< 1.2						
Manganese	< B	0	0.57	18	< 0.0012	< 0.38						
Mercury	< 0.4	< 4.9	< 0.005	< 0.16	< 0.00060	< 0.2						
Nickel	< B	0	2.2	68	< 0.0060	< 2.0						
Selenium	< 5	< 62	< 0.01	< 0.31	< 0.0012	< 0.38						
Tellurium	< 25	< 310	< 5	< 160	< 0.60	< 200						
Tin	< 250	< 3100	< 1	< 31	< 0.12	< 38						
Titanium	< B	0	< 1	< 31	< 0.12	< 38						
Vanadium	< 5	< 62	< 0.1	< 3.1	< 0.012	< 3.8						
Zinc	< B	0	0.088	2.7	< 0.00060	< 0.2						
Chloride	11	140	15	470	< 0.047	< 15						
Fluoride	46	570	4.1	130	0.096	31						
Nitrates	0.2	2.5	0.44	14	0.008	2.4						
Sulfates	520	6400	32	1000	< 0.16 (SO <sub>2</sub> )	< 51 (SO <sub>2</sub> )						
Total POM	3.2	40	0.23	7.1	NR	--						
Total PCB	< 1	< 12	< 0.01	< 0.31	NR	--						

101

See notes on Table F-1

TABLE F-52. TRACE SPECIES AND ORGANICS EMISSIONS, PROCESS SAMPLES AND MASS BALANCES  
TEST 13-18, WOOD-BARK BOILER

Sample Type	Emission in Partic. < 3 µm	Total Emission Concen.	Total Emission Rate	Coal Fuel Input		Wood Fuel Input		Boiler Ash Output		Dust Collector Ash Output		Mass Balance	Emission Ratio	
Sample Number	740 + 282	SASS		1038		1032		1033		1034		(SASS + Output) Input	SASS (Input - Output)	
Sample Weight/Vol.	2.3693 g	11.25 m <sup>3</sup>	10.8 m <sup>3</sup> /s	1100 g/s		640 g/s		37 g/s		69 g/s				
Units	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s	µg/g	µg/s	µg/g	µg/s	µg/g	µg/s	µg/g	µg/s	--	--	
Antimony	NES	140 < 840	1500 < 9100	< 50	< 55000	< 50	< 32000	< 50	< 1900	< 50	< 3500	< DL	< DL	
Arsenic		350	370 < 420	4000 < 4500	< 3	< 3300	< 3	< 1900	< 3	110	60	4140	> 1.6	> 4.4
Barium	NES	31 < 55	335 < 590	5	5500	5	3200	165	6100	300	21000	3.20	-0.018	
Beryllium	NES	< 8.6	< 93	2	2200	< 0.5	< 320	4.3	160	5.5	380	0.25 < 0.29	< 0.06	
Cadmium	NES	1.9 < 9.8	21 < 110	< 0.5	< 550	0.5	320	4.5	170	4.3	300	1.5	-0.14 < 0.05	
Calcium	NES	24000	260000	140	150000	5000	3200000	275	10000	35000	2400000	0.81	0.29	
Chromium	NES	270	2900	10	11000	3.5	2200	86	3200	71	4900	0.85	0.59	
Cobalt	NES	< 55	< 590	< 25	< 28000	< 25	< 16000	< 25	< 930	< 25	< 1700	< DL	< DL	
Copper	NES	59	640	5.5	6100	3	1900	40	1500	64	4400	0.82	0.30	
Iron	NES	2600	28000	6200	6800000	650	420000	345000	1300000	45000	3100000	0.62	0.01	
Lead	NES	9.8 < 28	110 < 300	10	11000	< 5	< 3200	17	630	93	6400	0.65	0.03	
Manganese	NES	250	2700	14	15000	125	80000	85	3200	700	48000	0.57	0.06	
Mercury		0.080	0.11 < 52	1.5 < 560	< 0.5	< 550	< 0.5	< 320	< 0.5	< 19	< 0.5	< 35	< DL	< DL
Nickel	NES	260	2800	5.0	5500	< 1	< 640	50	1900	48	3300	1.5 > 1.3	9.3 > 3.1	
Selenium	NES	< 67	< 720	< 5	< 5500	< 5	< 3200	< 5	< 190	6.5	450	> 0.52	< DL	
Tellurium	NES	< 2700	< 29000	< 25	< 28000	< 25	< 16000	< 25	< 930	< 25	< 1700	< DL	< DL	
Tin	NES	< 3600	< 39000	< 250	< 280000	< 250	< 160000	< 250	< 9300	< 250	< 17000	< DL	< DL	
Titanium	NES	470	5100	700	770000	240	150000	14000	520000	5200	360000	0.96	0.13	
Vanadium	NES	< 110	< 1200	15.0	17000	5	3200	135	5000	120	8300	0.65 < 0.71	< 0.9	
Zinc	NES	110	1200	12	13000	18	12000	18.5	680	185	13000	0.61	0.11	
Chloride	NES	1200	13000	< 13	< 14000	405	260000	< 13	< 480	255	18000	0.12	0.05	
Fluoride		920	2700	29000	67	74000	31	20000	160	5900	133	9200	0.47	0.37
Nitrates	NES	190	2100	11	12000	15	9600	< 5	< 190	< 5	< 350	0.095 < 0.12	0.098	
Sulfates	NES	22000	240000	1800	2000000	132	84000	675	25000	25500	1800000	0.97	0.77	
Total POM		6.3	350	3800										
Total PCB		< 0.2	< 14	< 150										

502

See notes on Table F-1

TABLE F-53. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY  
TEST 13-18, WOOD-BARK BOILER

Sample Type	Combined Solids		XAD-2 Resin		Combined Liquids		Total Emission Concen.	Total Emission Rate
	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.
	13-18 A, B & C	2.9143 g	13-18 D	139 g	13-18 E	3990 ml	11.25 m <sup>3</sup>	10.8 m <sup>3</sup> /s
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s
Antimony	110	28	< 0.2	< 2.5	< 0.004	< 1.4	28 < 32	300 < 43
Arsenic	790 < MC	200 < MC	< B	0	< 0.0025	< 0.87	200 < MC	2200 < MC
Barium	26 < MC	0.67 < MC	= B	0	0.051	18	19 < MC	200 < MC
Beryllium	1.7	0.44 < MC	< 0.2	< 2.5	< 0.004	< 1.4	0.44 < MC	4.8 < MC
Cadmium	32	8.3	< 0.4	< 4.9	< 0.007	< 2.5	8.3 < 16	90 < 170
Calcium	MC	MC	< B	0	< B	0	MC	MC
Chromium	160 < MC	40 < MC	< B	0	0.90	320	360 < MC	3900 < MC
Cobalt	28	7.3	< 0.1	< 1.2	0.020	7.1	14 < 16	160 < 170
Copper	87 < MC	23 < MC	1	12	< B	0	35 < MC	380 < MC
Iron	MC	MC	= B	0	1.5	540	540 < MC	5900 < MC
Lead	17 < MC	4.5 < MC	< 0.9	< 11	0.03	11	16 < MC	170 < MC
Manganese	MC	MC	= B	0	0.059	21	21 < MC	230 < MC
Mercury	NR	--	NR	--	NR	--	NR	--
Nickel	420	110	1.1	14	0.40	140	260	2900
Selenium	58	15	< 0.2	< 2.5	< 0.015	< 5.3	15 < 23	160 < 250
Tellurium	33	8.6 < 8.7	< 0.2	< 2.5	< 0.004	< 1.4	8.6 < 13	93 < 140
Tin	110	28	< 0.2	< 2.5	< 0.004	< 1.4	28 < 32	300 < 340
Titanium	11 < MC	2.7 < MC	< B	0	0.0032	1.1	3.8 < MC	41 < MC
Vanadium	51 < MC	13 < MC	0.092	1.1	< B	0	14 < MC	150 < MC
Zinc	MC	MC	< B	0	< B	0	MC	MC
Chlorine	240 < MC	62 < MC	< B	0	< B	0	62 < MC	670 < MC
Fluorine	38 < MC	10 < MC	< B	0	< B	0	10 < MC	110 < MC

See notes on Table F-1

TABLE F-54. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY (Continued)  
TEST 13-18, WOOD-BARK BOILER

Sample Type	Combined Solids		XAD-2 Resin		Combined Liquids		Total Emission Concen.	Total Emission Rate
Sample Number	13-18 A, B, & C		13-18 D		13-18 E			
Sample Weight/Vol.	2.9143		139 g		3990 ml		11.25 m <sup>3</sup>	10.8 m <sup>3</sup> /s
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s
Aluminum	MC	MC	3	37	0.28	98	140 < MC	1500 < MC
Bismuth	8.4	2.2	< 0.2	< 2.5	< 0.008	< 2.8	2.2 < 7.5	24 < 81
Boron	580 < MC	150 < MC	= B	0	0.53	190	340 < MC	3700 < MC
Bromine	46	12	0.7	8.6	0.00040	0.14	21	220
Cerium	150	39	< 0.2	< 2.5	0.0039	1.4	40 < 43	440 < 460
Cesium	19	4.8	< 0.2	< 2.5	< 0.0023	0.81	5.6 < 8.1	61 < 88
Dysprosium	3.6	0.94	< 0.2	< 2.5	< 0.004	< 1.4	0.94 < 4.8	10 < 52
Erbium	1.7	0.44	< 0.2	< 2.5	< 0.004	< 1.4	0.44 < 4.3	4.8 < 47
Europium	1.7	0.44	< 0.2	< 2.5	< 0.004	< 1.4	0.44 < 4.3	4.8 < 47
Gadolinium	2.7	0.70	< 0.2	< 2.5	< 0.004	< 1.4	0.70 < 4.6	7.6 < 50
Gallium	74 < MC	1.9 < MC	< 0.2	< 2.5	< 0.004	< 1.4	19 < MC	210 < MC
Germanium	5.4 < MC	1.4 < MC	< 0.2	< 2.5	< 0.004	< 1.4	1.4 < MC	15 < MC
Gold	< 0.10	< 0.026	< 0.2	< 2.5	< 0.004	< 1.4	< 3.9	< 42
Hafnium	1.7	0.44	< 0.2	< 2.5	< 0.004	< 1.4	0.44 < 4.3	4.8 < 47
Holmium	1.8	0.49	< 0.2	< 2.5	< 0.004	< 1.4	0.49 < 4.4	5.29 < 47
Iodine	11	2.9	< B	0	0.0034 < 0.0054	1.2 < 1.9	4.1 < 4.8	44 < 52
Iridium	< 0.10	< 0.026	< 0.2	< 2.5	< 0.004	< 1.4	< 3.9	< 42
Lanthanum	46	12	< 0.2	< 2.5	0.0084	3.0	15 < 18	160 < 190
Lithium	36	9.3	< B	0	0.0027	0.97	10	110
Lutetium	0.21 < 0.22	0.054 < 0.056	< 0.2	< 2.5	< 0.004	< 1.4	0.054 < 4.0	0.58 < 43
Magnesium	MC	MC	1	12	< B	0	12 < MC	130 < MC
Molybdenum	120	32	< B	0	0.031	11	43	
Neodymium	16	4.2	< 0.2	< 2.5	< 0.004	< 1.4	4.2 < 8.1	45 < 87
Niobium	40	10	< 0.2	< 2.5	< 0.004	< 1.4	10 < 14	110 < 150
Osmium	< 0.18	< 0.047	< 0.2	< 2.5	< 0.004	< 1.4	< 3.9	< 43

See note on Table F-1

TABLE F-55. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY (Continued)  
TEST 13-18, WOOD-BARK BOILER

Sample Type	Combined Solids		XAD-2 Resin		Combined Liquids		Total Emission Concen.	Total Emission Rate
Sample Number	13-18 A, B, & C		13-18 D		13-18 E			
Sample Weight/Vol.	2.9143 g		139 g		3990 ml		11.25 m <sup>3</sup>	10.8 m <sup>3</sup> /s
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s
Palladium	3.4	0.89	< 0.2	< 2.5	< 0.004	< 1.4	0.89 < 4.8	9.6 < 52
Platinum	< 0.26	< 0.068	< 0.2	< 2.5	< 0.004	< 1.4	< 4.0	< 43
Phosphorus	MC	MC	< B	0	< B	0	MC	MC
Potassium	MC	MC	9	110	1.5 < MC	550 < MC	660 < MC	7100 < MC
Praseodymium	5.9	1.5	< 0.2	< 2.5	< 0.004	< 1.4	1.5 < 5.4	16 < 58
Rhenium	< 0.10	< 0.026	< 0.2	< 2.5	< 0.004	< 1.4	< 3.9	< 42
Rhodium	< 0.18	< 0.047	< 0.2	< 2.5	< 0.004	< 1.4	< 3.9	< 43
Rubidium	56	15	< B	0	0.0023	0.83	16	170
Ruthenium	< 0.10	< 0.026	< 0.2	< 2.5	< 0.004	< 1.4	< 3.9	< 42
Samarium	9.0	2.3	< 0.2	< 2.5	< 0.004	< 1.4	2.3 < 6.2	25 < 67
Scandium	17	4.3	< 0.1	< 1.2	< 0.002	0.71	5.0 < 5.1	54 < 55
Silicon	MC	MC	< B	0	< B	0	MC	MC
Silver	14	3.5	0.7	8.6	MC	MC	12 < MC	130 < MC
Sodium	MC	MC	48	590	MC	MC	590 < MC	6400 < MC
Sulfur	MC	MC	= B	0	MC	MC	MC	MC
Strontium	0.48	0.12	3.7	3.7	< B	0	3.8	41
Tantalum	< 0.56	< 0.15	< 0.2	< 2.5	< 0.004	< 1.4	< 4.1	< 44
Thallium	41	11	< 0.2	< 2.5	< 0.004	< 1.4	11 < 15	120 < 160
Terbium	0.89 < 0.90	0.23	< 0.2	< 2.5	< 0.004	< 1.4	0.23 < 4.1	2.5 < 45
Thorium	14	3.6 < 3.7	< 0.2	< 2.5	< 0.004	< 1.4	3.6 < 7.6	39 < 82
Thulium	0.35 < 0.36	0.09	< 0.2	< 2.5	< 0.004	< 1.4	0.09 < 4.0	0.97 < 43
Tungsten	10	2.6	< 0.2	< 2.5	< 0.004	< 1.4	2.6 < 6.5	28 < 70
Uranium	12	3.1	< 0.2	< 2.5	< 0.004	< 1.4	3.1 < 7.0	33 < 76
Ytterbium	1.8	0.47	< 0.2	< 2.5	< 0.004	< 1.4	0.47 < 4.4	< 47
Yttrium	36	9.4	0.2	2.5	< 0.004	< 1.4	12 < 13	130 < 144
Zirconium	260	67	= B	0	< B	0	67	720

See note on Table F-1

TABLE F-56. POM COMPOUNDS BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY  
LOCATION 13, WOOD-BARK BOILER

POM Component	Stack Exit, Test 13-18					
	Cyclone Wash 605,606,607,333		XAD-2 Resin 530		Module Wash 264,331	
	ng/ml	ng/m <sup>3</sup>	ng/g	ng/m <sup>3</sup>	ng/ml	ng/m <sup>3</sup>
Anthracene	0.0045	0.54	0.12	1.4	0.019	0.60
Phenanthrene	--	--	0.018	0.22	--	--
Methyl Anthracenes	--	--	0.019	0.23	--	--
Fluoranthene	0.0009	0.11	0.43	0.53	0.0075	0.23
Pyrene	--	--	0.013	0.15	--	--
*Benzo(c)phenanthrene	--	--	--	--	--	--
Chrysene	0.0022	0.26	0.0026	0.032	0.03	0.93
Benz(a)anthracene	--	--	--	--	--	--
Methyl Chrysenes	--	--	--	--	--	--
*7,12-Dimethylbenz(a) anthracene	--	--	--	--	--	--
Benzo Fluoranthenes	--	--	0.0046	0.056	--	--
*Benz(a)pyrene	--	--	0.0031	0.039	--	--
Benz(e)pyrene	--	--	0.0034	0.042	--	--
Perylene	--	--	--	--	--	--
*3-Methylcholanthrene	--	--	--	--	--	--
Indeno(1,2,3-cd)pyrene	--	--	--	--	--	--
Benzo(ghi)perylene	--	--	--	--	--	--
*Dibenzo(a,h)anthracene	--	--	--	--	--	--
*Dibenzo(c,g)carbazole	--	--	--	--	--	--
*Dibenz(ai and ah)pyrenes	--	--	--	--	--	--
Total	0.0077	0.91	0.22	2.7	0.057	1.8

\* Compounds required to be identified for this contract

Note: Values in this table are expressed in nonograms (ng), (1 ng = 10<sup>-9</sup> g).  
Values in other trace species and organics tables in this report are  
expressed in micrograms (µg), (1 µg = 10<sup>-6</sup> g).

TABLE F-57. TRACE SPECIES AND ORGANIC EMISSIONS, SASS SOLIDS SECTION COLLECTION  
TEST 13-24, WOOD-BARK BOILER

Sample Type	Nozzle, Probe, 10 µm Cyclone Solids		3 µm Cyclone Solids		1 µm Cyclone Solids		Filters		Solid Section Wash	
	Sample Number	739	731	735	284	Sample Weight/Vol.	0.4806 g	0.3527 g	1.2542 g	~ 1.2 g
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Antimony	< 140	< 6.0	< 170	< 5.4	< 170	< 19	< 100	11	< 0.5	< 83
Arsenic	140	6.0	300	9.5	260	29	120	13	< 0.01	< 1.7
Barium	430	19	420	13	420	47	460	49	< 0.05	< 8.3
Beryllium	7	0.31	7	0.22	7	0.79	13	1.4	< 0.005	< 0.83
Cadmium	16	0.69	13	0.41	18	2.0	76	8.2	0.01	1.7
Calcium	100000	4300	57000	1800	65000	7300	67000	7200	100	17000
Chromium	140	6.0	100	3.2	100	11	170	18	0.05	8.3
Cobalt	< 70	< 3.0	< 80	< 2.5	< 80	< 9.0	< 50	5.4	< 0.05	< 8.3
Copper	160	6.9	160	5.1	180	20	480	52	0.09	15
Iron	33000	1400	31000	980	28000	3100	21000	2300	5.9	980
Lead	370	16	350	11	330	37	13000	1400	0.08	13
Manganese	3900	170	4000	130	5000	560	3400	370	2.0	330
Mercury	1.4	0.060	< 1.5	< 0.047	< 1.5	< 0.17	1.0	0.11	< 0.005	< 0.83
Nickel	110	4.7	66	2.1	62	7.0	110	12	0.10	17
Selenium	17	0.73	33	1.0	20	2.2	20	2.1	< 0.01	< 1.7
Tellurium	< 70	< 3.0	< 80	< 2.5	< 80	< 9.0	< 50	5.4	< 5	< 830
Tin	< 700	< 30	< 800	< 25	< 800	< 90	< 500	54	< 1	< 170
Titanium	4600	200	5700	180	4800	540	4400	470	< 1	< 170
Vanadium	130	5.6	120	3.8	130	15	210	23	< 0.1	< 17
Zinc	1300	56	1400	44	1500	170	7600	820	0.47	78
Chloride	NES	--	NES	--	130	15	NES	--	2.1	350
Fluoride	920	40	1300	41	1100	120	1200	130	< 0.20	< 33
Nitrates	NES	--	NES	--	< 5	< 0.56	NES	--	1.1	180
Sulfates	NES	--	NES	--	140000	16000	NES	--	45	7400
Total POM	NES	--							0.010	1.7
Total PCB	NES	--							< 0.005	< 0.83

See notes on Table F-1

TABLE F-58. TRACE SPECIES AND ORGANIC EMISSIONS, SASS ORGANIC AND LIQUIDS SECTION COLLECTION TEST 13-24, WOOD-BARK BOILER

Sample Type	KAD-2 Resin		Organic Module Rinse		Condensate		Impinger No. 1		Impinger No. 2		Impinger No. 3	
	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.
	531	167 g	609	298 ml	13-24 B	4048 ml	Combined with Condensate					
Units	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Antimony	< 50	< 750	< 0.5	< 13	0.35	130						
Arsenic	< 3	< 45	< 0.01	< 0.27	< 0.0099	< 3.6						
Barium	< 3	< 45	< 0.05	< 1.3	< 0.049	< 18						
Beryllium	< 0.5	< 7.5	< 0.005	< 0.13	< 0.0049	< 1.8						
Cadmium	< 0.5	< 7.5	< 0.01	< 0.27	0.016	5.9						
Calcium	< B	0	< 0.05	< 1.3	0.15	56						
Chromium	2.5	37	0.46	12	0.47	170						
Cobalt	< 25	< 370	< 0.05	< 1.3	< 0.049	< 18						
Copper	1.0	15	0.02	0.53	0.11	40						
Iron	< B	0	9.6	260	3.0	1100						
Lead	5	75	< B	0	< 0.030	< 11						
Manganese	< B	0	0.28	7.5	0.096	35						
Mercury	< 0.5	< 7.5	< 0.005	< 0.13	< 0.0049	< 1.8						
Nickel	< B	0	1.4	37	0.42	150						
Selenium	< 5	< 75	< 0.01	< 0.27	< 0.0099	< 3.6						
Tellurium	< 25	< 370	< 5	< 130	< 4.9	< 1800						
Tin	< 250	< 3700	< 1	< 27	< 0.99	< 360						
Titanium	15	220	< 1	< 27	690	250000						
Vanadium	< 5	< 75	< 0.1	< 2.7	< 0.099	< 36						
Zinc	< B	0	0.038	1.0	0.069	25						
Chloride	26	390	11	290	< B	0						
Fluoride	36	540	3.3	88	5.4	2000						
Nitrates	3.0	45	0.22	5.9	0.46	79						
Sulfates	22	330	5.0	130	17000 (SO <sub>2</sub> )	3000000 (SO <sub>2</sub> )						
Total POM			0.23	6.1								
Total PCB			< 0.010	< 0.27								

See notes on Table F-1

508

TABLE F-59. TRACE SPECIES AND ORGANICS EMISSIONS, PROCESS SAMPLES AND MASS BALANCES  
TEST 13-24, WOOD-BARK BOILER

Sample Type	Emission in Partic. < 3 µm	Total Emission Concn.	Total Emission Rate	Coal Fuel Input		Wood Fuel Input		Boiler Ash Output		Dust Collector Ash Output		Mass Balance	Emission Ratio
Sample Number	755 + 284	SASS		1039		1035		1036		1037		(SASS + Output)	SASS (Input - Output)
Sample Weight/Vol.	~2.5	11.17 m <sup>3</sup>	11.0 m <sup>3</sup> /s	1100 g/s		640 g/s		37 g/s		69 g/s		Input	
Units	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s	µg/g	µg/s	µg/g	µg/s	µg/g	µg/s	µg/g	µg/s	--	--
Antimony	11 < 30	130 < 980	1400 < 11000	< 50	< 55000	< 50	< 32000	< 50	< 1900	< 50	< 3500	< DL	< DL
Arsenic	42	58 < 110	640 < 1200	< 3	< 3300	< 3	< 1900	< 3	< 110	83	5700	> 1.2	< DL
Barium	96	130 < 200	1400 < 2200	5	5500	< 3	< 1900	180	6700	310	21000	0.76	0.52
Beryllium	2.2	2.7 < 13.4	30 < 150	1.3	1400	< 0.5	< 320	13	480	7.3	500	0.72	0.071
Cadmium	2.8	19 < 26	210 < 290	0.3	330	0.5	320	6.0	220	3.3	230	1.0	1.1 < 1.5
Calcium	15000	23000	250000	350	390000	1800	1200000	18000	670000	18500	1300000	1.4	0.63
Chromium	29	270	3000	11	12000	2	1900	89	3300	66	4600	0.78	0.49
Cobalt	5.4 < 14	< 420	< 4600	< 25	< 28000	< 25	< 16000	< 25	< 930	< 25	< 1700	< DL	< DL
Copper	72	150	1700	4	4400	1.5	960	42	1600	59	4100	1.4	5.7
Iron	5400	9800	110000	12000	13x10 <sup>6</sup>	390	250000	51000	1900000	41000	2800000	0.37	0.013
Lead	1400	1600	18000	10	11000	5	3200	30	1100	115	7900	1.9	3.6
Manganese	930	1500	17000	17	19000	110	70000	170	6300	800	55000	0.88	0.61
Mercury	0.11 < 0.28	0.17 < 11	1.9 < 120	< 0.5	< 550	< 0.5	< 320	< 0.5	< 19	< 0.5	< 35	< DL	< DL
Nickel	19	230	2500	5.0	5500	< 1	< 640	100	3700	47.5	3500	1.7	-1.7 > -2.8
Selenium	4.3	6.2 < 87	68 < 960	< 5	< 5500	5	3200	10	370	< 5	< 350	0.14	0.024
Tellurium	5.4 < 14	< 3100	< 34000	< 25	< 28000	< 25	< 16000	< 25	< 930	< 25	< 1700	< DL	< DL
Tin	54 < 140	< 4500	< 50000	< 250	< 280000	< 250	< 160000	< 250	< 9300	< 250	< 17000	< DL	< DL
Titanium	1000	250000	2800000	950	1000000	120	77000	14000	520000	6150	420000	3.4	18
Vanadium	38	46 < 180	510 < 2000	15	17000	< 5	< 3200	250	9300	125	8600	1.1	-0.51 < 0.26
Zinc	990	1200	13000	10.5	12000	19	12000	35	1300	175	12000	1.1	1.2
Chloride	15	1100	12000	< 13	< 14000	61.9	40000	13.0	480	280	19000	0.78 > 0.57	0.57 > 0.34
Fluoride	250	3000	33000	63	69000	22.6	14000	57.4	2100	106	7300	0.51	0.45
Nitrates	< 0.56	310	3400	11.5	13000	14.8	9500	5.0	190	< 5	< 350	0.14 < 15	0.13
Sulfates	16000	24000	260000	3600	4000000	< 120	77000	650	24000	24700	1700000	0.47	0.10
Total POM		7.9	87										
Total PCB		< 1.1	< 12										

605

See notes on Table F-1

TABLE F-60. TRACE SPECIES AND ORGANIC EMISSIONS, SASS SOLIDS SECTION COLLECTION  
TEST 14-2, STEEL OPEN HEARTH FURNACE

Sample Type	Nozzle, Probe, 10 µm Cyclone Solids		3 µm Cyclone Solids		1 µm Cyclone Solids		Filters		Solid Section Wash	
	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.	Sample Number	Sample Weight/Vol.
	556	8.8596 g	574	2.0105 g	568	7.0748 g	14 J	4.8611 g	14 K	1683 ml
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Antimony	< 50	< 37	< 100	< 17	< 150	< 89	< 150	< 61	< 0.5	< 70
Arsenic	75	56	70	12	80	47	75	31	0.025	3.5
Barium	20	15	30	5.0	20	12	16	6.5	< 0.05	< 7.0
Beryllium	< 0.5	< 0.37	< 0.5	< 8.4	< 0.5	< 2.9	< 1.5	< 0.61	< 0.005	< 0.7
Cadmium	130	96	280	47	280	170	550	220	0.11	15
Calcium	30000	22000	49000	8200	18000	11000	27000	11000	1.6	230
Chromium	320	240	380	64	330	200	310	130	0.21	30
Cobalt	< 25	< 19	< 50	< 840	< 25	< 15	< 25	< 10	< 0.05	< 7.0
Copper	940	700	1500	250	1500	890	1700	690	0.52	.73
Iron	240000	180000	340000	57000	270000	160000	270000	110000	120	17000
Lead	9500	7000	22000	3700	12000	7100	62000	25000	9.1	1300
Manganese	2200	1600	2700	450	2100	1200	2300	940	1.2	170
Mercury	< 0.5	< 0.37	< 0.6	< 1.0	< 0.5	< 0.3	< 0.7	< 0.28	< 0.005	< 0.7
Nickel	130	96	150	25	130	77	130	53	0.10	14
Selenium	< 5	< 3.7	< 10	< 1.7	< 5	< 3.0	< 16	< 6.5	< 0.01	< 1.4
Tellurium	50	37	250	42	380	220	730	300	< 5	< 700
Tin	< 250	< 190	< 500	< 84	< 500	< 300	< 800	< 330	< 1	< 140
Titanium	500	370	1000	170	500	300	830	340	< 1	< 140
Vanadium	60	44	50	840	50	30	66	27	< 0.1	< 14
Zinc	65000	48000	160000	27000	130000	77000	120000	49000	20	2800
Chloride	400	300	1800	300	1800	1100	2.6	1.1	2.7	380
Fluoride	560	420	600	100	290	170	250	100	< B	0
Nitrates	11.0	8.2	16	2.7	190	110	850	350	3.9	550
Sulfates	19000	14000	23000	3900	29000	17000	19000	7700	5.0	700
Total POM	70.5	52	NES	--	104	62	NES	--	NR	--
Total PCB	< 1	< 0.7	NES	--	< 1	< 0.6	NES	--	NR	--

See notes on Table F-1

TABLE F-61. TRACE SPECIES AND ORGANIC EMISSIONS, SASS ORGANIC AND LIQUIDS SECTION COLLECTION TEST 14-2, STEEL OPEN HEARTH FURNACE

Sample Type	XAD-2 Resin		Organic Module Rinse		Condensate		Impinger No. 1		Impinger No. 2		Impinger No. 3	
Sample Number	532		616		14 L		Combined with		Combined with		Combined with	
Sample Weight/Vol.	147 g		430 ml		4293 ml		Condensate		Condensate		Condensate	
Units	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Antimony	< 50	< 620	< 0.5	< 18	0.33	120						
Arsenic	< 3	< 37	< 0.01	< 0.36	< 0.01	< 3.6						
Barium	< 2.5	< 31	< 0.05	< 1.8	< 0.049	< 18						
Beryllium	< 0.5	< 6.2	< 0.005	< 0.18	< 0.0049	< 1.8						
Cadmium	< 0.5	< 6.2	0.046	1.7	0.028	10						
Calcium	= B	0	< 0.005	< 0.18	0.96	340						
Chromium	= B	0	5.3	190	4.4	1600						
Cobalt	< 25	< 310	0.15	5.4	0.14	50						
Copper	= B	0	0.05	1.8	0.054	19						
Iron	15	180	41	1500	28	10000						
Lead	< 5	< 62	< 0.03	< 1.1	< B	0						
Manganese	= B	0	0.43	15 <sup>φ</sup>	0.17	61						
Mercury	< 0.5	< 6.2	< 0.005	< 0.18	< 0.0049	< 1.8						
Nickel	1.5	18	7.0	250	4.4	1600						
Selenium	5	62	< 0.01	< 0.36	< 0.01	< 3.6						
Tellurium	< 25	< 310	< 5	< 180	< 4.9	< 1800						
Tin	< 250	< 3100	< 1	< 36	< 1.0	< 360						
Titanium	15	180	< 1	< 36	< 1.0	< 360						
Vanadium	< 5	< 62	< 0.1	< 3.6	< 0.1	< 36						
Zinc	0.5	6.2	0.045	1.6	0.1	37						
Chloride	= B	0	29	1000	< B	0						
Fluoride	--	--	20	720	37	13000						
Nitrates	36	440	0.84	30	1.0	370						
Sulfates	100	1200	3.0	110	400 (SO <sub>2</sub> )	140000 (SO <sub>2</sub> )						
Total POM	9.5	120	0.027	0.97	NR	--						
Total PCB	0.194	2.4	< 0.01	< 0.36	NR	--						

511

See notes on Table F-1

TABLE F-62. TRACE SPECIES AND ORGANICS EMISSIONS, PROCESS SAMPLES AND MASS BALANCES  
TEST 14-2, STEEL OPEN HEARTH FURNACE

Sample Type	Emission in Partic. < 3 µm	Total Emission Concen.	Total Emission Rate	No. 6 Fuel Oil		Mass Balance
				1031		
Sample Number	568 + 14 J	SASS	SASS	1031		SASS Fuel
Sample Weight/Vol.	11.9359 g	11.95 m <sup>3</sup>	48.3 m <sup>3</sup> /s	402 g/s		
Units	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s	µg/g	µg/s	--
Antimony	< 150	120 < 1000	5800 < 48000	< 25	< 10000	> 0.58
Arsenic	78	150 < 190	7200 < 9200	< 2	< 800	> 9.0
Barium	19	38 < 92	1800 < 4400	< 5	< 2000	> 0.91
Beryllium	< 3.5	0.37 < 10	18 < 480	< 0.3	< 120	> 0.15
Cadmium	390	570 < 580	28000	< 0.3	< 120	> 230
Calcium	22000	53000	2.6x10 <sup>6</sup>	31	12000	220
Chromium	330	2400	120000	< 5	< 2000	> 58
Cobalt	< 25	120 < 430	5800 < 21000	< 10	< 4000	> 1.4
Copper	1600	2700	130000	< 3	< 1200	> 110
Iron	270000	530000	26x10 <sup>6</sup>	39	16000	1600
Lead	32000	44000	2.1x10 <sup>6</sup>	< 3	< 1200	>1800
Manganese	2100	3000	140000	1.0	400	350
Mercury	< 3.3	< 10	< 480	< 0.1	< 40	< DL
Nickel	130	2100	100000	10	4000	25
Selenium	< 9.5	62 < 81	3000 < 3900	< 1	< 400	> 7.4
Tellurium	520	590 < 3500	28000 < 170000	< 25	< 10000	> 2.8
Tin	< 630	< 4400	< 210000	< 25	< 10000	< DL
Titanium	640	1300 < 1900	63000 < 92000	< 250	< 100000	> 0.62
Vanadium	57	110 < 230	5300 < 11000	33	13000	0.41 < 0.85
Zinc	130000	200000	9.7x10 <sup>6</sup>	3	1200	8000
Chloride	1100	3100	150000	< 17.1	< 6900	> 22
Fluoride	270	15000	720000	38.0	15000	47
Nitrates	460	1600	77000	NR	--	--
Sulfates	25000	45000	2.2x10 <sup>6</sup>	NR	--	--
Total PCM	62	230	11000	NR	--	--
Total PCB	< 0.6	2.4 < 4.1	< 17	NR	--	--

See notes on Table F-1

TABLE F-63. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY  
TEST 14-2, STEEL OPEN HEARTH FURNACE

Sample Type	Combined Solids		XAD-2 Resin		Combined Liquids		Total Emission Concn.	Total Emission Rate	Input No. 6 Fuel Oil		SSMS Mass Balance	Best Balance AA & SS
	Sample Number	14 A	14 B	14 C	SASS	1031	Emission Input	AA or SS Emission AA or SS Input				
Sample Weight/Vol.	22.8060 g		147 g		4713 ml		11.95 m <sup>3</sup>	48.3 m <sup>3</sup> /s	402 g/s			
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s	µg/g	µg/s		
Antimony	23	44	< 0.3	< 3.7	< 0.003	< 1.2	44 < 49	2100 < 2400	< 0.25	< 100	> 21	0.58 < 4.8
Arsenic	98	190	< 0.3	< 3.7	< 0.002	< 0.79	190	9200 < 9400	0.05 < 0.1	20 < 40	460	360
Barium	MC	MC	2.5	31	< B	0	31 < MC	1500 < MC	0.85	340	4.4 < MC	5.3 < MC
Beryllium	0.8	1.5	< 0.3	< 3.7	< 0.001	< 0.39	1.5 < 5.6	72 < 270	< 0.25	< 100	> 0.72	> 0.72
Cadmium	3	5.2	< 0.35	< 4.3	< 0.006	< 2.4	5.2 < 12	250 < 570	< 0.35	< 140	> 1.8	> 1.8
Calcium	MC	MC	94	1200	MC	MC	1200 < MC	5800 < MC	34	14000	4.2 < MC	185
Chromium	540	1000	6	74	9.0	3500	4600	220000	0.55	220	1000	550
Cobalt	36	69	< 0.1	1.2	< 0.003	< 1.2	70 < 71	3400	0.025 < 0.075	10 < 30	340 > 110	340 > 1.4
Copper	320	610	1	12	< B	0	620	30000	1	400	75	75
Iron	MC	MC	39	480	MC	MC	480 < MC	23000 < MC	29	12000	2.0 < MC	1.5 < 1700
Lead	210	400	< 1	< 12	< 0.006	< 2.4	400 < 410	19000 < 20000	0.5 < 0.85	200 < 340	95	95
Manganese	MC	MC	0.35	4.3	0.17	68	72 < MC	3500 MC	0.35	140	25 < MC	7.3 < 1000
Mercury	NR	--	NR	--	NR	--	NR	--	NR	--	--	< DL
Nickel	110	210	1	12	6.0	2400	2600	130000	8.5	3400	38	23
Selenium	36	69	0.45	5.5	< 0.01	< 3.9	75 < 78	3600 < 3900	< 0.75	< 300	> 12	> 7.5
Tellurium	< 0.7	< 1.3	< 0.5	6.2	< 0.003	< 1.2	6.2 < 8.7	300 < 420	< 0.25	< 100	> 3.0	> 2.8
Tin	24	46	0.4 < 0.55	4.9 < 6.8	< 0.003	< 1.2	51 < 52	2500	< 0.25	< 100	> 25	> 25
Titanium	MC	MC	7.6	93	= B	0	93 < MC	4500 < MC	1	400	11 < MC	11 < 160
Vanadium	220	420	0.05 < 0.1	0.62 < 1.2	< B	0	420	20000	16.5	6600	3.0	0.80
Zinc	MC	MC	0.5	6.2	< B	0	6.2 < MC	300 < MC	2	800	0.37 < MC	8000
Chlorine	440	840	< B	0	< B	< B	840	41000	3.5	1400	29	29
Fluorine	160	310	2	25	< B	0	340	16000	14	5600	2.8	1.1

See notes on Table F-1

513

TABLE F-64. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY (Continued)  
TEST 14-2, STEEL OPEN HEARTH FURNACE

Sample Type	Combined Solids		XAD-2 Resin		Combined Liquids		Total Emission Concn.	Total Emission Rate	Input No. 6 Fuel Oil		SSMS Mass Balance
Sample Number	14 A		14 B		14 C		SASS		1031		Emission Input
Sample Weight/Vol.	22.8060 g		147 g		4713 ml		11.95 m <sup>3</sup>	48.3 m <sup>3</sup> /s	402 g/s		
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s	µg/g	µg/s	
Aluminum	MC	MC	60	740	< B	0	740 < MC	36000 < MC	2.4	960	37 < MC
Bismuth	2	3.8	< 0.3	3.7	< 0.003	< 1.2	7.5 < 8.7	360 < 420	< 0.25	< 100	> 3.6
Boron	MC	MC	< B	0	< B	0	MC	MC	3	1200	MC
Bromine	45	86	< B	0	0.073	29	120	5600	0.45 < 0.55	180 < 220	31 < 25
Cerium	91	170	0.15 < 0.3	1.8 < 3.7	< 0.0017	< 0.66	170	8300 < 8400	< 0.25	< 100	> 83
Cesium	4	7.6	< 0.1	< 1.2	< 0.003	< 1.2	7.6 < 10	370 < 480	< 0.25	< 100	> 3.7
Dysprosium	5	9.5	< 0.3	< 3.7	< 0.003	< 1.2	9.5 < 14	460 < 700	< 0.25	< 100	> 4.6
Erbium	2	3.8	< 0.3	< 3.7	< 0.003	< 1.2	3.8 < 8.7	180 < 420	< 0.25	< 100	> 1.8
Europium	2	3.8	< 0.3	< 3.7	< 0.003	< 1.2	3.8 < 8.7	180 < 420	< 0.25	< 100	> 1.8
Gadolinium	3	5.7	< 0.3	< 3.7	< 0.003	< 1.2	5.7 < 11	280 < 510	< 0.25	< 100	> 2.8
Gallium	78	150	0.25	3.1	< 0.003	< 1.2	150	7400 < 7500	< 0.15	60	> 120
Germanium	66	130	< 0.25	< 3.1	< 0.003	< 1.2	130	6300 < 6500	< 0.25	< 100	> 63
Gold	< 0.1	< 0.19	< 0.3	< 3.7	< 0.003	< 1.2	< 5.1	< 250	< 0.25	< 100	< DL
Hafnium	0.5	0.95	< 0.3	< 3.7	< 0.003	< 1.2	0.95 < 5.9	46 < 280	< 0.25	< 100	> 0.46
Holmium	3	5.7	< 0.3	< 3.7	< 0.003	< 1.2	5.7 < 11	280 < 510	< 0.25	< 100	> 2.8
Iodine	6	11	0.2 < 0.35	2.5 < 4.3	0.00083	0.33	14 < 16	670 < 740	< 0.25	< 100	> 6.7
Iridium	< 0.1	< 0.19	< 0.3	< 3.7	< 0.003	< 1.2	< 5.1	< 250	< 0.25	< 100	< DL
Lanthanum	49	94	< 0.45	5.5	< 0.000057	< 0.026	100	4800	< 0.25	< 100	> 48
Lithium	33	63	0.1 < 0.15	1.2 < 1.8	< B	0	64 < 65	3100	0.3	120	26
Lutetium	0.3	0.57	< 0.3	< 3.7	< 0.003	< 1.2	5.7 < 11	280 < 510	< 0.25	< 100	> 28
Magnesium	MC	MC	8	98	< B	0	98 < MC	4700 < MC	7	2800	1.7 < MC
Molybdenum	53	100	< B	0	0.47	190	290	14000	6.5	2600	5.4
Neodymium	26	50	< 0.3	< 3.7	< 0.003	< 1.2	50 < 55	2400 < 2700	< 0.25	< 100	> 24
Niobium	27	52	< 0.3	< 3.7	< 0.003	< 1.2	52 < 57	2500 < 2700	< 0.25	< 100	> 25
Osmium	< 0.1	< 0.19	< 0.3	< 3.7	< 0.003	< 1.2	< 5.1	< 250	< 0.25	< 100	< DL

See note on Table F-1

TABLE F-65. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY (Continued)  
TEST 14-2, STEEL OPEN HEARTH FURNACE

Sample Type	Combined Solids		XAD-2 Resin		Combined Liquids		Total Emission Concent.	Total Emission Rate	Input No. 6 Fuel Oil		SSMS Mass Balance	
	Sample Number	Sample Weight/Vol.	Units	Units	Units	Units	Units	Units	Units	Units	Emission Input	
	14 A	22.8060 g	$\mu\text{g/g}$	$\mu\text{g/m}^3$	$\mu\text{g/g}$	$\mu\text{g/m}^3$	$\mu\text{g/ml}$	$\mu\text{g/m}^3$	$\mu\text{g/s}$	$\mu\text{g/g}$	$\mu\text{g/s}$	
	14 B	147 g	$\mu\text{g/g}$	$\mu\text{g/m}^3$	$\mu\text{g/ml}$	$\mu\text{g/m}^3$	$\mu\text{g/m}^3$	$\mu\text{g/s}$	$\mu\text{g/g}$	$\mu\text{g/s}$		
	14 C	4713 ml	$\mu\text{g/g}$	$\mu\text{g/m}^3$	$\mu\text{g/ml}$	$\mu\text{g/m}^3$	$\mu\text{g/m}^3$	$\mu\text{g/s}$	$\mu\text{g/g}$	$\mu\text{g/s}$		
	SASS	11.95 m <sup>3</sup>										
	1031	402 g/s										
Palladium	< 0.1	< 0.19	< 0.3	< 3.7	< 0.003	< 1.2	< 5.1	< 250	< 0.25	< 100	< DL	
Platinum	< 0.1	< 0.19	< 0.3	< 3.7	< 0.003	< 1.2	< 5.1	< 250	< 0.25	< 100	< DL	
Phosphorus	MC	MC	17	210	MC	MC	210 < MC	10000 < MC	5.5	2200	4.5 < MC	
Potassium	MC	MC	220	2800	MC	MC	2800 < MC	140000 < MC	18	7200	19 < MC	
Praseodymium	12	23	0.15 < 0.3	1.8 < 3.7	< 0.003	< 1.2	25 < 28	1200 < 1300	< 0.25	< 100	> 12	
Rhenium	< 0.1	< 0.19	< 0.3	< 3.7	< 0.003	< 1.2	< 5.1	< 250	< 0.25	< 100	< DL	
Rhodium	< 0.1	< 0.19	< 0.3	< 3.7	< 0.003	< 1.2	< 5.1	< 250	< 0.25	< 100	< DL	
Rubidium	200	380	< B	0	< 0.0029	< 1.1	380	18000	< 0.25	< 100	> 180	
Ruthenium	< 0.1	< 0.19	< 0.3	< 3.7	< 0.003	< 1.2	< 5.1	< 250	< 0.25	< 100	< DL	
Samarium	6	11	< 0.3	< 3.7	< 0.003	< 1.2	11 < 15	530 < 720	< 0.25	< 100	> 5.3	
Scandium	15	29	= B	0	< 0.001	< 0.39	29	1400	0.15 < 0.2	60 < 80	23 > 17	
Silicon	MC	MC	400	4900	MC	MC	4900 < MC	240000 < MC	59	24000	10 < MC	
Silver	5	9.5	7	86	MC	MC	96 < MC	4600 < MC	0.1 < 0.25	40 < 100	114	
Sodium	MC	MC	7.5	920	MC	MC	920 < MC	44000 < MC	33	13000	3.3 < MC	
Sulfur	MC	MC	8	98	MC	MC	98 < MC	4700 < MC	160 < MC	64000 < MC	0.07	
Strontium	760	1500	0.7	8.6	< B	0	1500	72000 < 73000	0.35	141	510 < 520	
Tantalum	< 0.8	< 1.5	< 0.3	< 3.7	< 0.003	< 1.2	< 6.4	< 310	< 0.25	< 100	< DL	
Thallium	28	53	< 0.3	< 3.7	< 0.003	< 1.2	53 < 58	2600 < 2800	< 0.25	< 100	> 26	
Terbium	1	1.9	< 0.3	< 3.7	< 0.003	< 1.2	1.9 < 5.1	92 < 250	< 0.25	< 100	> 0.92	
Thorium	22	42	< 0.3	< 3.7	< 0.003	< 1.2	42 < 47	2000 < 2300	< 0.25	< 100	20	
Thulium	0.4	7.6	< 0.3	< 3.7	< 0.003	< 1.2	7.6 < 13	370 < 600	< 0.25	< 100	> 3.7	
Tungsten	7	13	< 0.3	< 3.7	< 0.003	< 1.2	13 < 18	630 < 860	< 0.25	< 100	> 6.3	
Uranium	17	32	< 0.3	< 3.7	< 0.003	< 1.2	32 < 37	1500 < 1800	< 0.25	< 100	> 15	
Ytterbium	2	3.8	< 0.3	< 3.7	< 0.003	< 1.2	3.8 < 8.7	180 < 420	< 0.25	< 100	> 1.8	
Yttrium	39	74	0.15 < 0.3	1.8 < 3.7	< 0.003	< 1.2	76 < 79	3700 < 3800	< 0.25	< 100	> 37	
Zirconium	100	190	= B	0	< B	0	190	9200	1.5	600	15	

See note on Table F-1

515

TABLE F-66. POM COMPOUNDS BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY  
LOCATION 14, OPEN HEARTH STEEL FURNACE

POM Component	Stack Exit Test 14-2			
	XAD-2 Resin 532		Module Wash 616	
	ng/g	ng/m <sup>3</sup>	ng/ml	ng/m <sup>3</sup>
Anthracene	0.38	4.7	0.0094	0.48
Phenanthrene	0.022	0.27	--	--
Methyl Anthracenes	0.098	1.2	--	--
Fluoranthene	0.20	2.5	0.0023	0.12
Pyrene	0.047	0.58	--	--
*Benzo(c)phenanthrene	--	--	--	--
Chrysene	0.020	0.25	--	--
Benz(a)anthracene	--	--	--	--
Methyl Chrysenes	--	--	--	--
*7,12-Dimethylbenz(a) anthracene	--	--	--	--
Benzo Fluoranthenes	0.0071	0.087	--	--
*Benz(a)pyrene	--	--	--	--
Benz(e)pyrene	--	--	--	--
Perylene	--	--	--	--
*3-Methylcholanthrene	--	--	--	--
Indeno(1,2,3-cd)pyrene	--	--	--	--
Benzo(ghi)perylene	--	--	--	--
*Dibenzo(a,h)anthracene	--	--	--	--
*Dibenzo(c,g)carbazole	--	--	--	--
*Dibenz(ai and ah)pyrenes	--	--	--	--
Total	0.78	9.6	0.012	0.60

\* Compounds required to be identified for this contract

Note: Values in this table are expressed in nonograms (ng), (1 ng = 10<sup>-9</sup> g).  
Values in other trace species and organics tables in this report are  
expressed in micrograms (µg), (1 µg = 10<sup>-6</sup> g).

TABLE F-67. TRACE SPECIES AND ORGANIC EMISSIONS, SASS SOLIDS SECTION COLLECTION  
TEST 15-10, DIESEL ENGINE

517

Sample Type	Nozzle, Probe, 10 µm Cyclone Solids		3 µm Cyclone Solids		1 µm Cyclone Solids		Filters		Solid Section Wash	
	Sample Number	Sample Weight/Vol.	Units	Units	Units	Units	Units	Units	Units	Units
Sample Number	563	0.0032 g								
Sample Weight/Vol.										
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Antimony	NES						< 200	< 2.7	< 0.5	< 40
Arsenic	NES						< 8.0	< 0.11	< 0.005	< 0.4
Barium	NES						< 80	< 1.1	< 0.1	< 8.0
Beryllium	NES						< 4.0	< 0.053	< 0.005	< 0.4
Cadmium	NES						< 4.0	< 0.053	< 0.005	< 0.4
Calcium	NES						68000	0.90	0.04	3.2
Chromium	NES						64	0.85	0.03	2.4
Cobalt	NES						32	0.43	< 0.2	< 16
Copper	NES						20	0.27	< 0.02	< 1.6
Iron	NES						1300	17	0.38	30
Lead	NES						< 40	< 0.53	< 0.05	< 4.0
Manganese	NES						40	0.53	0.12	9.6
Mercury	NES						< 0.16	< 0.0021	< 0.005	< 0.4
Nickel	NES						20	0.27	0.47	38
Selenium	NES						16	0.21	< 0.010	< 0.8
Tellurium	NES						< 200	< 2.7	< 0.3	< 24
Tin	NES						< 400	< 5.3	< 1	< 80
Titanium	NES						< 1200	< 16	< 1	< 80
Vanadium	NES						< 80	< 1.1	< 0.1	< 8.0
Zinc	NES						670	8.9	0.15	12
Chloride	NES						NES	--	1.6	130
Fluoride	NES						< 5	< 0.067	< 0.1	< 8.0
Nitrates	NES						NES	--	0.12	9.6
Sulfates	NES						NES	--	= B	0
Total POM	NES						NES	--	NR	
Total PCB	NES						NES	--	NR	

See notes on Table F-1

TABLE F-68. TRACE SPECIES AND ORGANIC EMISSIONS, SASS ORGANIC AND LIQUIDS SECTION COLLECTION TEST 15-10, DIESEL ENGINE

Sample Type	XAD-2 Resin		Organic Module Rinse		Condensate		Impinger No. 1		Impinger No. 2		Impinger No. 3	
	Sample Number	Sample Weight/Vol.	Units	Units	Units	Units	Units	Units	Units	Units	Units	Units
	1041	150 g	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
	898	398 ml	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
	15-10 B	3877 ml	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
	Combined with Condensate	Combined with Condensate	Combined with Condensate	Combined with Condensate	Combined with Condensate	Combined with Condensate	Combined with Condensate					
Antimony	< 23	< 200	< 0.5	< 11	< 0.49	< 110						
Arsenic	0.1	0.85	0.02	0.45	0.010	2.2						
Barium	< B	0	< 0.1	< 2.3	< 0.10	< 22						
Beryllium	0.46	3.9	< 0.005	< 0.11	< 0.0049	< 1.1						
Cadmium	< B	0	0.03	0.68	0.013	2.9						
Calcium	< B	0	0.08	1.8	0.41	91						
Chromium	< B	0	2.0	45	0.39	85						
Cobalt	< B	0	< 0.2	< 4.5	< 0.20	< 44						
Copper	< B	0	0.10	2.3	0.034	7.4						
Iron	5	43	3.2	73	1.5	340						
Lead	< 2.3	< 20	< 0.05	< 1.1	< 0.031	< 6.8						
Manganese	0.3	2.6	0.09	2.0	0.064	14						
Mercury	< 0.02	< 0.17	< 0.005	< 0.11	< 0.0049	< 1.1						
Nickel	2.3	20	0.51	12	0.23	51						
Selenium	1.9	16	0.05	1.1	0.020	4.4						
Tellurium	< 23	< 200	< 0.3	< 6.8	< 0.31	< 68						
Tin	< 46	< 390	< 1	< 23	< 1.0	< 220						
Titanium	< 140	< 1200	< 1	< 23	< 1.0	< 220						
Vanadium	< 9.3	< 79	< 0.1	< 2.3	< 0.10	< 22						
Zinc	2.4	20	0.13	2.9	0.13	30						
Chloride	53	450	0.54	12	3.1	680						
Fluoride	< B	0	0.21	4.8	0.28	63						
Nitrates	55	470	0.06	1.4	< B	0						
Sulfates	90	770	19	430	1300 (SO <sub>2</sub> )	290000 (SO <sub>2</sub> )						
Total POM	< 0.1	< 0.9	NES	--	NR	--						
Total PCB	< 1	< 9	NES	--	NR	--						

518

See notes on Table F-1

TABLE F-69. TRACE SPECIES AND ORGANICS EMISSIONS, PROCESS SAMPLES AND MASS BALANCE  
TEST 15-10, DIESEL ENGINE

Sample Type	Emission in Partic. < 3 µm	Total Emission Concen.	Total Emission Rate	Fuel Input No. 2 Diesel Oil		Mass Balance
Sample Number	541	SASS	SASS	1042		<u>Emission</u>
Sample Weight/Vol.	0.2335 g	17.55 m <sup>3</sup>	0.575 m <sup>3</sup> /s	26.4 g/s		<u>Input</u>
Units	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s	µg/g	µg/s	--
Antimony	< 2.7	< 360	< 210	< 25	< 660	< DL
Arsenic	< 0.11	4.1	2.4	< 2	< 53	> 0.05
Barium	< 1.1	< 34	< 20	30	790	> 0.03
Beryllium	< 0.053	3.9 < 5.6	2.2 < 3.2	< 0.3	< 7.9	> 0.28
Cadmium	< 0.053	3.6 < 4.1	2.1 < 2.4	< 0.3	< 7.9	> 0.26
Calcium	0.90	1000	580	30	790	0.73
Chromium	0.85	140	81	< 5	< 130	> 0.62
Cobalt	0.43	0.43 < 68	0.25 < 39	< 10	< 260	< DL
Copper	0.27	9.7 < 11	5.6 < 6.3	< 3	< 79	> 0.071
Iron	17	510	290	< 5	< 130	> 2.2
Lead	< 0.53	< 32	< 18	< 5	< 130	< DL
Manganese	0.53	30	17	1.0	26	0.65
Mercury	< 0.0021	< 1.8	< 1.0	< 0.1	< 2.6	< DL
Nickel	0.27	120	69	< 1.0	< 2.6	> 2.7
Selenium	0.21	22 < 23	13	< 1.0	< 2.6	> 0.5
Tellurium	< 2.7	< 300	< 170	< 25	< 660	< DL
Tin	< 5.3	< 740	< 430	< 25	< 660	< DL
Titanium	< 16	< 1500	< 860	< 250	< 6600	< DL
Vanadium	< 1.1	< 110	< 63	< 5	< 130	< DL
Zinc	8.9	74	43	10	260	0.17
Chloride	--	1100	630	< 10	< 260	> 2.4
Fluoride	< 0.067	68 < 74	39 < 43	12.5	330	0.12 < 0.13
Nitrates	--	480	280	1.95	52	5.4
Sulfates	--	1200	690	44.3	1200	0.38
Total POM	NES	< 0.9	< 0.5	NR	--	--
Total PCB	NES	< 9	< 5	NR	--	--

See notes on Table F-1

TABLE F-70. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY  
TEST 15-10, DIESEL ENGINE

Sample Type	Combined Solids		XAD-2 Resin		Combined Liquids		Total Emission Concen.	Total Emission Rate	Input No. 2 Diesel Oil		SSMS Mass Balance	Best Balance AA & SS
Sample Number	15-10 E & A'		15-10 F		15-10 G		SASS		15-10 H (1042)		Emission Input	AA or SS Emission
Sample Weight/Vol.	0.2335		150 g		4275 ml		17.55 m <sup>3</sup>	0.575 m <sup>3</sup> /s	26.4 g/s			AA or SS Input
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s	µg/g	µg/s		
Antimony	240	3.2	< 0.1	< 0.85	0.009	2.2	5.4 < 6.3	3.1 < 3.6	0.009	0.24	13 < 15	13 < 15
Arsenic	190	2.5	< 0.1	< 0.85	0.026	6.5	9.0 < 9.9	5.2 < 5.7	0.008	0.21	25 < 27	11
Barium	3800	50	< B	0	< B	0	50	29	0.07	1.8	16	16
Beryllium	< 120	< 1.6	< 0.1	< 0.85	< 0.001	< 0.24	< 2.7	< 1.5	< 0.004	< 0.11	< DL	> 20
Cadmium	1 < 120	0.057 < 1.6	< 0.1	< 0.85	0.0053	1.3	1.4 < 3.8	7.8 < 2.2	< 0.008	< 0.21	> 3.7	> 0.99
Calcium	MC	MC	< B	0	MC	MC	MC	MC	1	26	MC	0.73
Chromium	1000	14	< B	0	< B	0	14	8.1	0.01	0.26	30	31
Cobalt	200	2.7	< 0.1	< 0.85	0.068	17	20 < 21	11 < 12	0.002	0.053	210 < 220	4.7 < 740
Copper	1600	2.2	< 0.1	0	< B	0	2.2	1.3	0.08	2.1	0.60	0.62
Iron	30000	400	= B	0	6.1	1500	1900	1100	0.1	2.6	410	110
Lead	4400	59	< 0.5	< 4.3	0.19	46	110	60	0.06	1.6	33 < 40	< 11
Manganese	230	3.1	< 0.1	< 0.85	0.021	5.1	8.2 < 9.1	4.7 < 5.2	0.005	0.13	36 < 39	6.5
Mercury	NR	--	NR	--	NR	--	NR	--	NR	--	--	< DL
Nickel	3900	52	< B	0	< B	0	52	30	0.02	5.3	57	5.7
Selenium	480	6.4	< 0.1	< 0.85	< 0.01	< 2.4	6.4 < 9.7	3.7 < 5.5	< 0.01	< 0.26	14 < 21	> 0.50
Tellurium	< 120	< 1.6	< 0.1	< 0.85	< 0.003	< 0.73	< 3.2	< 1.8	< 0.004	< 0.11	< DL	< DL
Tin	13 < 130	1.4 < 1.8	< 0.1	< 0.85	< 0.008	< 1.9	1.4 < 4.6	0.81 < 2.6	< 0.004	< 0.11	> 7.6	> 7.4
Titanium	760	10	< B	0	0.18	44	54	31	0.05	1.3	24	24
Vanadium	1800	24	= B	0	0.011	2.7	27	15	0.003	0.079	190	190
Zinc	1800 < MC	24 < MC	< B	0	0.0056	1.4	25 < MC	15 < MC	0.4	11	1.4 < MC	1.4 < MC
Chlorine	180	2.4	= B	0	< B	0	2.4	1.4	0.3	7.9	0.17	0.18
Fluorine	MC	MC	1	8.5	< B	0	8.5 < MC	4.9 < MC	0.4	11	0.46 < MC	0.44

See notes on Table F-1

TABLE F-71. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY (Continued)  
TEST 15-10, DIESEL ENGINE

Sample Type	Combined Solids		XAD-2 Resin		Combined Liquids		Total Emission Concn.	Total Emission Rate	Input No. 2 Diesel Oil		SSMS Mass Balance
Sample Number	15-10 E & A'		15-10 F		15-10 G		SASS		15-10 H (1042)		Emission Input
Sample Weight/Vol.	0.2335		150 g		4275 ml		17.55 m <sup>3</sup>	0.575 m <sup>3</sup> /s	26.4 g/s		
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s	µg/g	µg/s	
Aluminum	> 2300	> 31	= B	0	> 3.7	> 900	> 930	< 540	0.06	1.6	> 340
Bismuth	0.4 < 120	0.0053 < 1.6	< 0.1	< 0.85	< 0.003	< 0.73	0.0053 < 1.6	0.0030 < 0.91	< 0.004	< 0.11	> 0.029
Boron	1100	14	< B	0	< B	0	14	8.1	0.02	0.53	15
Bromine	65	0.87	< B	0	< B	0	0.87	0.50	0.02	0.53	0.95
Cerium	240	3.2	< 0.1	< 0.85	0.0061	1.5	4.7 < 5.6	2.7 < 3.2	0.01	0.26	10 < 12
Cesium	180	2.4	< 0.1	< 0.85	0.0025	0.62	3.0 < 3.9	1.7 < 2.2	< 0.002	< 0.053	> 33
Dysprosium	< 120	< 1.6	< 0.1	< 0.85	< 0.003	< 0.73	< 3.2	< 1.8	< 0.004	< 0.11	< DL
Erbium	< 120	< 1.6	< 0.1	< 0.85	< 0.003	< 0.73	< 3.2	< 1.8	< 0.004	< 0.11	< DL
Europium	< 120	< 1.6	< 0.1	< 0.85	0.004	0.97	0.97 < 3.4	5.6 < 2.0	< 0.004	< 0.11	> 5.3
Gadolinium	< 120	< 1.6	< 0.1	< 0.85	< 0.003	< 0.73	< 3.2	< 1.8	< 0.004	< 0.11	< DL
Gallium	1 < 61	0.013 < 0.82	< 0.1	< 0.85	0.004	0.97	0.98 < 2.6	0.57 < 1.5	0.003	0.079	7.1 < 19
Germanium	< 120	< 1.6	< 0.1	< 0.85	< 0.002	< 0.49	< 2.9	< 1.7	< 0.004	< 0.11	< DL
Gold	< 120	< 1.6	< 0.1	< 0.85	< 0.003	< 0.73	< 3.2	< 1.8	< 0.006	< 0.16	< DL
Hafnium	< 120	< 1.6	< 0.1	< 0.85	< 0.003	< 0.73	< 3.2	< 1.8	< 0.004	< 0.11	< DL
Holmium	< 120	< 1.6	< 0.1	< 0.85	< 0.003	< 0.73	< 3.2	< 1.8	< 0.004	< 0.11	< DL
Iodine	190	2.6	0.2	1.7	< B	0	4.3	2.5	0.009	0.24	10
Iridium	< 120	< 1.6	< 0.1	< 0.85	< 0.003	< 0.73	< 3.2	< 1.8	< 0.004	< 0.11	< DL
Lanthanum	420	5.6	< 0.1	< 0.85	0.034	8.4	14 < 15	8.1 < 8.5	0.01	0.26	30 < 32
Lithium	0.5 < 6.5	0.0067 < 0.087	0.1	0.85	< B	0	0.86 < 0.94	0.49 < 0.54	< 0.001	< 0.026	> 19
Lutetium	< 120	< 1.6	< 0.1	< 0.85	< 0.003	< 0.73	< 3.2	< 1.8	< 0.004	< 0.11	< DL
Magnesium	25000	330	6	51	MC	MC	380 < MC	220 < MC	0.2	5.3	41 < MC
Molybdenum	3000	40	< B	0	< B	0	40	23	0.1	2.6	8.7
Neodymium	0.3 < 120	0.0040 < 1.6	< 0.1	< 0.85	0.1	2.4	2.4 < 4.9	1.4 < 2.8	< 0.004	< 0.11	> 13
Niobium	0.3 < 120	0.0040 < 1.6	< 0.1	< 0.85	0.004	0.97	0.97 < 11	0.56 < 6.4	< 0.004	< 0.11	> 5.3
Osmium	< 120	< 1.6	< 0.1	< 0.85	< 0.003	< 0.73	< 3.2	< 1.8	< 0.004	< 0.11	< DL

See note on Table F-1

TABLE F-72. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY (Continued)  
TEST 15-10, DIESEL ENGINE

Sample Type	Combined Solids		XAD-2 Resin		Combined Liquids		Total Emission Concen.	Total Emission Rate	Input No. 2 Diesel Oil		SSMS Mass Balance
Sample Number	15-10 E & A'		15-10 F		15-10 G		SASS		15-10 H (1042)		Emission Input
Sample Weight/Vol.	0.2335		150 g		4275 ml		17.55 m <sup>3</sup>	0.575 m <sup>3</sup> /s	26.4 g/s		
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s	µg/g	µg/s	
Palladium	< 120	< 1.6	< 0.1	< 0.85	< 0.003	< 0.73	< 3.2	< 1.8	< 0.004	< 0.11	< DL
Platinum	< 120	< 1.6	< 0.1	< 0.85	< 0.003	< 0.73	< 3.2	< 1.8	< 0.004	< 0.11	< DL
Phosphorus	MC	MC	6	51	MC	MC	51 < MC	29 < MC	0.2	5.3	5.5 < MC
Potassium	27000 < MC	360 < MC	< B	0	< B	0	360 < MC	210 < MC	0.7	18	11 < MC
Praseodymium	120	1.6	< 0.1	< 0.85	0.006	1.5	3.1 < 4.0	1.8 < 2.3	< 0.004	< 0.11	> 17
Rhenium	< 120	< 1.6	< 0.1	< 0.85	< 0.003	< 0.73	< 3.2	< 1.8	< 0.004	< 0.11	< DL
Rhodium	< 120	< 1.6	< 0.1	< 0.85	< 0.003	< 0.73	< 3.2	< 1.8	< 0.004	< 0.11	< DL
Rubidium	43	0.57	< 0.1	< 0.85	< B	0	0.57 < 1.4	0.33 < 0.82	0.001	0.026	12 < 31
Ruthenium	< 120	< 1.6	< 0.1	< 0.85	< 0.003	< 0.73	< 3.2	< 1.8	< 0.004	< 0.11	< DL
Samarium	< 120	< 1.6	< 0.1	< 0.85	< 0.01	< 2.4	< 4.9	< 2.8	< 0.004	< 0.11	< DL
Scandium	< 60	< 0.80	< 0.1	< 0.85	< 0.004	< 0.97	< 2.6	< 1.5	< 0.001	< 0.026	< DL
Silicon	14000 < MC	190 < MC	< B	0	< B	0	190 < MC	110 < MC	0.4	11	10 < MC
Silver	18000	240	0.1	0.85	MC	MC	240 < MC	140 < MC	0.02	0.53	260 < MC
Sodium	360 < MC	4.8 < MC	> 320	> 2700	MC	MC	2700 < MC	1600 < MC	0.4	11	150 < MC
Sulfur	870 < MC	12 < MC	25	210	MC	MC	220 < MC	130 < MC	1	26	4.8 < MC
Strontium	5300	71	< B	0	0.12	30	100	58	0.01	0.26	220
Tantalum	< 120	< 1.6	< 0.1	< 0.85	< 0.003	< 0.73	< 3.2	< 1.8	< 0.004	< 0.11	< DL
Thallium	< 120	< 1.6	< 0.1	< 0.85	< 0.003	< 0.73	< 3.2	< 1.8	< 0.004	< 0.11	< DL
Terbium	< 120	< 1.6	< 0.1	< 0.85	< 0.003	< 0.73	< 3.2	< 1.8	< 0.004	< 0.11	< DL
Thorium	2 < 1200	0.027 < 16	< 0.1	< 0.85	< 0.003	< 7.3	0.027 < 24	0.016 < 4	0.05	1.3	0.012 < 11
Thulium	< 120	< 1.6	< 0.1	< 0.85	< 0.003	< 0.73	< 3.2	< 1.8	< 0.004	< 0.11	< DL
Tungsten	6 < 130	0.080 < 1.7	< 0.1	< 0.85	< B	0	0.080 < 2.6	0.046 < 1.5	< 0.004	< 0.11	0.44 < 14
Uranium	11 < 1200	0.15 < 16	< 0.1	< 0.85	0.036	8.9	9.1 < 26	5.2 < 15	0.06	1.6	313 < 9.3
Ytterbium	< 120	< 1.6	< 0.1	< 0.85	< 0.003	< 0.73	< 3.2	< 1.8	< 0.004	< 0.11	< DL
Yttrium	1 < 120	0.013 < 1.6	< 0.1	< 0.85	0.003	0.73	0.74 < 3.2	0.43 < 1.8	< 0.004	< 0.11	4.0
Zirconium	500	< 6.7	= B	0	< B	0	6.7	3.9	0.07	1.8	2.1

522

See note on Table F-1

TABLE F-73. TRACE SPECIES AND ORGANIC EMISSIONS, SASS SOLIDS SECTION COLLECTION TEST 15-11, DIESEL ENGINE

Sample Type	Nozzle, Probe, 10 µm Cyclone Solids		3 µm Cyclone Solids		1 µm Cyclone Solids		Filters		Solid Section Wash	
	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Sample Number	NONE		NONE		NONE		542		15-11 A	
Sample Weight/Vol.							0.2364 g		1416 ml	
Units	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Antimony							< 100	< 1.3	< 0.5	< 39
Arsenic							< 16	< 0.2	< 0.005	< 0.39
Barium							< 280	< 3.7	< 0.1	< 7.9
Beryllium							< 2	< 0.026	< 0.005	< 0.39
Cadmium							< 2	< 0.026	< 0.005	< 0.39
Calcium							< 60000	< 790	0.75	59
Chromium							25	0.33	0.01	0.79
Cobalt							17	0.22	< 0.2	< 16
Copper							34	0.45	< 0.02	< 1.6
Iron							< 1000	< 13	0.14	11
Lead							< 10	< 0.13	< 0.05	< 3.9
Manganese							< 34	< 0.45	0.03	2.4
Mercury							< 0.08	< 0.0011	< 0.005	< 0.39
Nickel							< 10	< 0.13	0.11	8.7
Selenium							< 4	< 0.053	< 0.01	< 0.79
Tellurium							< 100	< 1.3	< 0.3	< 24
Tin							< 200	< 2.6	< 1	< 79
Titanium							< 600	< 7.9	< 1	< 79
Vanadium							< 40	< 0.53	< 0.1	< 7.9
Zinc							2700	35	0.18	14
Chloride							NES	--	0.54	42
Fluoride							NES	--	< 0.1	< 7.9
Nitrates							NES	--	= B	0
Sulfates							NES	--	2.0	160
Total POM							NES	--	NR	--
Total PCB							NES	--	NR	--

See notes on Table F-1

523

TABLE F-74. TRACE SPECIES AND ORGANIC EMISSIONS, SASS ORGANIC AND LIQUIDS SECTION COLLECTION TEST 15-11, DIESEL ENGINE

Sample Type	XAD-2 Resin		Organic Module Rinse		Condensate		Impinger No. 1		Impinger No. 2		Impinger No. 3	
Sample Number	1044		941		15-11 B		Combined with		Combined with		Combined with	
Sample Weight/Vol.	154 g		402 ml		4062 ml		Condensate		Condensate		Condensate	
Units	µg/g	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>	µg/ml	µg/m <sup>3</sup>
Antimony	< 23	< 200	< 0.5	< 11	< 0.49	< 110						
Arsenic	5.5	47	0.01	0.22	< 0.0049	< 1.1						
Barium	100	860	< 0.1	< 2.2	< 0.10	< 23						
Beryllium	< 0.46	< 3.9	< 0.005	< 0.11	< 0.0049	< 1.1						
Cadmium	< B	0	0.03	0.67	0.0084	1.9						
Calcium	< B	0	0.10	2.2	0.39	89						
Chromium	< B	0	0.82	18	0.12	27						
Cobalt	0.7	6.0	< 0.2	< 4.5	< 0.20	< 45						
Copper	2.1	18	0.04	0.89	< 0.013	< 2.8						
Iron	< B	0	1.5	34	0.42	94						
Lead	--	--	< 0.05	< 1.1	< 0.032	< 7.2						
Manganese	= B	0	0.04	0.89	0.015	3.4						
Mercury	< 0.02	< 0.17	< 0.005	< 0.11	0.0049	1.1						
Nickel	< 2.3	< 20	0.25	5.6	0.010	23						
Selenium	< 0.91	< 7.8	0.04	0.89	0.02	4.5						
Tellurium	< 23	< 200	< 0.3	< 6.7	< 0.30	< 67						
Tin	< 46	< 390	< 1	< 22	< 1.0	< 230						
Titanium	< 140	< 1200	< 1	< 22	< 1.0	< 230						
Vanadium	< 9.1	< 78	< 0.1	< 2.2	< 0.1	< 23						
Zinc	< B	0	= B	0	0.14	32						
Chloride	< 11	< 94	0.54	.12	54	12000						
Fluoride	< B	0	< 0.1	< 2.2	0.21	47						
Nitrates	1.5	13	0.02	0.45	< B	0						
Sulfates	< 50	< 430	5.2	120	1300 (SO <sub>2</sub> )	290000 (SO <sub>2</sub> )						
Total POM	< 0.1	< 0.9	< 0.001	< 0.02	NR	--						
Total PCB	< 1	< 9.0	< 0.001	< 0.02	NR	--						

See notes on Table F-1

TABLE F-75. TRACE SPECIES AND ORGANICS EMISSIONS, PROCESS SAMPLES AND MASS BALANCE  
TEST 15-11, DIESEL ENGINE

Sample Type	Emission in Partic. < 3 µm	Total Emission Concen.	Total Emission Rate	Fuel Input No. 2 Diesel Oil		Mass Balance
Sample Number	542	SASS		1045		Emission Input
Sample Weight/Vol.	0.2364	18.00 m <sup>3</sup>	0.582 m <sup>3</sup> /s	26.4 g/s		
Units	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/s	µg/g	µg/s	--
Antimony	< 1.3	< 360	< 210	< 25	< 660	< DL
Arsenic	< 0.2	47 < 49	27 < 29	< 2	< 53	> 0.51
Barium	< 3.7	830 < 890	480 < 520	< 5	< 130	> 3.7
Beryllium	< 0.026	< 5.6	< 3.3	< 0.3	< 7.9	< DL
Cadmium	< 0.026	2.6 < 3	1.5 < 1.7	< 0.3	< 7.9	> 0.19
Calcium	< 790	160 < 780	93 < 450	30	790	0.12
Chromium	0.33	46	27	< 5	< 130	> 0.21
Cobalt	0.22	6.1 < 72	3.6 < 42	< 10	< 260	< DL
Copper	0.45	19 < 24	11 < 14	< 3	< 79	> 0.14
Iron	< 13	140 < 150	81 < 87	< 5	< 130	> 0.62
Lead	< 0.13	< 12	< 7.0	< 5	< 130	< DL
Manganese	< 0.45	6.7 < 7.2	3.9 < 4.2	0.3	7.9	0.49
Mercury	< 0.0011	< 1.8	< 1.0	< 0.1	< 2.6	< DL
Nickel	< 0.13	3.7 < 56	2.2 < 33	< 1	< 26	> 0.085
Selenium	< 0.053	5.4 < 14	3.1 < 8.1	< 1	< 26	> 0.12
Tellurium	< 1.3	< 290	< 170	< 25	< 660	< DL
Tin	< 2.6	< 720	< 420	< 25	< 660	< DL
Titanium	< 7.9	< 1500	< 870	< 250	< 6600	< DL
Vanadium	< 0.53	< 110	< 64	< 5	< 130	< DL
Zinc	35	89	52	< 0.5	< 13	> 4
Chloride	NES	12000	7000	< 9	< 240	> 29
Fluoride	NES	47 < 56	27 < 33	13.6	360	0.075
Nitrates	NES	13	7.6	7.84	210	0.036
Sulfates	NES	280 < 710	160 < 410	48.0	1300	0.12
Total POM	NES	< 0.92	< 0.5	NR	--	--
Total PCB	NES	< 9.0	< 5.2	NR	--	--

See notes on Table F-1

TABLE F-76. POM COMPOUNDS BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY  
LOCATION 15, DIESEL ENGINE

POM Component	XAD-2 Resin 1041		Stack Exit	
	ng/g	ng/m <sup>3</sup>	Module Wash 941 ng/ml	ng/m <sup>3</sup>
Anthracene	17	148	0.0028	0.062
Phenanthrene	0.11	0.93	--	--
Methyl Anthracenes	14	122	--	--
Fluoranthene	0.16	1.4	0.0017	0.039
Pyrene	--	--	--	--
*Benzo(c)phenanthrene	0.0027	0.023	--	--
Chrysene	0.0079	0.068	0.011	0.24
Benz(a)anthracene	0.0008	0.0068	--	--
Methyl Chrysenes	0.0018	0.015	--	--
*7,12-Dimethylbenz(a) anthracene	--	--	--	--
Benzo Fluoranthenes	0.0035	0.030	0.0040	0.094
*Benz(a)pyrene	0.0028	0.024	--	--
Benz(e)pyrene	0.0027	0.023	--	--
Perylene	--	--	--	--
*3-Methylcholanthrene	--	--	--	--
Indeno(1,2,3-cd)pyrene	--	--	--	--
Benzo(ghi)perylene	--	--	--	--
*Dibenzo(a,h)anthracene	--	--	--	--
*Dibenzo(c,g)carbazole	--	--	--	--
*Dibenz(ai and ah)pyrenes	--	--	--	--
Total	32	273	0.02	0.44

\* Compounds required to be identified for this contract

Note: Values in this table are expressed in nonograms (ng), (1 ng = 10<sup>-9</sup> g).  
Values in other trace species and organics tables in this report are  
expressed in micrograms (µg), (1 µg = 10<sup>-6</sup> g).

APPENDIX G

SASS TRAIN EVALUATION TEST

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## SECTION G-1.0

### INTRODUCTION

The Aerotherm prototype SASS train was delivered to KVB for evaluation tests conducted on a boiler in the KVB laboratory burning West Virginia Pittsburgh No. 8 coal. The purpose of these tests was to determine the ability of the train to collect all of the trace elements and organics required for the current program. By weighing and analysis of the coal and all solid ashes and comparison with train catch, the ability of the train to establish mass balances on the desired elements could be established. In addition to evaluation of the chemical performance of the train, mechanical performance and suitability for field testing was evaluated and recommendations made for improved operation.

SECTION G-2.0

SOURCE ASSESSMENT SAMPLING SYSTEM TEST

An evaluation test of the Source Assessment Sampling System (SASS) was conducted on July 21, 1976.

The test was conducted on a KVB laboratory boiler firing Pittsburgh No. 8 coal. The SASS train and pulverized coal were obtained from Aerotherm. The train was completely disassembled and cleaned according to IERL-RTP SASS procedures (Report EPA 600/2-76-160a, June 1976).

XAD-2 organic absorbent was obtained from Arthur D. Little and loaded into two canisters obtained from TRW. The canisters each held 150 g of XAD-2.

A broken weld on the 1  $\mu$ m cyclone had to be rewelded by KVB. Also many of the fittings on the train had been previously overtightened and caused difficulty during assembly and filter changes during the test. Most of the mechanical problems occurred with the cyclone assembly. The remainder of the train functioned satisfactorily.

Samples were taken in a 0.28 m (11 inch) diameter stack above the boiler. A velocity traverse indicated uniform flow to within  $\pm 10\%$  of the average velocity of 12 m/s (40 ft/sec). A 15.87 mm (5/8 inch) probe nozzle was used. The sampling rate was set for 4 actual CFM (.1133  $\text{m}^3/\text{min}$ ) at 478  $^\circ\text{K}$  (400  $^\circ\text{F}$ ) to obtain the calibrated cut points on the 3 cyclones. Nominal cut points ( $D_{50}$ ) are 12, 3 and 1  $\mu\text{m}$  at this flow. EPA-PMB\* (Bill Kuykendahl) had indicated that the cyclones were to be redesigned for 4 SCFM (.1133  $\text{m}^3/\text{min}$ ) so that 30  $\text{m}^3$  could be collected in the 4.4 hour sampling period. However, as the train had not been run at the higher flow rate, nor had the cyclones been calibrated at that flow, it was decided to operate at the original design rate for a period of 7.5 hours, to collect 30  $\text{m}^3$  (1060  $\text{ft}^3$ ).

\*EPA - Process Measurements Branch

The sampling run required 11.75 hours elapsed time for 7.53 hours of actual sampling. Dryerite was changed 5 times and the filter was changed twice (1-2 hour required per change). Filter change required removal of the complete cyclone-filter assembly because of "frozen" fittings. During the second change, one filter holder fitting galled and silastic sealant was required to seal the fitting.

The objective established for train operation was to maintain a 4 ACFM (.1133 am<sup>3</sup>/min) sample rate at the cyclones within  $\pm 10\%$  and to maintain isokinetic sampling within  $\pm 10\%$ . The sampling rate varied from 3.62 to 4.58 ACFM (.102-.130 am<sup>3</sup>/min) and the percentage of isokinetic flow varied from 82% during initial start-up to a high of 106%. For the majority of the sampling time, the sampling rate was within  $\pm 5\%$  of isokinetic conditions. The sample probe was traversed to 3 points in the stack. The total sample collected was 33.4 m<sup>3</sup> (1180 ft<sup>3</sup>) registered on the dry gas meter or 30.0 sm<sup>3</sup> (1060 SCF).

A total of 1558 kg (3427 lb) of coal was burned in 16.7 hours of boiler firing. Following the test, ashes cleaned from the boiler were:

	<u>kg</u>	<u>lb</u>	<u>%</u>
Furnace tube	51.4	113	42.64
Firetubes	25.9	57	21.51
Stack surfaces	1.4	3	1.13
Baghouse	<u>41.8</u>	<u>92</u>	34.72
	120.5	265	

Data from Aerotherm indicate ash content by 2 analyses of 7.53 and 7.84%. Ash yield for the amount of coal burned should be 117-122 kg (258-268 lb). Collected ash was within this range.

A total of 1125 kg (2475 lb) of coal was burned during the 11.75 hour period from the start of sampling until sampling was terminated. For the 7.53 hr of actual sampling train on time the coal burned is estimated to be 721 kg (1586 lb). At an ash content of 7.5-7.8% and 35% of the ash transmitted out of the boiler to the baghouse, the expected particulates isokinetic catch in the train is 61.3-63.8 g. This is based on a duct to nozzle area ratio of 310/1. The actual catch was:

	<u>grams</u>
Probe solids	.0939
10 um cyclone	38.5477
3 um cyclone	23.7844
1 um cyclone	11.2979
Filters (3)	<u>3.3463</u>
	77.0702

This catch is 20% greater than expected on the basis of coal burned. The collected solid particulate concentration was 2.6 g/DSCM (1.12 gr/DSCF) or 950 ng/J (2.23 lb/10<sup>6</sup> Btu). The operating results are summarized in Table G-1.

Samples from the train and boiler ashes were recovered according to IERL-TRP procedures with assistance by a TRW representative. Samples were split into two equal parts with the exception of probe, cyclone and filter washes. The two sample batches and blanks were delivered to TRW, Redondo Beach, CA, and to Calspan, Buffalo, New York for analysis.

Conclusions from the test are:

1. The train functioned properly throughout the test with respect to sample acquisition capability.
2. Mechanical problems with the cyclone assembly are attributed to the type of connecting fittings used. The Swagelok fittings are not well suited for repeated use since deformation of mating surfaces (rendering separation difficult) is not easily avoided when a leak-free

TABLE G-1. KVB BOILER TEST RESULT SUMMARY

	<u>Total Boiler Operation Period</u>	<u>SASS Train Sampling Period</u>
Operating time, min	1002	452
Boiler firing rate, GJ/h ( $10^6$ Btu/h)	2.98 (2.8)	3.05 (2.9)
Coal burned, kg (lb)	1558 (3427)	721 (1586)
Ash collected, kg (lb)		
Furnace tube	51.4 (113)	23.6 (52)
Firetubes	25.9 (57)	11.8 (26)
Stack surface	1.4 (3)	.5 (1)
Baghouse	41.8 (92)	19.5 (43)
Total	<u>120.5 (265)</u>	<u>55.4 (122)</u>
Stack conditions (average)		
Velocity m/s <sub>3</sub> (ft/s), Diam = 0.28 m		12.7 (41.7)
Flow rate sm <sup>3</sup> /min (SCFM), wet		21.5 (760)
Gas temperature, K (°F)		629 (673)
Excess oxygen, % dry		5.9
Moisture, %		5.0
Total gas Volume, m <sup>3</sup> (ft <sup>3</sup> )		9232 (326,028)
SASS train conditions		
Actual cyclone flow rate am <sup>3</sup> /s (ACFM), wet		.1133 (4.0) ± 10%
Total meter volume, m <sup>3</sup> (ft <sup>3</sup> ), dry		33.4 (1180)
Total standard volume, m <sup>3</sup> (ft <sup>3</sup> ), dry		30.0 (1060)
Oven temperature, K (°F)		478±2 (400±5)
XAD-2 module temperature, K (°F)		328±2 (130±5)
Isokinetic rate, %		100.6
Particulate collected, g		77.07
Particulate loading, g/DSCM (gr/DSCF)		2.6 (1.12)
Emission factor, ng/J (lb/MMBtu)		957 (2.23)

joint is desired. The threaded parts also have a tendency to gall at elevated temperatures when no lubricants are used. Various possible lubricants will be investigated and Aerotherm plans modifications to improve the assembly and sealing.

3. Ice consumption was excessive, 122 kg (270 lb) were used. Insulating the ice bath from surrounding air may help to maximize its cooling effectiveness.
4. No condensation occurred in the XAD-2 module operated at 328 K (130 °F). This temperature is above the dew point for coal fuel and IERL-PMB is considering a reduced temperature. The XAD-2 module satisfactorily maintained the adsorbent temperature within 3 °K (5 °F) of the desired temperature.
5. Boiler ash recovered was close to 100% of expected ash. SASS train particulate catch was 20% higher than expected. These results should provide a good basis for mass balance of the trace elements.
6. Pluggage of the sampling filter necessitated renewal of the filter element two times during the test. Particulate grain loadings were similar to those encountered upstream of particulate removal devices at conventional pulverized coal fired boilers. To minimize downtime for filter changes, a large filter design should be pursued to allow a 4 to 5 hour run period per filter.

As a result of the relatively successful test, fabrication of a new train for KVB field was performed. All modifications possible for improved operation were incorporated. Cyclone design flow remained at 0.113 am<sup>3</sup>/min (4 ACFM).

Costs for SASS train support and spare equipment were significantly higher than expected. One important factor is the XAD-2. Original costs were estimated on the basis of Tenax and with the assumption that Tenax could be recycled. Both XAD-2 and Tenax can be recycled if analysis is only done for organics. However, post-use cleaning only provides for organic removal. Inorganics may build up to unacceptable background levels and prevent reuse.

## SECTION G-3.0

### SASS TESTS ON KVB BOILER, ASH ANALYSES

Samples of the coal and ashes collected in the SASS at KVB were submitted to Accu-Labs (A-L) and Commercial Testing and Engineering (CTE) for standard analysis. The results for the coal are presented in Table G-2. Sample analyses provided to KVB by Aerotherm are also included. These analyses were for the coal prior to shipment to KVB. Two analyses were performed by A-L and CTE on a "total composite" sample of all coal burned during the entire KVB boiler run. Also, two analyses were run for a composite sample collected for the coal only during the period of time when the SASS train was actually collecting samples. The composite samples were compiled by extracting equal amounts of coal from 26 sample containers accumulated during the entire boiler operating period.

Except for moisture content, the three analyses performed by CTE are quite consistent indicating little variation in coal properties. The variation between laboratories on a given sample appears to be greater than the variation between samples.

A primary purpose in obtaining these analyses was to determine ash content for comparison with total ash collected in the boiler. The average of as received ash analysis for all three samples is 7.66% compared with 7.63% for the total composite sample and 7.68% for the SASS train run composite sample. Analyses were also performed on the collected boiler ashes. Table G-3 indicates the amount of each ash type recovered, carbon content, moisture and amount recovered on a carbon-free, dry basis. Carbon content in the firetube ash was the highest (26%). The total amount of carbon in all ash samples is about 12 kg (26 lb). A total of 1554 kb (3427 lb) of coal was burned. At 76% carbon in the coal (1181 kg) the carbon combustion efficiency was 98.98%, indicating that the boiler was properly operating. At the average ash content for the coal (7.63%), a total of 119 kg (262 lb) should have been recovered. Table G-3 indicates 108.1 kg (238 lb) of carbon and moisture-free ash were actually recovered, or 91% of the expected value.

TABLE G-2. PITTSBURGH #8 COAL ANALYSES

Sample Number	From Aerotherm				Total Test Composite Sample				Composite Sample During SASS Run			
	PTL		CTE		CTE		Accu-Labs		CTE		Accu-Labs	
	AR	Dry	AR	Dry	AR	Dry	AR	Dry	AR	Dry	AR	Dry
<u>Proximate (% weight)</u>												
Moisture	1.19	-	1.92	-	1.66	-	0.96	-	1.50	-	0.89	-
Volatile	37.00	37.45	36.73	37.45	37.65	38.29	36.80	37.15	37.89	38.47	37.08	37.41
Fixed carbon	53.97	54.62	53.82	54.87	53.17	54.06	54.52	55.05	53.15	53.96	54.14	54.63
Ash	7.84	7.93	7.53	7.68	7.52	7.65	7.73	7.80	7.46	7.57	7.89	7.96
Sulfur	2.56	2.59	2.58	2.63	2.67	2.72	2.75	2.78	2.69	2.73	2.81	2.84
J/g	31814	32197	31972	32597	31902	32442	32058	32369	31827	32311	31841	32128
(Btu/lb)	13678	13843	13746	14015	13716	13948	13783	13917	13684	13892	13690	13813
<u>Ultimate (% weight)</u>												
Moisture	-	-	1.92	-	1.66	-	0.96	-	1.5	-		
Carbon	-	77.23	76.33	77.82	76.15	77.44	75.92	76.65	76.28	77.44	76.05	76.73
Hydrogen	-	5.15	5.07	5.17	5.11	5.20	5.09	5.14	5.19	5.27	5.10	5.14
Nitrogen	-	1.23	1.17	1.19	1.37	1.39	1.32	1.33	1.39	1.41	1.30	1.32
Sulfur	-	2.59	2.58	2.63	2.67	2.72	2.75	2.78	2.69	2.73	2.81	2.84
Chlorine	-	-	0.02	0.02	0.03	0.03	-	-	0.04	0.04	-	-
Ash	-	7.93	7.53	7.68	7.52	7.65	7.73	7.80	7.46	7.57	7.89	7.96
Oxygen (diff)	-	5.87	5.38	5.49	5.49	5.57	6.23	6.29	5.45	5.54	5.96	6.02

536

TABLE G-3. ANALYSES OF BOILER ASHES

Sample	Amount Recovered kg (lb) (%)	Sample No.	Lab*	AR	Dry	% Moisture	Amount Collected Carbon Free and Dry kg (lb)
Furnace slag chunks	27.2 (60) (22.6%)	None 199/200	CTE A-L	0.18	0.18	0.03	27.2 (59.9)
Furnace slag powder	24.0 (53) (19.9%)	175 174	CTE A-L	2.91 2.68	2.92 2.69	0.37 0.22	23.3 (51.3) 23.3 (51.5)
Firetube ash	25.8 (57) (21.4%)	177 176	CTE A-L	26.60 26.20	27.22 26.60	2.29 1.47	18.4 (40.5) 18.7 (41.2)
Lower stack ash	1.4 (3) (1.1%)	All used for T.E. analysis					1.2 (2.7) est.
Horz. duct ash	.5 (1) (.4%)	All used for T.E. analysis					.4 (.9) est.
Baghouse ash	41.8 (92) (34.6%)	173 172	CTE A-L	9.62 9.87	9.68 9.92	0.63 0.48	37.5 (82.6) 37.4 (82.5)
Totals	120.7 (266)						108.1 (238.3)

CTE - Commercial Testing & Engineering, Chicago, IL  
A-L - Accu-Labs, Denver, CO

537

## SECTION G-4.0

### KVB BOILER SASS TEST SAMPLE ANALYSIS, INORGANICS

Table G-4 presents results for the major elements barium, calcium, and titanium. There was a substantial difference in concentration of barium between the two coal samples (58  $\mu\text{g/g}$  in the composite sample of total coal burned versus 81  $\mu\text{g/g}$  in the coal sample collected only during the SASS run). For calcium, the SASS run coal sample was 40% higher than the total sample. Titanium was within 3% for both coal samples.

The total coal sample and SASS run coal sample were composite samples obtained from 26 separate coal samples collected during the run. The majority of the elements appeared to be consistent between the two samples. Elements that showed a fairly large difference include: antimony, arsenic, barium, cadmium, and fluoride. The mercury content in both samples was  $< 0.03 \mu\text{g/g}$ . Calspan had the SASS run coal sample analyzed by CTE using a gold amalgamation-AA method and a value of  $0.03 \mu\text{g/g}$  was obtained, exactly equal to the Calspan AA detection limit.

Boiler ash collection appeared very good. Total ash barium content was 93% of the total coal sample barium content but only 66% of the SASS run coal sample content. Comparison of the boiler ash samples with the total coal sample rather than the SASS run coal is more appropriate since the ash was generated by the total amount of coal burned. For calcium, the ash content was 138% of total coal calcium and 108% of the SASS run coal content. For titanium, the ash content was 95% of the total coal content and 92% of the SASS run coal sample.

SASS train collections of barium, calcium and titanium were also very good. The majority of these three elements was collected in the solids portion of the train. The specific concentrations ( $\mu\text{g/g}$ ) in the cyclone solids are comparable to the specific concentrations in the boiler baghouse ash. Total stack emissions of the three major elements were estimated by three methods:

TABLE G-4. KVB BOILER SASS TRAIN TEST MASS BALANCE OF MAJOR ELEMENTS

Sample	Quantity During Train Run	Barium		Calcium		Titanium	
		Relative Amount	Total	Relative Amount	Total	Relative Amount	Total
<b>Fuel</b>							
153 Total Coal	719.3 kg	58 µg/g	41.7 g	1100 µg/g	791 g	840 µg/g	604 g
154 SASS Run Coal	719.3 kg	81 µg/g	58.3 g	1400 µg/g	1007 g	870 µg/g	626 g
<b>Boiler Ashes</b>							
180 Slag Chunks	12.6 kg	>1000 µg/g	12.6 +g	3000 µg/g	378 g	9700 µg/g	122 g
167 Slag Powder	11.1 kg	720 µg/g	7.99 g	17000 µg/g	189 g	9400 µg/g	104 g
169 Firstube	12.0 kg	630 µg/g	7.56 g	5600 µg/g	67 g	8200 µg/g	98 g
171 Stack	.6 kg	310 µg/g	.19 g	8200 µg/g	5 g	8200 µg/g	5 g
179 Duct	.2 kg	330 µg/g	.07 g	3500 µg/g	1 g	1600 µg/g	.3 g
165 Baghouse	19.5 kg	530 µg/g	10.34 g	23000 µg/g	449 g	12500 µg/g	244 g
Total Ash	56.0 kg		38.75 +g		1089 g		573 g
% of Total/SASS Coal			93/66		138/108		95/92
<b>Train Samples</b>							
Comb. P,N,C,F Washes	365 ml	.64 µg/ml	234 µg	14.6 µg/ml	5.3 mg	3.5 µg/ml	1.3 mg
182 10 µm Solids	38.5758 g	900 µg/g	34718 µg	2100 µg/g	810 mg	11000 µg/g	424 mg
184 3 µm Solids	23.7092 g	600 µg/g	14225 µg	24000 µg/g	569 mg	13500 µg/g	320 mg
186 1 µm Solids	11.3035 g	420 µg/g	4747 µg	17000 µg/g	192 mg	14000 µg/g	158 mg
188 Filters	3.3463 g	480 µg/g	1606 µg	26000 µg/g	87 mg	9200 µg/g	31 mg
151 XAD2 Resin	151.4 g	4 µg/g	606 µg	98 µg/g	15 mg	<50 µg/g	0
139 XAD2 Wash	274 ml	.13 µg/g	36 µg	.8 µg/ml	.2 mg	<2 µg/ml	0
108 Imping. #1(1)	937 ml	.10 µg/ml	94 µg	<.02 µg/ml	0	<2 µg/ml	0
109 Imping. #1(2)	980 ml	.076 µg/ml	75 µg	.04 µg/ml	.4 mg	<2 µg/ml	0
110 Imping. #2	1295 ml	.044 µg/ml	57 µg	.12 µg/ml	.2 mg	<2 µg/ml	0
112 Imping. #3	558 ml	.080 µg/ml	45 µg	.08 µg/ml	.04 mg	<2 µg/ml	0
Total Train Catch			56443 µg		1679 mg		934 mg
µg/m <sup>3</sup>			1880		55929		31112
% as Vapor			1.6		0.9		0
<b>Total Stack Emission:</b>							
Area Ratio = 309 (Duct/Nozzle)			17.44 g		519 g		289 g
Volume Ratio = 308 (9232/30 m <sup>3</sup> )			17.38 g		517 g		288 g
Solids Ratio = 253 (19500/77 g)			14.28 g		424 g		236 g
% Mass Balance A,V, S Ratio - Total Coal			110/109/102		147/146/135		102/101/94
% Mass Balance A,V, S Ratio - SASS Coal			79/79/73		115/114/106		99/98/90

1. Area Ratio = Duct Area/SASS Nozzle Area = 309
2. Volume Ratio = Total Stack Volume/SASS Sample Volume = 308
3. Solids Ratio = Baghouse Ash Weight/SASS Solids Weight = 253

These ratios are based on:

Duct Area at Sample Point =  $0.0613 \text{ m}^2$

SASS Nozzle Area =  $0.000198 \text{ m}^2$

Total Stack Volume = 9232 SCM, dry

SASS Sample Volume = 30.02 SCM, dry

Baghouse Ash Weight = 19,500 g

SASS Solids Weight = 76.9 g

Mass balances based on each ratio and for the two coal samples are shown in the table. The balance was made by subtracting baghouse ash content from total ash content, adding the stack emission obtained by train collection and dividing by the coal content. The various balance values vary from 73 to 146%. The mass balance on titanium was from 90 to 105%. These are considered to be excellent results and indicate that the basic sample collection procedure was properly conducted.

Table G-5 presents preliminary results for four of the more volatile elements. Each element is discussed below.

#### Arsenic

The total arsenic collected in the boiler ashes is 94% of the total coal arsenic (141% of SASS run coal content). This suggests that the arsenic did not behave as a volatile element. The baghouse ash contained 38% of the arsenic collected in the ashes and the baghouse total ash was 35% of the total boiler ash. Arsenic content of the total coal sample was  $1.5 \text{ } \mu\text{g/g}$  or  $19.7 \text{ } \mu\text{g/g}$  if considered to be present only in the coal ash at an ash content of 7.63%. Boiler ash concentrations varied from 12 to  $26 \text{ } \mu\text{g/g}$  of arsenic (see Appendix A) or an average of  $18.1 \text{ } \mu\text{g/g}$ . It would appear that all arsenic remained in the boiler ash. Essentially all of the arsenic collected in the SASS train was present in the solids section, consistent with the above. However, the train solids concentrations were higher ( $40\text{-}100 \text{ } \mu\text{g/g}$ ) than in the ashes and the resultant total mass balance varied from 176 to 303%. Arsenic collected by the train, converted to total emission by the 3 ratios, exceeds the total coal arsenic content.

TABLE G-5. KVB BOILER SASS TRAIN TEST MASS BALANCE OF VOLATILE TRACE ELEMENTS

<u>Sample</u>	<u>Quantity During Train Run</u>	<u>Arsenic</u>	<u>Antimony</u>	<u>Selenium</u>	<u>Mercury</u>
<u>Fuel</u>					
153 Total Coal	719.3 kg	1079 mg	14386 mg	<2158 mg	<21.6 mg
154 SASS Run Coal	719.3 kg	719 mg	7193 mg	<2158 mg	21.6 mg
<u>Boiler Ashes</u>					
180 Slag Chunks	12.6 kg	151 mg	5.04 mg	25.2 mg	<.378 mg
167 Slag Powder	11.1 kg	144 mg	5.55 mg	33.3 mg	.77 mg
169 Firstube	12.0 kg	312 mg	3.60 mg	108.0 mg	1.440 mg
171 Stack	.6 kg	15 mg	<.06 mg	6.6 mg	.060 mg
179 Duct	.2 kg	3 mg	.02 mg	8.8 mg	.042 mg
165 Baghouse	19.5 kg	390 mg	<1.95 mg	156.0 mg	1.560 mg
<b>Total Ash</b>	<b>56.0 kg</b>	<b>1015 mg</b>	<b>14.21 mg</b>	<b>337.9 mg</b>	<b>3.879 mg</b>
<b>% of Total/SASS Coal</b>		<b>94/141</b>	<b>.1/.2</b>	<b>-/-</b>	<b>-/18</b>
<u>Train Samples</u>					
Comb. P,N,C,F Washes	365 ml	22 µg	292 µg	<44 µg	<.5 µg
182 10 µm Solids	38.5758 g	1544 µg	5786 µg	<116 µg	7.7 µg
184 3 µm Solids	23.7092 g	2371 µg	4740 µg	<71 µg	<2.4 µg
186 1 µm Solids	11.3035 g	848 µg	2034 µg	<34 µg	<1.5 µg
188 Filters	3.3463 g	251 µg	301 µg	<15 µg	1.0 µg
151 XAD2 Resin	151.4 g	<151 µg	1514 µg	<454 µg	<15.1 µg
139 XAD2 Wash	274 ml	<11 µg	219 µg	<33 µg	2.2 µg
108 Imping. #1 (1)	937 ml	<4 µg	2998 µg	<112 µg	4.3 µg
109 Imping. #1 (2)	980 ml	<4 µg	3136 µg	<118 µg	4.2 µg
110 Imping. #2	1295 ml	<5 µg	1036 µg	<155 µg	11.1 µg
112 Imping. #3	558 ml	<2 µg	446 µg	<67 µg	6.7 µg
<b>Total Train Catch</b>		<b>5036 µg</b>	<b>&lt;22502 µg</b>	<b>1219 µg</b>	<b>37.2 µg</b>
<b>µg/m<sup>3</sup></b>		<b>168</b>	<b>750</b>	<b>-</b>	<b>1.24</b>
<b>% as Vapor</b>		<b>0</b>	<b>40</b>	<b>-</b>	<b>77.</b>
<u>Total Stack Emissions</u>					
Area Ratio = 309		1556 mg	6953 mg	-	11.5 mg
Volume Ratio = 308		1551 mg	6931 mg	-	11.5 mg
Solids Ratio = 253		1247 mg	5693 mg	-	9.4 mg
<b>% Mass Balance, A,V,S Ratio - Total Coal</b>		<b>202/202/176</b>	<b>48/48/40</b>	<b>-/-/-</b>	<b>-/-/-</b>
<b>% Mass Balance, A,V,S Ratio - SASS Coal</b>		<b>303/303/264</b>	<b>97/97/79</b>	<b>-/-/-</b>	<b>64/64/54</b>

### Antimony

Only 0.1 to 0.2% of the antimony was retained in the boiler ashes. This suggests that almost all antimony was vaporized and train collection would be expected to occur in the impinger sections. Such was not the case. Sixty percent of the antimony was collected in the train solids section. Total antimony mass balance was 79 to 97% based on the SASS coal sample, indicating excellent collection of antimony. The high unexpected fraction found in the solid section may indicate that as the sample is cooled from 625 K (665°F) stack temperature to 478 K (400°F) cyclone temperature, condensation of antimony may occur. However, if that were the case, the antimony would be enriched on the small particles and that did not occur as indicated below:

	<u>Antimony</u>	
	<u>µg/g</u>	<u>mg</u>
10 µm solids	150	5786
3 µm solids	200	4740
1 µm solids	180	2034
Filter	90	301

There was no significant increase in antimony concentration for smaller particle size.

### Selenium

Selenium concentrations were below detection limits for both coal samples and all SASS train samples. All boiler ash samples were above detection limits. No conclusions can therefore be drawn regarding selenium collection.

### Mercury

Coal mercury content was relatively low (0.03 µg/g) compared with typical coal concentrations (about 0.15 µg/g). Only 18% of the mercury was retained in the boiler ashes. Some mercury was collected in the 10 micron cyclone and on the filter but 77% was collected in the XAD2 wash and impingers. The total mass balance was about 60% with the largest amount collected in Impinger No. 2. If all train samples for which mercury was below detection, were taken at the detection limit values, total mercury collected would still be only 89% of coal mercury.

### Blank Values

Comparison of test results for blanks and samples for the XAD2 resin and the filter indicates that blank trace element contents were in several instances higher than in the samples.

### Conclusions

Based on major trace element mass balances, the KVB SASS test appears to have been a satisfactory test run. For volatile elements of main interest, arsenic was collected in excess of the expected amount, antimony collection was excellent on a mass balance basis, selenium was not present in sufficient quantities to evaluate collection, and only about 60% of the mercury was recovered by the train.

## SECTION G-5.0

### KVB BOILER TEST PARTICLE SIZE ANALYSIS

The SASS train cyclones were designed for nominal cut sizes of 10, 3, and 1 microns. A particle sizing analysis was obtained by KVB from Calspan Corporation. The sizing was performed by a Coulter Counter which optically analyzes particles suspended in a liquid. The result is a volume-based diameter while the actual desired result should be based on aerodynamic diameter. Sizing was done for the 1, 3, and 10 micron cyclone particulate collected. Sizing of the filter collection was requested but no results were obtained since the Coulter technique is valid only for particles over 1 micron.

Figures G-1, G-2, and G-3 present the results for the 10, 3, and 1 micron cyclone respectively. The 50% cut point for the 10 micron cyclone (Fig. G-1) was 10.7 microns and 54% of the particulate was over 10 microns. Since the basic design is based on a 50% collection at 10 microns, this is an extremely accurate result. Ninety percent of the particulate was between 3.7 and 23 microns.

For the 3 micron cyclone, particles theoretically should be from 3 to 10 microns. Results of Figure G-2 show 73% of the particulate between 3 and 10 microns. The 50% cut point was 6.7 microns and 90% of the particles were between 2.8 and 17 microns.

For the 1 micron cyclone, particles should theoretically be between 1 and 3 microns. The results for the 1 micron cyclone are shown in Figure G-3. The 50% cut point was 2.7 microns and 63% was between 1 and 3 microns. Ninety percent was between 1.3 and 5.7 microns.

These results were obtained at a cost less than \$100. They appear to substantiate the design sizing of the cyclones. However, the design is based on an aerodynamic diameter while the Coulter Counter provides a volume based diameter independent of particulate density.

Figure G-1.

 <b>COULTER COUNTER<sup>®</sup> Model T &amp; TA.</b>		<b>PARTICLE SIZE ANALYSIS</b>				<small>COULTER ELECTRONICS INC.</small> <small>.15 - 200 μ</small> <small>X PERCENT</small> <small>500 W 20 ST.</small> <small>MALEAH, FLA. 33010</small>							
ORGANIZATION <b>Calspan</b>		$k = d \sqrt{\frac{2}{\pi}}$ <small>FOR MODEL T</small>				$\frac{\Delta Z}{\Delta t} = \left(\frac{d_2}{d_1}\right)^3$ when $W_2 = W_1$ $\frac{\Delta Z}{\Delta t} = \left(\frac{d_1}{d_2}\right)^3$ when $W_2 = W_1$ <small>FOR MODEL TA</small>				SAMPLE SETTINGS			
OPERATOR		APERT. SIZE		SERIAL		PART DIA.		W		± SA		A	
EQUIPMENT		SAMPLE		ELECTROLYTE		DISPERSANT							
		KVB #182, 10 <sup>+</sup> μm cyclone, KVB Boiler Test											
		D <sub>50</sub> = 10.7 μm (volume)     54% > 10 μm											
		90% between 3.7-2.3 μm											

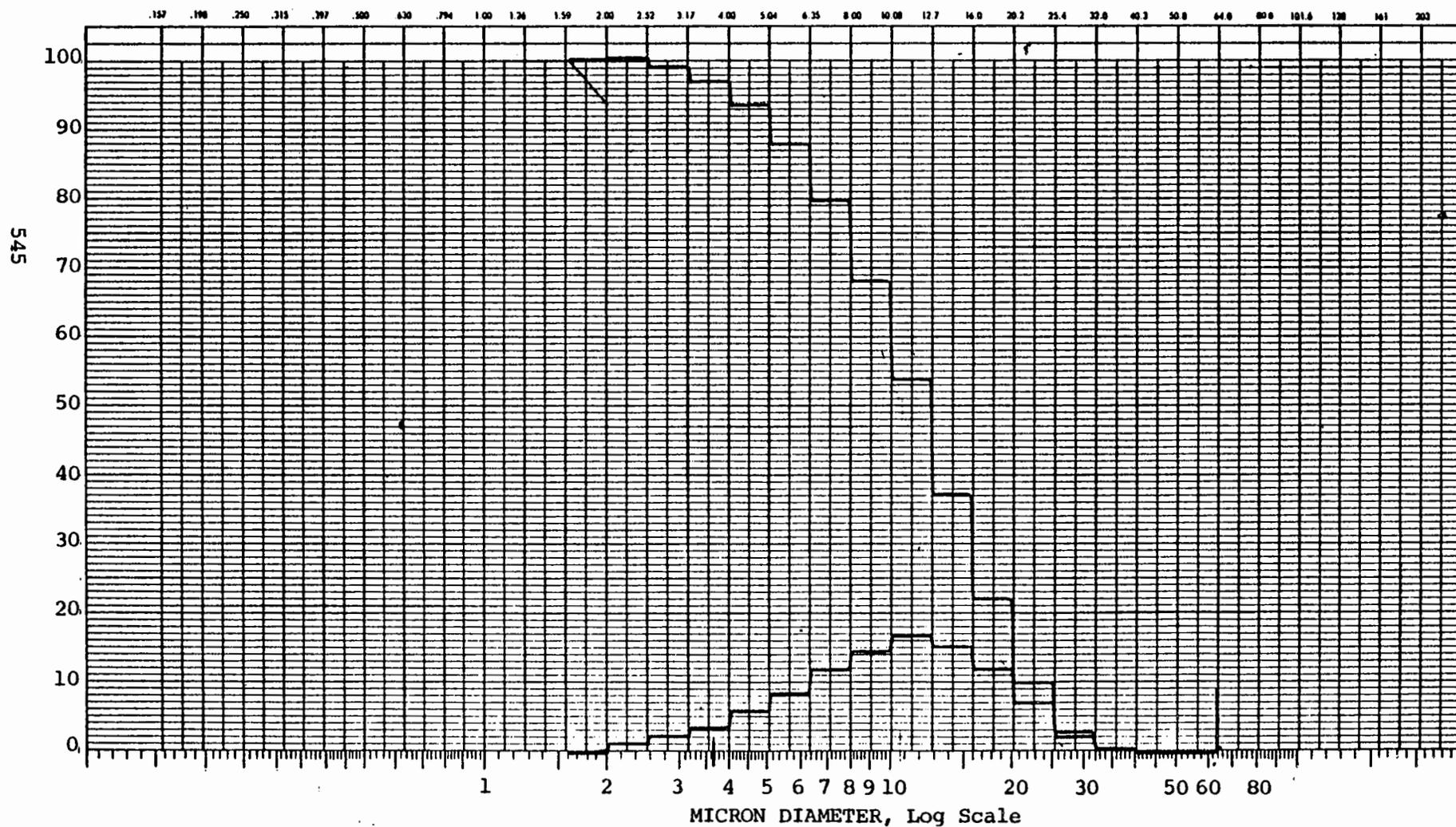
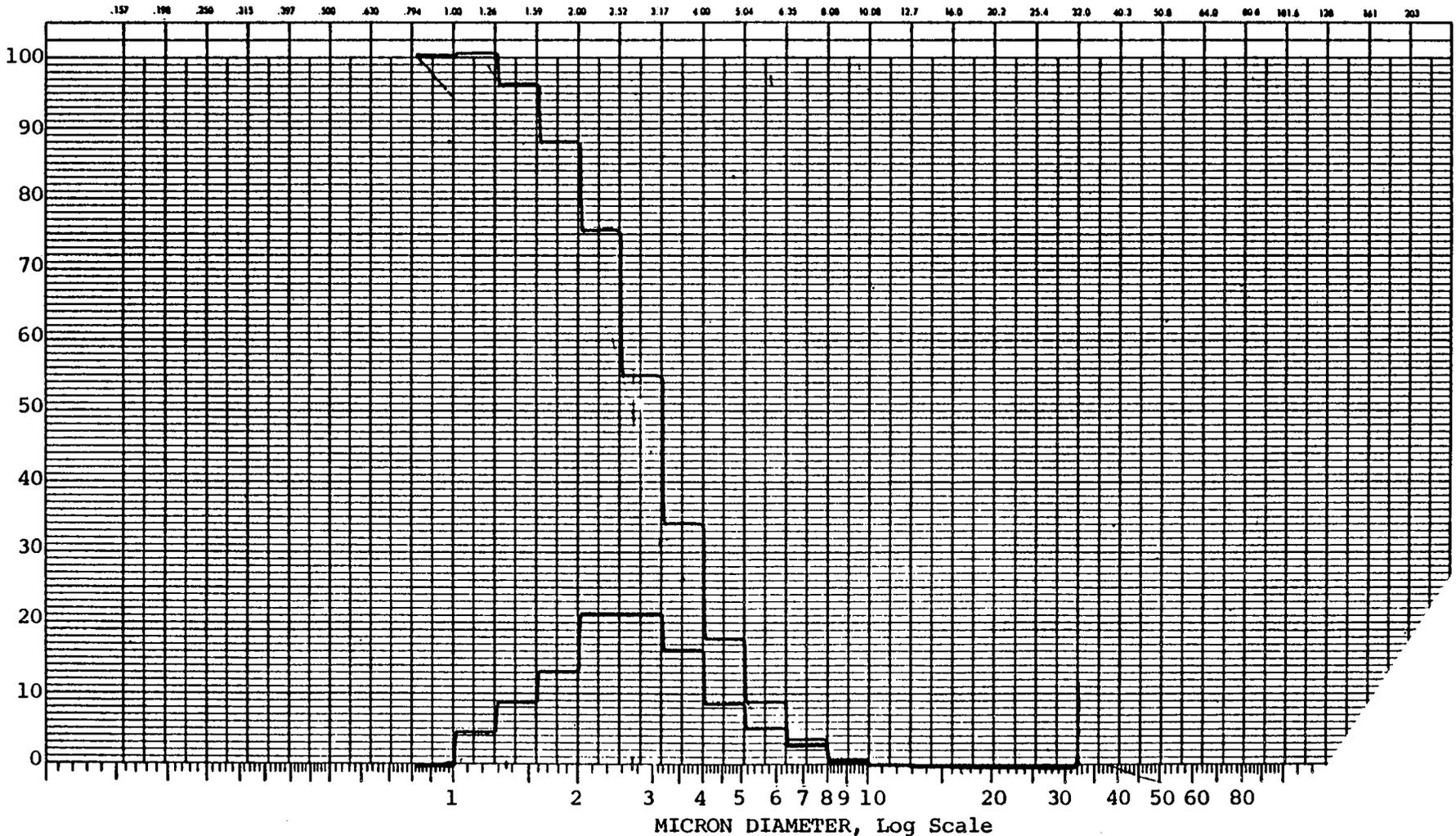


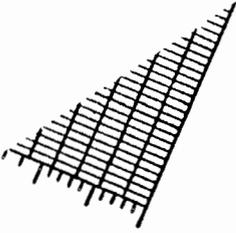


Figure G-3.

 <b>COULTER COUNTER Model T &amp; TA</b>		<b>PARTICLE SIZE ANALYSIS</b>				.15 - 200 μ X PERCENT		COULTER ELECTRONICS INC. 590 W 30 ST. MABLEAN, FLA. 33070							
ORGANIZATION <b>Calspan</b>		$L = d \sqrt[3]{\frac{2m}{\rho}}$						$\frac{A_2}{A_1} = \left(\frac{d_2}{d_1}\right)^3$ when $W_2 = W_1$				$\frac{A_2}{A_1} = \left(\frac{d_1}{d_2}\right)^3$ when $W_2 = W_1$		SAMPLE SETTINGS	
OPERATOR		FOR MODEL T						FOR MODEL TA							
EQUIPMENT		APER. SIZE	SERIAL					PART DIA.	W	± 1A	A	DIA.	W	± 1A	A
SAMPLE	ELECTROLYTE	DISPERSANT													
KVB #186, 1-3 μ cyclone, KVB Boiler Test															
$D_{50} = 2.7 \mu\text{m (volume)}$															
63% between 1-3 μ															
90% between 1.3-5.7 μ															

547





## SECTION G-6.0

### ORGANICS

Analysis of polycyclic organic matter (POM) and polychlorinated biphenyls (PCB) in samples collected during the initial SASS train test on the KVB boiler was performed. The results are presented in Table G-6. Total POM in the coal burned during the sampling time was 94 grams. The total ash content was 272 mg of total POM of which the majority, 264 mg, was in the firetube ash and 3.5 mg in the baghouse ash.

Total POM collected in the SASS train was 6.6 mg. Of this, 83% or 5.5 mg was collected in the XAD-2 module wash and 15% or 1.0 mg was collected in the XAD-2 resin. The remainder was present in the 1  $\mu\text{m}$  cyclone solids (0.097 mg) and in the 3  $\mu\text{m}$  cyclone solids (0.018 mg). Based on 30  $\text{m}^3$  of stack gas collected by the train, the total POM emission was 220  $\mu\text{g}/\text{m}^3$  or, on a heat input basis, 0.081 ng/J. Total POM in samples from nozzle, probe, cyclone, and filter washes, the filter itself, and from the impingers were all below the detectable limit. The potential total undetected amount is 1.1 mg of total POM.

The gas chromatograms for POM did not show any distinct peaks that could be attributed to any of the eight specific POM compounds required to be identified. Compound separation was substantial based on a review of Calspan calibration runs. However there are evidently so many compounds present in the samples where total POM amount is high that identification of specific POM by GC analysis alone is not adequate. As a result of this test, samples with high POM content were subjected on a selected basis to analysis by GC/MS for compound identification.

Calspan results for total PCB content of all samples were below the limit of detectability in all samples.

TABLE G-6. POM AND PCB EMISSIONS FROM KVB BOILER TEST OF SASS TRAIN

Sample No.	Sample Type	Quantity During Train Run	Total POM		Total PCB Concentration
			Concentration	Amount	
<u>FUEL</u>					
153	Total Coal	719.3 kg	229 µg/g	165 g	< 10 µg/g
154	SASS Coal	719.3 kg	130 µg/g	94 g	< 10 µg/g
<u>BOILER ASHES</u>					
180	Slag Chunks	12.6 kg	< 0.2 µg/g	---	< 10 µg/g
167	Slag Powder	11.1 kg	0.17 µg/g	1.9 mg	< 10 µg/g
169	Firetube Ash	12.0 kg	22.0 µg/g	264.0 mg	< 10 µg/g
171	Stack Ash	0.6 kg	4.2 µg/g	2.5 mg	< 10 µg/g
179	Duct Ash	0.2 kg	< 0.2 µg/g	---	< 10 µg/g
165	Baghouse Ash	19.5 kg	0.18 µg/g	3.5 mg	< 10 µg/g
	Total Ash	56.0 kg		271.9 mg	
<u>TRAIN SAMPLES</u>					
Comb.	* Solid Section Washes	365 ml	< 1 µg/ml	---	< 10 µg/ml
182	10 µm Solids	38.5758 g	< 0.2 µg/g	---	< 10 µg/g
184	3 µm Solids	23.7092 g	0.74 µg/g	18 µg	< 10 µg/g
186	1 µm Solids	11.3035 g	8.6 µg/g	97 µg	< 10 µg/g
188	Filter	3.3463 g	< 1 µg/g	---	< 10 µg/g
151	** XAD-2 Resin	151.4 g	6.7 µg/g	1014 µg	< 10 µg/g
139	* Org. Module Wash	274 ml	20.0 µg/ml	5480 µg	< 1 µg/ml
108,109	* Impinger #1	1917 ml	< 0.2 µg/ml	---	< 1 µg/ml
110	* Impinger #2	1295 ml	< 0.2 µg/ml	---	< 1 µg/ml
112	* Impinger #3	558 ml	< 0.2 µg/ml	---	< 1 µg/ml
	Total Train Catch			6600 µg	N.D.
	Stack Concentration			220 µg/m <sup>3</sup>	N.D.
	% as Vapor			98	
	Total Stack Emission by Volume Ratio of 327			2158 mg	

\*Blank values for all liquids: POM < 0.2 µg/ml, PCB < 1 µg/ml.

\*\*Blank values for XAD-2 resin: POM < 0.2 µg/g, PCB < 10 µg/g.

549



**TECHNICAL REPORT DATA**  
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-79-015a		2.		3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE Application of Combustion Modifications to Industrial Combustion Equipment				5. REPORT DATE January 1979	
				6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) S. C. Hunter, W. A. Carter, M. W. McElroy, S. S. Cherry, and H. J. Buening				8. PERFORMING ORGANIZATION REPORT NO. KVB 6002-743	
9. PERFORMING ORGANIZATION NAME AND ADDRESS KVB, Inc. 17332 Irvine Boulevard Tustin, California 92680				10. PROGRAM ELEMENT NO. EHE624A	
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16. ABSTRACT The report gives results of a field test program to evaluate the effect of minor combustion modifications on pollutant emissions from a variety of industrial combustion equipment types. Tested were 22 units, including refinery process heaters; clay and cement kilns; steel and aluminum furnaces; boilers burning black liquor, wood bark, and CO gas; internal combustion engines; and gas-turbine combined cycles. Process variables, fuel types, excess air reduction, burner adjustments, and staged combustion were evaluated primarily for their effect on NOx emissions. Emissions of NOx, SOx, CO, and HC were measured on all units. Emissions of particulate mass and size, trace species, and organics were measured on selected units. Baseline (as-found) NOx emissions from the test units varied from 35 to 1320 ng/J (52 to 2250 ppm corrected to 3% O2, dry basis). With combustion modifications NOx emissions from some units were reduced by up to 69%; however, for certain kinds of equipment, NOx reductions were low or insignificant. The main conclusion was that combustion modifications can be applied to many devices without process disruption; however, process limitations on certain types of equipment restrict the degree of NOx reduction that can be achieved.					
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a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS		c. COSATI Field/Group	
Air Pollution	Chemical Analysis	Air Pollution Control	13B	07D	
Combustion	Inorganic Compound	Stationary Sources	21B		
Boilers	Organic Compound	Combustion Modification	13A	07C	
Furnaces	Gas Turbine Engine	Particulate		21E	
Nitrogen Oxides	Reciprocating Engine	Excess Air	07B		
Fossil Fuels	Industrial Process	Staged Combustion	21D	21G	
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