Emission Characteristics of Paraho Shale Oil as Tested in a [illegible]tility Boiler

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Prepared by
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Rosemead, California
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ABSTRACT

Combustion tests of Crude Paraho Shale Oil (0.7% sulfur and 2% nitrogen) were conducted in a 45 MW Combustion Engineering boiler at SCE's Highgrove Generating Station. Shale oil was blended in various proportions with low sulfur oil before its combustion in the boiler so that the sulfur content of the fuel blend did not exceed 0.5%. Emission of air contaminants was determined when shale oil blends are burned in all burners (tank blending), and when the oil blend is burned in the lower boiler elevation only, followed by the combustion of low nitrogen fuels in the upper elevations. The segregation of the high and low nitrogen fuels, in two independent fuel systems, was originated by SCE and named "Dual Fuel Combustion".

NOx emissions were evaluated for both a developmental low NOx burner (LNB) and a conventional mechanical atomized Peabody burner using both tank blending and dual fuel combustion systems. The emission levels were determined under normal and off-stoichiometric (o/s) modes of combustion. The maximum reduction in emission level occurred during the fuel-rich combustion of shale oil in the lower boiler elevation followed by the combustion of natural gas in the upper elevation.

Both fuel nitrogen conversion into NOx and thermal NOx formation were found to be very dependent upon burner Air/Fuel ratio. The conversion efficiency of fuel nitrogen into NOx was calculated and found to be inversely proportional to the nitrogen content of the fuel.

The emission of particulate matter trace elements and polynuclear aromatic hydrocarbons from the combustion of shale oil was also evaluated during the study.

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EXECUTIVE SUMMARY

Combustion tests of crude Paraho Shale Oil were conducted at SCE's Highgrove Generating Station in a 45 MW Combustion Engineering boiler. The boiler is equipped with six front-face mounted oil burners, arranged in two rows, and rated at 85 million Btu/hr each. Shale oil was blended in various proportions with low sulfur oil before its combustion in the boiler so that the sulfur content of the fuel blend did not exceed 0.5%. The fuel handling system for the test boiler was modified to achieve the blending of the shale and low sulfur oils in the piping network. The fuel piping was arranged to either supply the shale oil blends to all six burners or to the bottom row burners only. Emission of air contaminants was determined when shale oil blend was burned in all six burners (tank blending) and when the oil blend was burned in the bottom row of burners only followed by the combustion of low nitrogen fuel in the upper burners elevation. The segregation of the high and low nitrogen fuels in two independent fuel systems was originally conceived by SCE and named "Dual Fuel Combustion".

Sampling was performed to determine NOx, particulates, and polynuclear aromatic hydrocarbons (PNA) emission at full boiler load when burning shale oil blends of various proportions. NOx emission levels under conventional and off-stoichiometric firing modes using both tank blending and dual fuel combustion were compared at each blend ratio. The NOx emissions level was evaluated for two different types of burners; a developmental low NOx burner (LNB), and a conventional mechanical atomized Peabody burner.

Particulate size distribution was determined by examining the electron microscope photographs of the collected particulates and calculating the distribution by weight based on number count. Several particulate catches were also analyzed for PNA content. The emission of trace elements when burning pure shale oil was also evaluated during the program. To meet SO2 Rules for the South Coast Air Quality Management District (SCAQMD), the boiler was operated during these tests at 25% load and the resulting flue gas was scrubbed in a 10 MW wet alkaline scrubber before it was discharged to the atmosphere.

Crude shale oil was found to be miscible in station fuel oil and compatible with station fuel storage and handling equipment. No smoke emission or combustion problems of any kind were experienced with the burning of the shale oil. As to be expected, NOx emission level under off-stoichiometric mode of firing was generally lower than under normal combustion. Significant reduction in NOx emission levels were achieved, however, during both O/S and normal combustion using the dual fuel combustion technique. The maximum reduction in emission levels occurred during the fuel-rich combustion of shale oil blends in the bottom row of burners followed by the combustion of natural gas in the upper burners elevation. The LNB displayed, in general, lower emission levels than the conventional Peabody burner for all tested operating conditions. The shale oil blend ratio corresponded to NOx emission level of 225 ppm (corrected to 3% O2) was 17% using the LNB, and 12% using the Peabody burner. Shale oil blend ratio as high as 58% was achieved, however, while maintaining the same emission level using dual fuel combustion with natural gas burned in the upper burner elevation.

The results showed that both fuel nitrogen conversion into NOx and thermal NOx formation are very dependent upon burner Air/Fuel ratio. Both mechanisms of NOx formation contributed less to emission levels under fuel-rich combustion. The conversion of fuel bound nitrogen into NOx was found to be inversely proportional to the nitrogen content of the fuel. Difference in nitrogen conversion efficiency between the developmental LNB and conventional Peabody burner, indicated that local stoichiometry within the burner flame affects the conversion efficiency of organically bound nitrogen.

The emission of particulate matter exhibited a large degree of scatter with a significant increase in emissions occuring as a result of blending of shale oil with low sulfur oil. The increase in particulate emission was far in excess of that to be expected as a result of increasing the ash content of fuel blends. It was postulated that the heavy distillation characteristics of the crude shale oil caused a large volume percent of the fuel to undergo pyrolysis during its combustion producing heavy residue and char and increasing the emission of particulate matter. The PNA emissions were found to be equivalent to 0.0000004 gr/SCFD. The amount of trace elements emitted depended upon the element, with titanium concentration in the gas particulate being the highest and beryllium being the lowest.

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Section 1.0

INTRODUCTION AND BACKGROUND

In an oil-fired utility boiler, nitric oxides are formed by two basic mechanisms; the thermal fixation of atmospheric nitrogen at elevated temperature within the flame zone, and the conversion of organically bound nitrogen in the fuel to NOx during the combustion process. NOx formation by thermal fixation, normally referred to as thermal NOx, is essentially dependent upon burner flame temperature. The conversion of organically bound nitrogen to NOx, is directly related, however, to the nitrogen content of the fuel.

The relatively high nitrogen content of the crude Paraho shale oil (nominally 2.0%) has posed a potential NOx emission problem if burned in a utility boiler. The high cost of nitrogen removal from shale oil, on the other hand, reduced the potential of using shale oil as an alternate fuel resource for utilities. It has therefore been considered important to identify methods of minimizing NOx emissions during combustion of crude shale oil without incurring the relatively high cost of fuel treatment.

Southern California Edison Company, being the only utility company among the seventeen companies participating in the Paraho Oil Shale Demonstration Project, became involved in the evaluation of shale oil as an alternate fuel resource for utility boilers. The evaluation was conducted in two phases. The first was carried out in May, 1975 to evaluate shale oil compatibility to fuel handling equipment and to examine the combustion characteristics of the fuel. The second was initiated in June, 1976 to characterize types of air contaminants generated from the combustion of shale oil and to develop advanced combustion modification techniques for the control of NOx emission. A brief summary for the results of the first phase of the program is presented below. Findings obtained during the second phase of the test program are the subject of this report.

1.1 FIRST PHASE OF TESTING

On July 24 and 25, 1975 combustion tests of Paraho shale oil were conducted at SCE's Highgrove Generating Station to evaluate the compatibility of shale oil to fuel handling equipment of a utility boiler. The test program was also initiated to examine the combustion qualities of the oil and to determine its approximate NOx emission characteristics. The tests were conducted at part boiler load to achieve compliance with local APCD SO2 regulations by scrubbing the flue gas in a 10 MW wet alkaline scrubber. Low load operation of the boiler, however, resulted in a high excess O2 environment within the boiler furnace.

The test program showed that there were no fuel handling or combustion problems with Paraho shale oil. NOx emission level, however, ranged between (800-1000) ppm. Although it was encouraging to show that the fuel handling and combustion characteristics of shale oil are acceptable for utility use, the high NOx emission level suggested that it cannot be used in its unrefined form unless blended with conventional fuels. Based on the preliminary test results, it was projected that a maximum shale oil blending ratio of 10% would be burned in the boiler without violating the South Coast Air Quality Management District (SCAQMD) regulation for NOx emissions (225 ppm corrected to 3% O2).

1.2 OBJECTIVES OF SECOND PHASE TESTING

The second phase of the test program was initiated to evaluate the level of air contaminants emission generated by the combustion of shale oil and to identify combustion modification techniques that could be used to minimize NOx emission when burning shale blends of various proportions. The specific objectives of the test program included the following:

1. Determine the maximum shale oil blend ratio that can be burned in a utility boiler while maintaining NOx emission below the 225 ppm limit allowed by local regulatory agencies.

2. Identify the optimum method of blending shale oil to minimize NOx emission.

3. Compare NOx emissions when burning various blends of shale oil using a developmental Low NOx Burner (LNB) and a conventional Peabody burner under both normal and off-stoichiometric modes of combustion.

4. Assess the effect of shale oil blend ratio upon particulate and PNA emission.

5. Analyze the shale oil for the concentration of 20 selected trace elements and measure trace element emissions resulting from the combustion of pure shale oil in a boiler equipped with a wet alkaline stack gas scrubber.

Section 2.0

DESCRIPTION OF HARDWARE

2.1 TEST BOILER

The combustion tests were conducted on Unit 4 at SCE's Highgrove Generating Station. The unit is a balanced-draft, 45 MW Combustion Engineering boiler equipped with six front-face mounted oil and gas fired burners each rated at 85 million Btu/hr. Fuel piping at the generating station was modified so that blending of the shale and low sulfur oils in various proportions could be achieved in the piping network before firing the blended oil in the boiler. The piping network was arranged so that the blended fuel could be either introduced to the three burners in the bottom row or to all six burners. The fuel system was also capable of handling the blended shale oil and pure low sulfur oil in two completely separate piping networks, so that the bottom three burners could be fired with blended shale oil and top three burners could be fired with pure low sulfur oil. A schematic drawing of the boiler configuration is shown in Figure 1.

2.2 LOW NOx BURNER

The LNB evaluated in the test program was a developmental burner that used steam assisted atomization. The basic design concept of the burner was to achieve intermixing between fuel and air in off-stoichiometric proportions along the burner flame front. This was obtained by injecting the fuel radially as shown in Figure 2 at a relatively low pressure (about 30 psi) with coaxial steam injection along each fuel stream to assist atomization and provide charge dilution for moderating flame temperature. The burner produced a conically-shaped thin flame that provided a large radiating surface to allow rapid dissipation of heat. The shape of the burner flame also insured extremely short residence time for atmospheric nitrogen in the high flame temperature zone where most of the thermally-fixed NOx forms. The operating variables of the low NOx burner were optimized to minimize NOx produced due to the thermal fixation of atmospheric

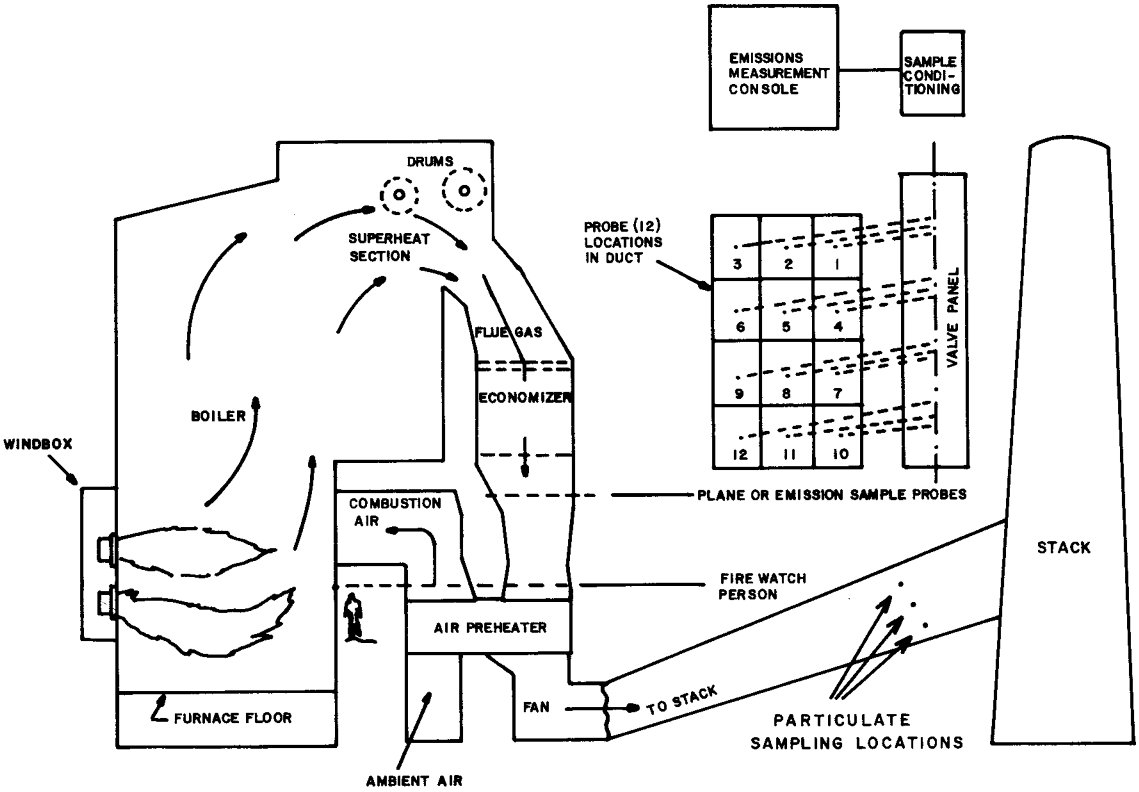

Figure 1. Test Boiler

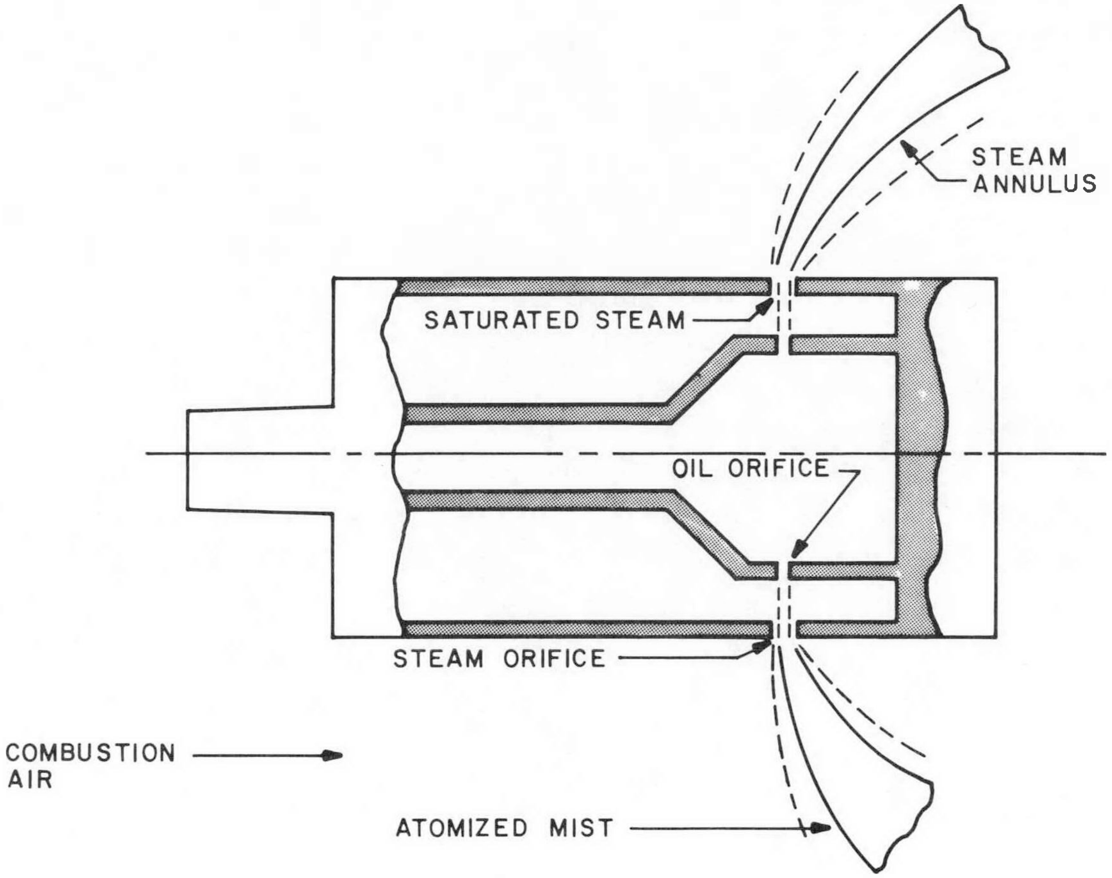

Figure 2. Schematic of the Low NOx Burner

nitrogen. It is suspected that the conversion of fuel nitrogen to NOx was also improved, however, by off-stoichiometric combustion characteristics as a function of linear distance along the burner flame front.

2.3 PEABODY BURNER

The Peabody burner utilized pressure differential to achieve mechanical atomization of the fuel. The atomizer assembly is shown in Figure 3.

Oil under high pressure is supplied through tangential slots (A) to a chamber (D) in which rapid rotary motion of the fuel occurs. The rotating fuel is then discharged into the furnace through orifice (B) in a finely divided solid spray. A secondary return line (C) permits part of the oil to return to the inlet of the differential pump. The quantity of oil sprayed into the furnace is regulated by varying the return line pressure. Flow control is achieved by increasing the return line pressure while maintaining a relatively constant differential pressure between the return and supply lines. This allows a uniform atomizing drop size and spray pattern as to the oil flow rate is varied to follow load demand on the generating unit.

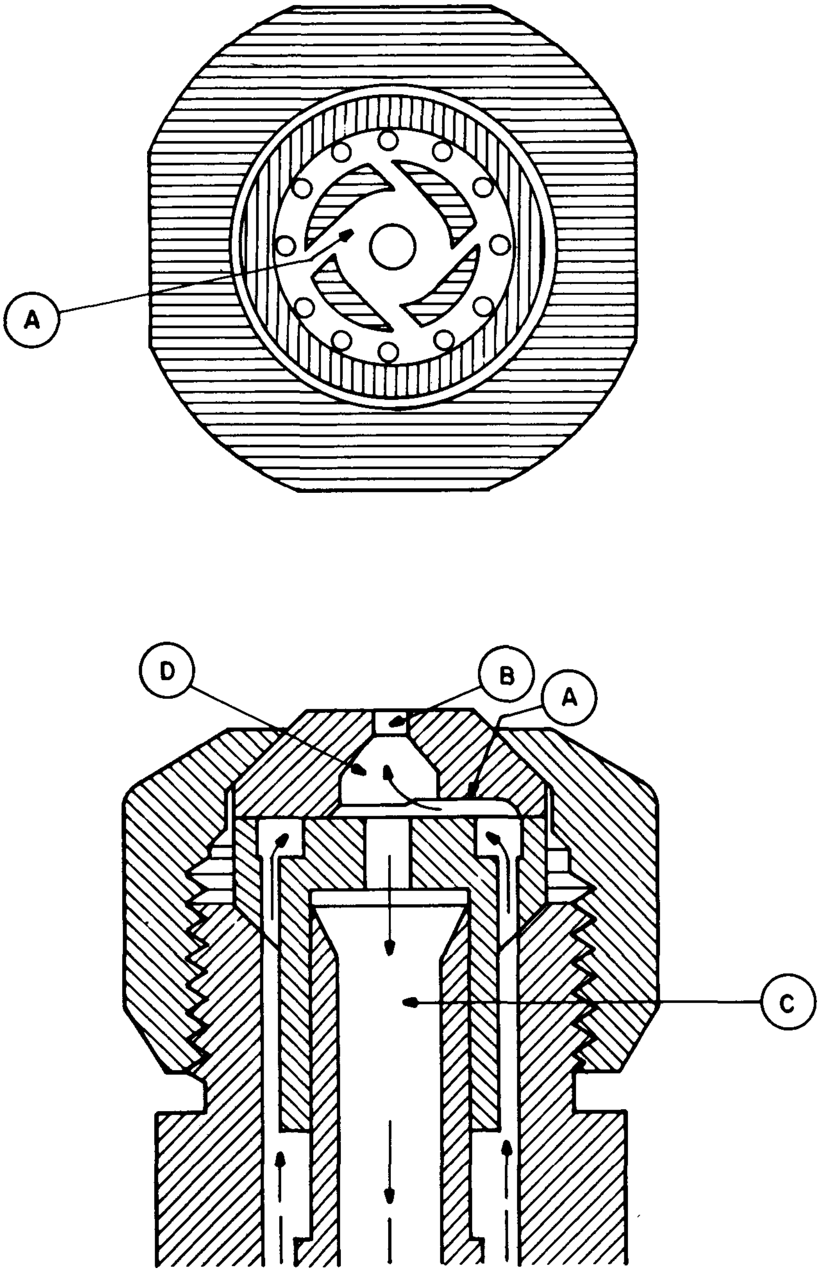

Figure 3. Schematic of the Peabody Burner

Section 3.0

ACQUISITION AND REDUCTION OF TEST DATA

3.1 SAMPLING OF AIR CONTAMINANTS

3.1.1 Gaseous Contaminants

The flue gas composition was measured utilizing the industrially acceptable, high quality emission measurement instrumentation. Capability was provided for sampling the concentration of oxides of nitrogen (NOx), carbon monoxide (CO), carbon dioxide (CO2), and oxygen (O2). Much of the equipment was contained in a portable air pollution measurement console located in the boiler control room. Special sampling probes were installed in the side of the fuel gas duct. The probes were constructed and modified as shown in Figure 4.

(A) Sampling System

The emission sampling system is shown schematically in Figure 5. It consists of:

- Stainless steel sampling probes (12)
- 300 foot 1/4-inch stainless steel tubing
- Pump, 0.5 cfm free air delivery stainless steel diaphragm pump
- Condensate trap (dry ice cooled)
- Gas Selector valves, manual, stainless steel
- Gauges to measure inlet pressure to emission instruments
- Metering valves

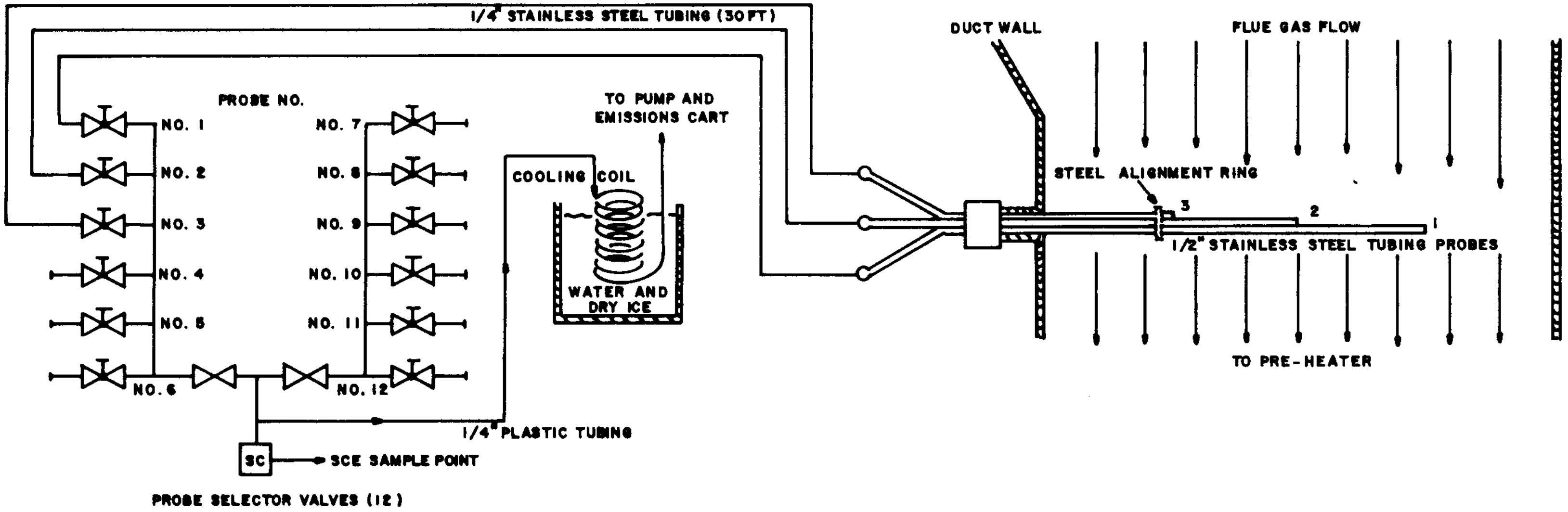

Figure 4. Probe Construction and Manifolding

- Gas analyzers
- Helium tank, to supply carrier gas to gas chromatograph
- Certified calibration gas "K": bottles (NO, NOx, CO, and CO2)
- Flow meters, total sample flow, NOx meter flow and NDIR analyzer flow
- Refrigeration (Hankinson freezer drier)

(B) Sampling Probes

The gas samples in the Highgrove facility were taken in the flue gas duct before entering the preheater wheel. Twelve sampling regions in a rectangular 3 by 4 matrix were used. The regions were numbered 1 through 12, each number corresponding to its respective probe. Each of the 12 probes consisted of 1/2-inch stainless steel tubing cut to length so that the end of the tube was situated in the middle of each region. The 12 probes were cantilevered horizontally in groups of three via 20-inch steel pipes welded to the duct walls. The three probes were spaced apart by a steel ring and oriented with the shorter probe on top, facing against the flow of hot flue gas. The samples drawn from each probe passed through 20- to 30-foot lengths of 1/4-inch stainless steel tubing into a valve assembly that manifolded any given probe or group of probes to the emissions console. The valve arrangement offered minimal sample column residence time. Previous sample gas that mixed with the new gas was easily and quickly purged by pumping.

(C) Sample Conditioning

The sample was conditioned with respect to temperature, pressure, particulate concentration, and moisture content before emissions analysis was conducted (Figure 5). Sample gas was conveyed through a dry ice cooled liquid water trap that collected water condensation formed as the gas cooled. The noncondensible gas was filtered to remove carbon granules and other solid particulates. A metering valve was used to regulate the flowrate as indicated on a flowmeter. A Hankinson freezer-drier completed the removal of water vapor prior to NO gas

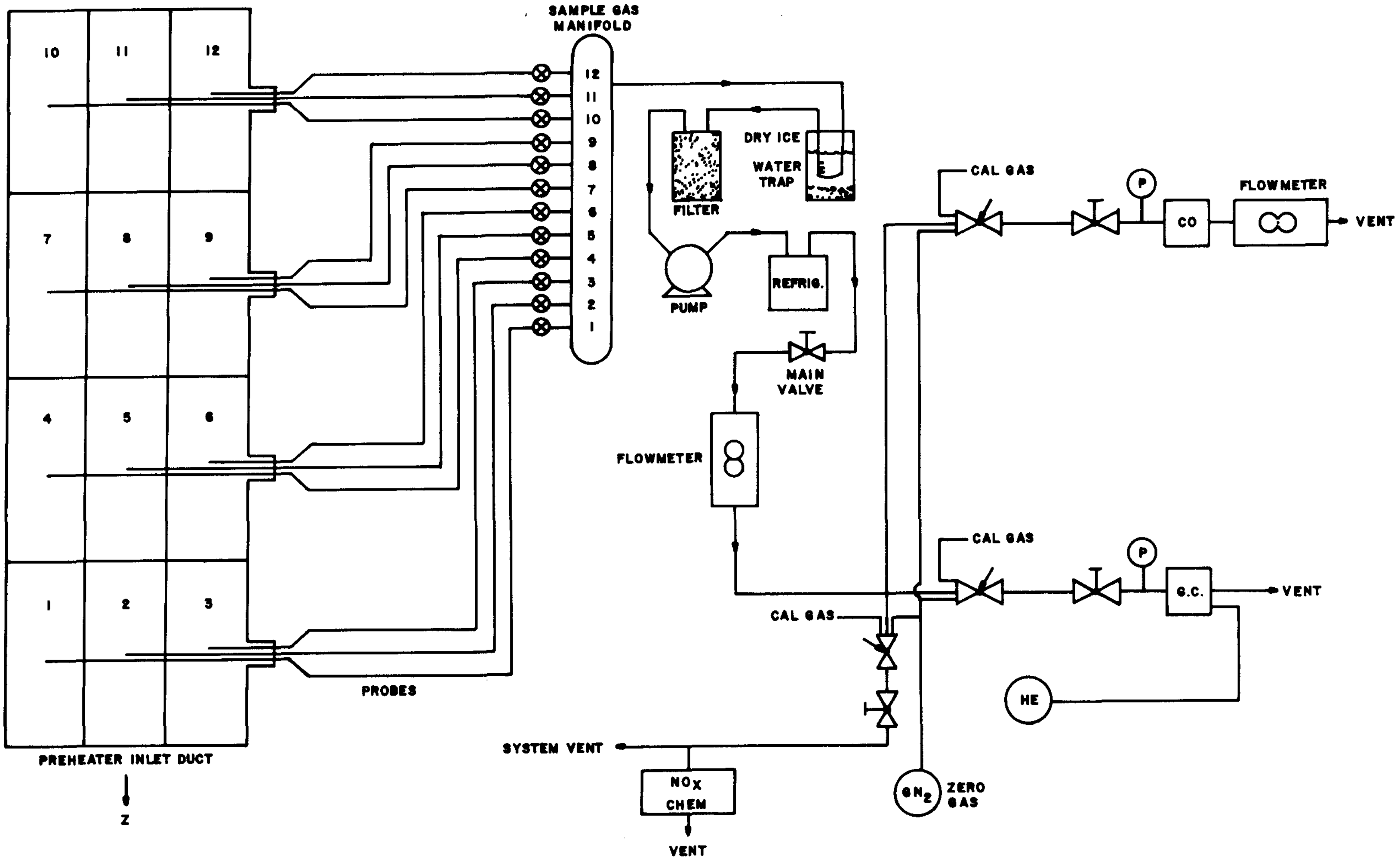

Figure 5. Emission Sampling System

analyses. The sample was distributed to the several different instruments via selector valves (all reported data refers to dry flue gas).

(D) Emissions Analysis Instrumentation

There were three different instruments used to measure the emission levels in the sample gas: Beckman Fieldlab Oxygen Analyzer (for O_2), Chemiluminescent Gas Analyzer (for NO-NO_x) and the Carle Basic Gas Chromatograph (for CO_2, O_2, CO, and N_2).

3.1.2 Particulate Emissions

Sampling ports were located downstream of the induced draft fan in the transition section between the fan and the stack, Figure 1. This location was chosen to provide the longest possible straight run of ducting. Sampling in the stack was avoided to simplify personnel access and support scaffolding required for testing.

At the start of the test period, velocity profiles with 40 and 24 traverse points were obtained to determine whether significant differences in calculating stack gas velocity would be observed. No significant differences in gas velocity were noticed and therefore most of the tests were performed using 24 traverse points.

The sampling tests were conducted according to EPA Method 5. This method requires isokinetic sampling for particulates at several points across the duct.

(A) Sampling Train

Sampling was performed using a Scientific Glass EPA method 5 sampling train. The sampling train consisted of a probe, a filter holder with a glass fiber filter to collect the particulates, followed by four impingers connected in series. The first, third and fourth impingers were the modified Greenburg-Smith type with the bottom compartment of the gas entry tube removed. The second impinger was a standard Greenburg-Smith type. The first two impingers contained 100 ml of distilled water, the third was dry, and the fourth contained 200 grams of silica gel. The volume of the impingers and weight of the silica gel were measured after each test in order to determine the percentage of moisture in the stack gas.

(B) Procedures

Sampling was done for three minutes at each traverse point. Isokinetic sampling was maintained by use of a nomograph adjusted to the gas temperature, percent moisture, nozzle diameter and stack gas velocity.

(C) Sample Recovery

After sampling, the impinger solutions were measured and placed in sample bottles. The filter was also placed in a separate sample bottle. The probe tip, probe and glassware up to the filter were rinsed with water and acetone. The water and acetone wash were placed in separate sample bottles. The sample bottles were labeled with the date, test run number and bottle contents.

(D) Analysis

When the samples were received at the laboratory, the acetone and water wash solutions were evaporated in preweighed beakers and weighed to determine the weight of particulates collected. The filter was placed in a dessicator for 24 hours and weighed to determine the amount of particulates collected. The weights of particulates collected were used to determine grain loading and mass emission rate. The filters and impinger solutions were stored in sealed brown glass bottles for further anaylsis.

3.2 FUEL ANALYSIS

Fuel samples of both shale and low sulfur oils were taken from sample taps located on the burner deck during the testing with both types of burners. The samples obtained were subsequently sent for lab analysis to determine fuel chemical composition (ultimate analysis), API gravity and heating value. The results of

Table 1
FUEL PROPERTIES

FUEL PROPERTIES	LOW SULFUR OIL FIRST SAMPLE	LOW SULFUR OIL SECOND SAMPLE	LOW SULFUR OIL AVERAGE	SHALE OIL FIRST SAMPLE	SHALE OIL SECOND SAMPLE	SHALE OIL AVERAGE	STATION FUEL LOW SULFUR	NATURAL GAS*
C	86.10	86.65	86.38	83.44	84.65	84.05	87.07	74.3
H	12.53	12.44	12.49	11.49	11.47	11.48	12.22	23.06
N	0.25	0.19	0.22	1.90	2.06	1.98	0.19	2.1
S	0.28	0.26	0.27	0.64	0.70	0.67	0.43	0
ASH	.007	.010	.009	0.025	0.018	.022	.015	0
O2	0.83	0.45	0.64	2.51	1.10	1.81	.06	0
API @ 60°F	22.4	26.8	24.6	20.4	20.2	20.3	23.3	--
Heating Value								
HHV	19,210	19,260	19,235	18,050	18,340	18,195	19,100	--
LHV	18,070	18,130	18,100	17,000	17,290	17,145	17,980	

*Obtained from Southern California Gas Company these lab analyses are presented in Table 1. The chemical composition of fuel blends burned during the various test runs was proportionately calculated using the fuel blend ratio and the ultimate analysis of the two fuels.

During the testing conducted using natural gas in top row burners, regular station low sulfur fuel was blended with shale oil and introduced to the bottom row of burners. The average sulfur content of the fuel burned in the boiler during these tests did not exceed 0.5% since natural gas contained no sulfur. To determine the composition of fuel blends burned during the tests, a sample of station fuel was also obtained and analyzed for composition. The chemical composition of natural gas was obtained from the Southern California Gas Company. The composition of fuel blends during these tests was proportioned based on the heat input for oil and gas during the tests. The calculated fuel properties for the various test runs are presented in Table 2.

3.3 COMBUSTION CALCULATIONS

Combustion calculations were performed to identify the effect of burner Air/Fuel ratio and organically bound fuel nitrogen on overall NOx emission level from the boiler. In examining the impact of fuel nitrogen on the emission level, the contribution of the individual burners to the total NOx emission was evaluated. The combustion and emission data and the results of the performed calculations are summarized in Tables 3, 4, 5 and 6. Method used and assumption made to perform the combustion calculations are described below and details of the performed calculations are provided in Appendix 1.

3.3.1 Combustion Air Volume

The fuel chemical composition and the measured concentration of CO2 in the flue gases were used in calculating combustion air volume. The combustion calculations were based on CO2 concentration rather than O2 since the CO2 concentration in flue gas is higher and therefore measurement errors are generally lower. The CO2 concentration was also selected since it is not directly affected by the leakage of atmospheric air into the exhaust ducting upstream from the sampling probe. The concentration of excess O2 in the flue gas was calculated and compared with experimentally measured concentrations. It was noted (Table 3) that the deviation between measured and calculated

Table 2

CALCULATED FUEL ULTIMATE ANALYSIS FOR VARIOUS TEST RUNS

TEST	DATE	FUEL ULTIMATE ANALYSES			
NO.	1976	C	H_2	O_2	N_2
1	12/2	86.38	12.49	0.64	0.22
2		86.38	12.49	0.64	0.22
3		86.12	12.38	0.77	0.41
4		85.91	12.29	0.88	0.57
5		85.65	12.18	1.01	0.77
6		85.45	12.10	1.11	0.92
7		85.21	12.00	1.23	1.10
8	12/3	86.38	12.49	0.64	0.22
9		86.12	12.38	0.77	0.41
10		85.98	12.32	0.84	0.52
11		85.77	12.23	0.95	0.68
12		85.47	12.10	1.10	0.91
13		85.23	12.00	1.22	1.09
14		84.83	11.82	1.42	1.39
15		86.38	12.49	0.64	0.22
16	12/4	86.38	12.49	0.64	0.22
17		86.14	12.39	0.76	0.40
18		85.86	12.27	0.90	0.62
19		85.68	12.19	1.00	0.75
20		85.39	12.07	1.14	0.96
21		85.18	12.00	1.24	1.12
22	12/4	86.38	12.49	0.64	0.22
23		85.98	12.32	0.84	0.52
24		86.67	12.19	1.00	0.76
25		85.28	12.01	1.20	1.05
26		84.99	11.89	1.34	1.27
27	12/20	86.38	12.49	0.64	0.22
28		86.12	12.38	0.77	0.42
29		85.92	12.29	0.87	0.56
30		85.65	12.18	1.00	0.77
31		85.46	12.10	1.10	0.91
32		85.19	12.00	1.24	1.12
33		86.38	12.49	0.64	0.22
34	12/22	86.38	12.49	0.64	0.22
35		86.10	12.37	0.78	0.43
36		85.91	12.29	0.88	0.58
37		85.64	12.18	1.00	0.78
38		85.36	12.06	1.15	0.99
39		85.47	11.96	1.25	1.14
40		85.25	11.83	1.40	1.37
41	12/22	83.14	15.47	0.47	0.72
42		82.70	15.37	0.65	1.02
43		82.38	15.22	0.82	1.26
44		82.10	15.14	0.94	1.46
45		81.35	14.84	1.31	2.01

Table 3

RESULTS OF COMBUSTION CALCULATIONS

TEST NO.	DATE 1976	COMBUSTION AIR MASS lb/lb OF FUEL	CALCULATED O_2 CONCENTRATION (PERCENT)	MEASURED O_2 CONCENTRATION (PERCENT)	PERCENT DEVIATION (±) OF EXPERIMENTAL AND THEORETICAL DATA
1	12/2	18.06	4.3	4.4	1.6
2		18.15	4.4	4.4	0.0
3		17.95	4.3	4.4	1.0
4		17.90	4.3	4.4	1.0
5		17.84	4.3	4.4	1.0
6		17.92	4.4	4.4	0.0
7		17.74	4.4	4.5	1.0
8	12/3	19.56	5.5	5.3	1.9
9		18.82	5.0	5.4	3.9
10		18.34	4.7	5.0	3.1
11		18.58	4.9	5.3	3.9
12		18.36	4.8	5.4	5.9
13		18.30	4.9	5.3	3.9
14		18.35	5.1	5.3	1.9
15		18.73	4.9	5.4	4.9
16	12/4	17.47	3.7	3.9	2.6
17		17.79	4.1	4.0	1.2
18		17.49	3.9	3.9	0
19		17.30	3.8	4.0	2.6
20		17.12	3.7	4.0	3.9
21		17.08	3.8	4.1	3.8
22	12/4	18.88	5.0	5.3	2.9
23		18.93	5.2	5.3	1.0
24		19.07	5.2	5.4	1.9
25		18.61	5.1	5.5	3.8
26		18.54	5.2	5.4	1.9
27	12/20	17.47	3.4	3.3	1.5
28		17.42	3.5	3.4	1.5
29		16.99	3.4	3.5	1.5
30		16.93	3.5	3.5	0
31		17.14	3.7	3.7	0
32		17.08	3.8	3.7	1.3
33		17.10	3.4	3.5	1.5
34	12/22	19.19	5.2	5.4	1.9
35		19.94	5.9	5.8	0.9
36		19.07	5.6	5.8	1.6
37		19.01	5.3	5.4	0.9
38		19.10	5.5	5.5	0
39		19.10	5.5	5.4	0.9
40		18.81	5.4	5.4	0
41	12/22	19.19	4.5	4.9	4.3
42		19.25	4.6	5.1	5.2
43		19.49	4.9	5.3	3.9
44		19.59	5.1	5.4	2.9
45		19.57	5.3	5.6	2.8

Table 4

COMBUSTION DATA

TEST NO.	DATE 1976	BOILER LOAD MW	SHALE OIL BLEND PERCENT OF TOTAL	FUEL TYPE BY BURNER ROW	
				TOP	BOTTOM
1	12/2	42.2	0	L.S.*	L.S.
2		42.8	0	L.S.	L.S.
3		42.8	11.0	L.S.	Blend
4		42.5	20.1	L.S.	Blend
5		42.3	31.2	L.S.	Blend
6		42.3	39.8	L.S.	Blend
7		42.2	50.1	L.S.	Shale
8	12/3	41.0	0	L.S.	L.S.
9		41.8	11.0	L.S.	Blend
10		41.8	17.1	L.S.	Blend
11		41.8	26.3	L.S.	Blend
12		41.8	39	L.S.	Blend
13		41.9	49.2	L.S.	Blend
14		41.9	66.7	L.S.	Shale
15		42.1	0	L.S.	L.S.
16	12/4	42.0	0	L.S.	L.S.
17		42.0	10.3	Blend	Blend
18		42.2	22.5	Blend	Blend
19		42.2	30.1	Blend	Blend
20		42.2	42.3	Blend	Blend
21		42.2	51.4	Blend	Blend
22	12/4	42.0	0	L.S.	L.S.
23		42.0	17.0	Blend	Blend
24		42.0	30.5	Blend	Blend
25		42.0	47.3	Blend	Blend
26		42.0	59.6	Blend	Blend
27	12/20	42.7	0	L.S.	L.S.
28		42.9	11.3	L.S.	Blend
29		43.0	19.6	L.S.	Blend
30		43.1	31.2	L.S.	Blend
31		43.4	39.4	L.S.	Blend
32		43.4	51.2	L.S.	Shale
33		43.0	0	L.S.	L.S.
34	12/22	43.3	0	L.S.	L.S.
35		43.0	11.9	L.S.	Blend
36		42.9	20.4	L.S.	Blend
37		43.0	31.6	L.S.	Blend
38		43.0	43.8	L.S.	Blend
39		43.2	52.1	L.S.	Blend
40		43.0	65.3	L.S.	Shale
41	12/22	43.4	0	N.G.**	L.S.
42		43.4	15.3	N.G.	Blend
43		43.2	29.4	N.G.	Blend
44		42.8	39.6	N.G.	Blend
45		42.0	71.8	N.G.	Blend

*Low Sulfur Oil

**Natural Gas

Table 4 (Continued)

SHALE OIL BLENDING METHOD	TYPE OF BURNER	FIRING MODE	AIR TO FUEL RATIO BY ROW		TEST NO.
			TOP	BOTTOM	
Bottom Row of Burners Only	LNB	Normal	17.9	18.3	1
			17.94	18.37	2
			17.79	18.12	3
			18.81	17.73	4
			17.86	17.86	5
			17.98	17.89	6
			18.0	17.5	7
Bottom Row of Burners Only	LNB	O/S	19.55	14.7	8
			18.75	14.12	9
			18.24	13.8	10
			18.55	13.95	11
			18.56	13.69	12
			18.59	13.61	13
			18.75	13.62	14
			18.7	14.1	15
Tank Blending	LNB	Normal	17.5		16
			17.81		17
			17.51		18
			17.31		19
			17.12		20
			17.06		21
Tank Blending	LNB	O/S	15.72		22
			15.8		23
			15.9		24
			15.5		25
			15.4		26
Bottom Row of Burners Only	Peabody	Normal	17.5	17.5	27
			17.7	17.2	28
			17.26	16.74	29
			17.33	16.55	30
			17.72	16.59	31
			17.76	16.45	32
			17.11	17.11	33
Bottom Row of Burners Only	Peabody	O/S	18.2	14.76	34
			19.0	15.33	35
			18.32	14.6	36
			18.22	14.57	37
			18.40	14.6	38
			18.61	14.52	39
			18.37	14.28	40
Bottom Row of Burners Only	Peabody	O/S			41
					42
					43
					44
					45

Table 5

EMISSION DATA

			STACK EMISSIONS		
TEST NO.	DATE 1976	SHALE OIL BLENDED PERCENT OF TOTAL	NOx CORRECTED TO 3% O_2	CO_2	O_2
1	12/2	0	212	12.4	4.4
2		0	219	12.3	4.4
3		11	273	12.4	4.4
4		20.1	296	12.4	4.4
5		31.2	307	12.4	4.4
6		39.8	319	12.4	4.4
7		50.1	323	12.4	4.5
8	12/3	0	175	11.4	5.3
9		11	215	11.8	5.4
10		17.1	224	12.1	5.0
11		26.3	238	11.9	5.3
12		39	262	12.0	5.4
13		49.2	271	12.0	5.3
14		66.7	299	11.9	5.3
15		0	184	11.9	5.4
16	12/4	0	201	12.8	3.9
17		10.3	265	12.5	4.0
18		22.5	300	12.7	3.9
19		30.1	351	12.8	4.0
20		42.3	398	12.9	4.0
21		51.4	426	12.9	4.1
22	12/4	0	189	11.8	5.3
23		17.0	262	11.7	5.3
24		30.5	318	11.7	5.4
25		47.3	366	11.8	5.5
26		59.6	398	11.8	5.4
27	12/20	0	248	12.8	3.3
28		11.3	331	12.8	3.4
29		19.6	389	13.1	3.5
30		31.2	432	13.1	3.5
31		39.4	471	12.9	3.7
32		51.2	522	12.9	3.7
33		0	254	13.1	3.5
34	12/22	0	179	11.6	5.4
35		11.9	226	11.1	5.8
36		20.4	250	11.6	5.8
37		31.6	268	11.6	5.4
38		43.8	282	11.5	5.5
39		52.1	292	11.5	5.4
40		65.3	306	11.6	5.4
41	12/22	0	134	11.3	4.9
42		15.3	164	11.2	5.1
43		29.4	187	11.0	5.3
44		39.6	203	10.9	5.4
45		71.8	239	10.8	5.6

Table 6

INDIVIDUAL BURNERS CONTRIBUTION TO NOx EMISSION LEVEL, AND FUEL NITROGEN CONVERSION EFFICIENCY TO NOx

TEST NO.	BURNERS CONTRIBUTION PER BURNER BY ROW, (ppm)		INCREASE IN NOx EMISSION DUE TO SHALE OIL BLENDING NOx (ppm)		COMBUSTION MODE
	TOP	BOTTOM	TOP	BOTTOM	
1	212	212	0	0	Normal Bottom Row Blending
2	219	219	0	0	
3	212	334	0	122	
4	212	380	0	168	
5	212	402	0	190	
6	212	426	0	214	
7	212	434	0	222	
8	233	195	0	0	O/S Bottom Row Blending
9	233	275	0	80	
10	233	293	0	98	
11	233	321	0	126	
12	233	369	0	174	
13	233	387	0	192	
14	233	443	0	248	
15	233	213	0	0	
16	201	201	0	0	Normal Tank Blending
17	265	265	64	64	
18	300	300	99	99	
19	351	351	150	150	
20	398	398	197	197	
21	426	426	225	225	
22	240	218	0	0	O/S Tank Blending
23	333	302	93	84	
24	404	367	164	149	
25	464	422	224	204	
26	505	459	264	241	
27	248	248	0	0	Normal Bottom Row Blending
28	248	414	0	166	
29	248	530	0	282	
30	248	616	0	368	
31	248	694	0	446	
32	248	796	0	548	
33	254	254	0	0	
34	273	176	0	0	O/S Bottom Row Blending
35	273	271	0	94	
36	273	319	0	141	
37	273	355	0	178	
38	273	383	0	206	
39	273	403	0	225	
40	273	431	0	254	

Table 6 (Continued)

TYPE OF BURNER	FUEL NITROGEN CONTENT PERCENT BY WEIGHT		NITROGEN CONVERSION EFFICIENCY BY ROW		TEST NO.
	TOP	BOTTOM	TOP	BOTTOM	
LNB*	0.22	0.22	---	---	1
	0.22	0.22	---	---	2
	0.22	0.61	---	25.3	3
	0.22	0.92	---	19.3	4
	0.22	1.32	---	13.9	5
	0.22	1.64	---	12.2	6
	0.22	1.98	---	10.2	7
LNB	0.22	0.22	---	---	8
	0.22	0.51	---	22.4	9
	0.22	0.67	---	17.4	10
	0.22	0.92	---	14.6	11
	0.22	1.25	---	13.7	12
	0.22	1.43	---	11.9	13
	0.22	1.98	---	11.4	14
	0.22	0.22	---	---	15
LNB	0.22	0.22	---	---	16
	0.40	0.40	28.8	28.8	17
	0.62	0.62	20.1	20.1	18
	0.75	0.75	22.9	22.9	19
	0.96	0.96	21.6	21.6	20
	1.12	1.12	20.3	20.3	21
LNB	0.22	0.22	---	---	22
	0.52	0.52	25.1	22.7	23
	0.76	0.76	24.6	22.4	24
	1.05	1.05	21.9	19.9	25
	1.25	1.25	20.8	20.0	26
Peabody	0.22	0.22	---	---	27
	0.22	0.61	---	34.2	28
	0.22	0.80	---	33.5	29
	0.22	1.32	---	27.5	30
	0.22	1.58	---	26.6	31
	0.22	1.98	---	25.2	32
	0.22	0.22	---	---	33
Peabody	0.22	0.22	---	---	34
	0.22	0.54	---	23.6	35
	0.22	0.92	---	16.5	36
	0.22	1.08	---	16.7	37
	0.22	1.41	---	14.1	38
	0.22	1.62	---	13.02	39
	0.22	1.98	---	11.7	40

*Low NOx Burner

oxygen concentrations was generally less than ± 3 percent over an excess oxygen content ranging from 3.4 to 5.6 percent. This agreement validates the degree of accuracy of the combustion calculations.

In determining the Air/Fuel ratio of the individual burners, it was assumed that the calculated combustion air volume was evenly distributed through all six air registers. The Air/Fuel ratio at each burner was obtained by dividing the mass of air flow through the register by the mass of fuel burned in the respective burners. In view of the fact that boiler parameters, such as wind box configuration, thermal convection and pressure gradients, generally prevent such uniform distribution of air, it is suspected that the calculated burner Air/Fuel ratios may not be exact. The difference between the actual and calculated Air/Fuel ratios at the various burners is not expected to be significant and should not affect the interpretation of test data.

3.3.2 Fuel Nitrogen Conversion to NOx

The increase in NOx emission levels that was noted due to the blending of shale oil with the low sulfur oil was caused by the increase in the nitrogen content of the fuel burned. This was due to the fact that variables influencing thermal NOx formation at the burners were maintained unchanged during the measurement of NOx emissions as shale oil blending ratio was varied.

To determine the conversion efficiency of fuel nitrogen into NOx, the overall increase in NOx emission from the boiler was allocated between rows of burners. The incremental increase in NOx emission, which can be attributed to fuel nitrogen conversion, was determined by subtracting the NOx levels obtained using the low sulfur oil from the higher NOx levels obtained with shale oil blending under the same combustion stoichiometries. The actual nitrogen conversion efficiency was then calculated using the proportionality relationship:

$$\begin{array}{l}\text{PERCENT FUEL}\\ \text{NITROGEN CONVERSION TO NOx}\end{array} = \frac{\begin{array}{c}\text{NOx attributed to fuel Nitrogen}\\ \text{ppm at 3\% }O_2\end{array}}{\begin{array}{l}\text{1235 ppm* x the increase of Nitrogen}\\ \text{content of the blended fuel, percent}\end{array}}$$

A detailed description and procedures to perform these calculations are presented in Appendix 1 and the results are summarized in Table 6.

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*1235 ppm is the NOx concentration in the Flue gases when 1.0% of fuel nitrogen is completely converted into NOx, corrected to 3% excess O_2.

Section 4.0

RESULTS AND DISCUSSION

The emission of NOx, particulate, PNA and trace elements were evaluated during the test program. Parameters that affected the emission of the various air contaminants were found to be as follows:

4.1 NOx EMISSION

NOx emission tests were intially performed during the program using the developmental Low NOx Burner (LNB). Different firing configurations and shale oil blending techniques were tested during this early phase to identify the optimum operating conditions that may achieve maximum NOx reduction. Both the dual fuel combustion system and off-stoichiometric firing mode were found to be the most effective techniques in controlling NOx formation. Fuel piping arrangement at the time of conducting these tests did not permit, however, the evaluation of the dual fuel combustion system using a wide range of shale oil blend ratios and therefore testing was temporarily interrupted until required piping modifications were installed. Data obtained during this preliminary phase of testing were summarized in Appendix 2.

Upon completing the necessary piping modifications, testing was continued to evaluate the NOx emission levels obtained with the LNB and a conventional Peabody burner when burning shale oil of various blend ratios. The test program had the primary objective of determining the maximum shale oil blend ratio that can be burned in a utiity boiler while maintaining NOx emission levels below the 225 ppm (corrected to 3% O2) limit allowed by local regulatory agencies. Most of the testing was conducted using the dual fuel combustion system in order to identify the maximum possible shale oil blend ratio that can be used in each type of burner without exceeding NOx limitations. To illustrate the effectiveness of the dual combustion in controlling emissions, additional testing was conducted with the LNB using tank blending and emission levels obtained with the two blending techniques were compared. NOx emission levels from the two burners were evaluated under both normal and off-stoichiometric modes of combustion. Factors that most significantly influenced NOx emission when burning shale oil were identified during the program to be as follows:

4.1.1 Combustion Mode

NOx emission levels under normal and off-stoichiometric modes of combustion were evaulated for the LNB and the conventional Peabody burner when burning shale oil of different blend ratios. Testing was only performed using the dual fuel combustion system in order to identify the maximum shale oil ratio that can be achieved with each type of burner without exceeding local NOx regulations. Shale oil blending, using the dual fuel system, was restricted as described earlier to the lower row of burners only and therefore a 10% overall shale oil blend ratio represented an actual lower row of burners blend ratio of 20% in the case of normal firing and approximately 14% in the case of off-stoichiometric firing. The off-stoichiometric mode of combustion was obtained by placing the middle burner in the upper row out of service and distributing fuel between burner elevations to have approximately 70% of the total fuel introduced to the lower row of burners and only 30% to the upper row. Maintaining uniform combustion air distribution to all burner locations caused the lower row of burners to operate at rich fuel stoichiometry (Air/Fuel ratio 14:1) and the upper burners to operate at normal or slightly lean stoichiometry (Air/Fuel ratio 18:1). In the case of normal combustion, both fuel and combustion air were evenly distributed to all burner locations to maintain a uniform Air/Fuel ratio within the boiler furnace.

NOx emission levels as a function of shale oil blend ratio under both modes of combustion for the LNB and the Peabody burner were compared in Figures 6 and 7 respectively. As to be expected, a reduction in NOx emission levels was obtained with both types of burners using the off-stoichiometric mode of combustion. Maintaining combustion stoichiometry fuel rich at the location where high nitrogen fuel was introduced was believed to be the most direct cause for the noted reduction. The relative reduction in emission levels between normal and off-stoichiometric firing varied noticeably with the type of burner, however, with a higher percent reduction occurring with the Peabody burner.

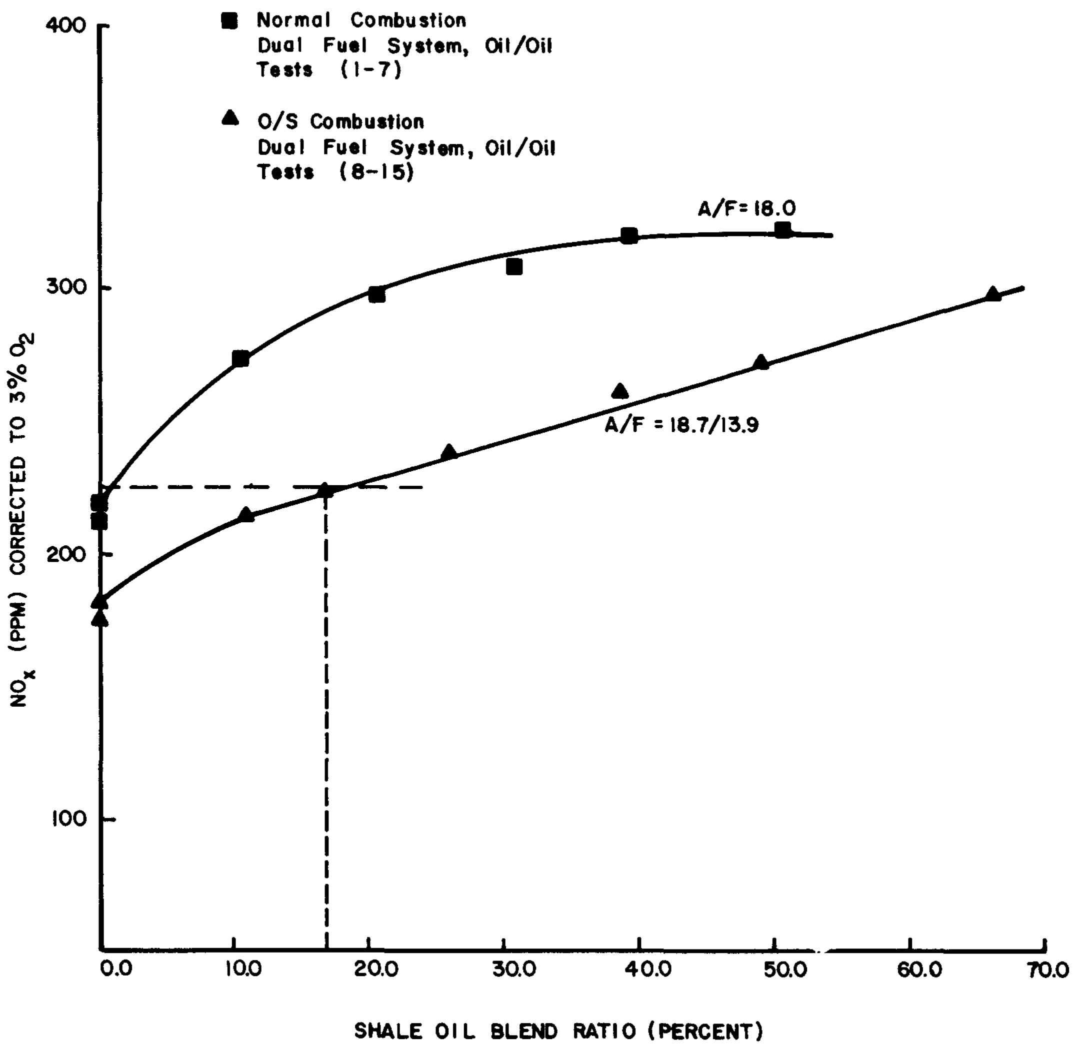

Figure 6. NOx Emission from the LNB

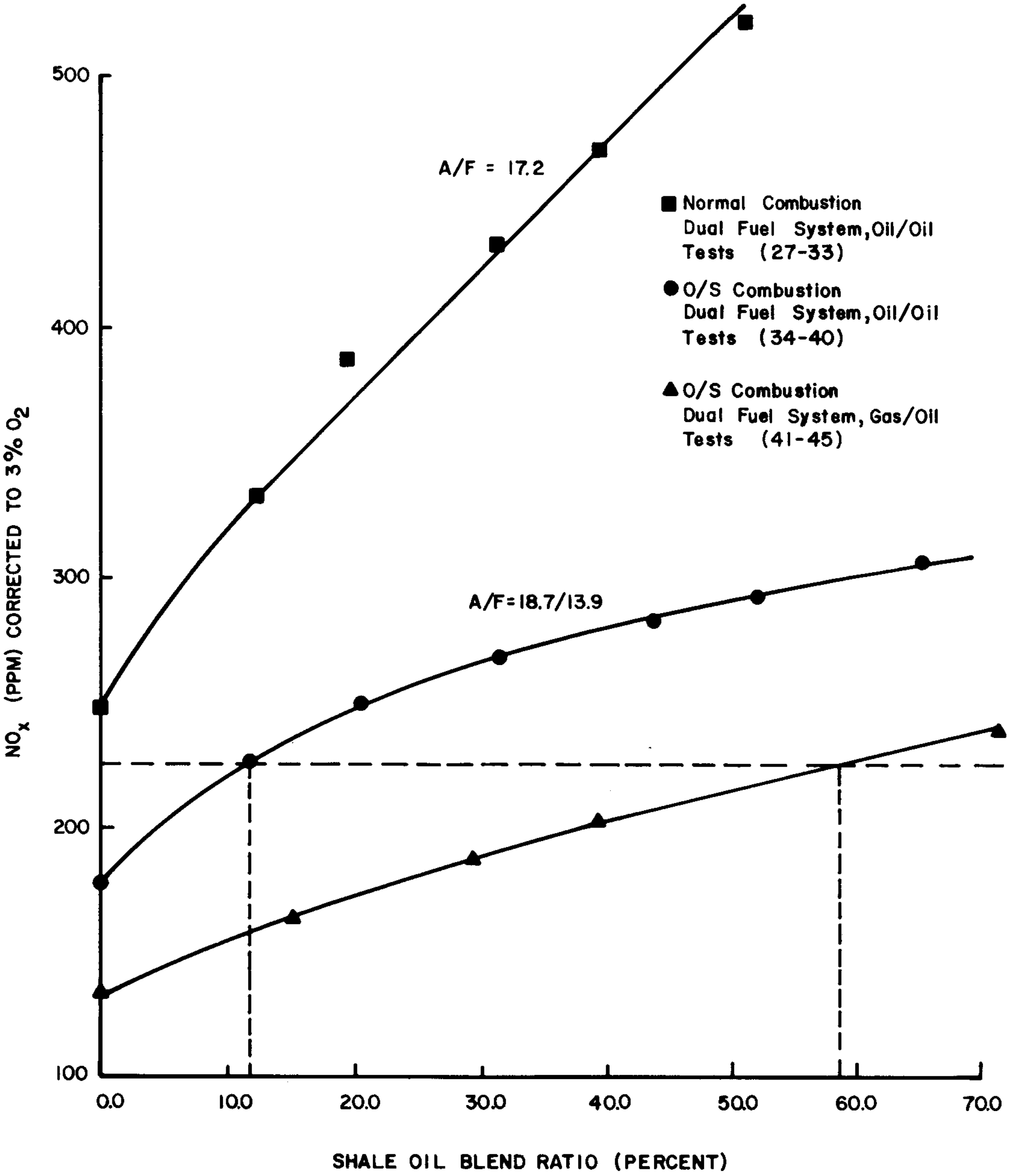

Figure 7. NOx Emission from the Peabody Burner

In order to accurately define the effect of burner stoichiometry on NOx emission level, NOx formation within the lower burners elevation during both normal and off-stoichiometric firing was calculated. The burners' emission was determined at different shale oil blend ratios and presented as a function of fuel nitrogen content in Figure 8. It was found that, although the Peabody burner under the normal mode of combustion contributes substantially higher NOx emission level than the LNB, it achieved a slightly lower emission level than the LNB when operated at rich fuel stoichiometry. The achieved reduction in emission was attributed to the Peabody burner fuel spray pattern which enhanced fuel vaporization within the core of the burner flame when operated under fuel rich stoichiometry. The formed fuel vapor within the flame core was burned in a reducing atmosphere with minimum NOx formation. The result indicated that the effect of burner stoichiometry on NOx formation is strongly dependent upon burner design parameters.

4.1.2 Type of Burners

NOx emission levels from the LNB and the Peabody burners were compared at different shale oil blend ratios when operated under both normal and off-stoichiometric modes of combustion. The LNB under normal combustion was found as shown in Figure 9 to achieve a significantly lower NOx emission level than the Peabody burner. The difference in emission level achieved by the two burners progressively increased as the nitrogen content of the fuel increased which indicated that the incremental increase in emission level is due to fuel nitrogen conversion into NOx. The capability of the LNB burner to control fuel nitrogen conversion was attributed to the burner's variable fuel stoichiometry along its flame front. The relatively fuel rich combustion achieved by the LNB in the post flame zone appeared to help nitrogen containing radicals within the flame zone to recombine forming a more stable chemical species rather than being oxidized to form NOx. The spray pattern developed by the Peabody burner, on the other hand, enhanced under normal mode of combustion fuel mixing with combustion air and provided virtually no control over local fuel stoichiometry within the flame.

In the case of off-stoichiometric firing, it was found, as shown in Figure 10, that differences in emission levels achieved by the two burners was rather small. The data showed that, under fuel rich stoichiometry, the Peabody burner is by far much less sensitive to the fuel nitrogen content.

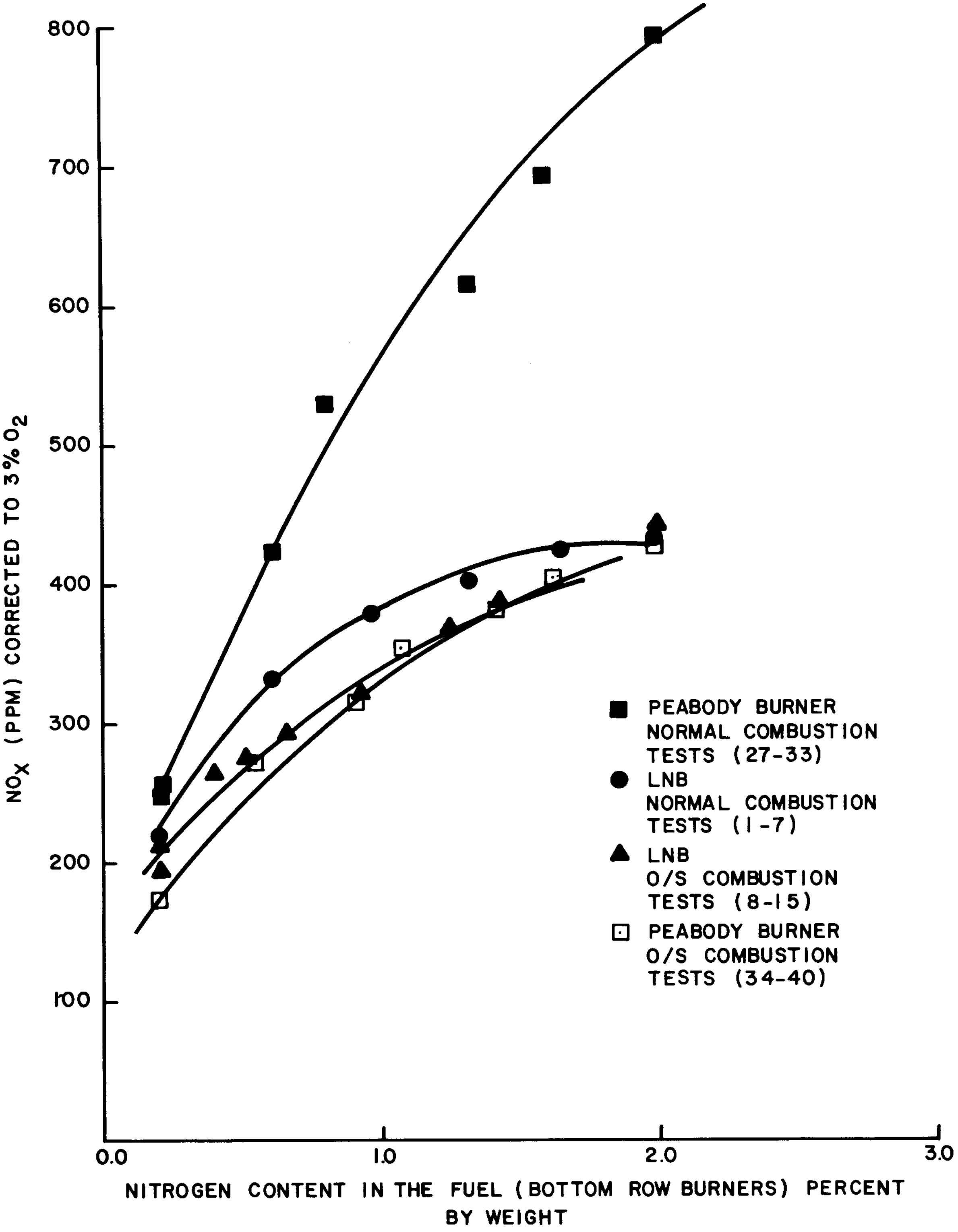

Figure 8. Bottom Burners Contribution to NOx Emission Level Using Dual Fuel System

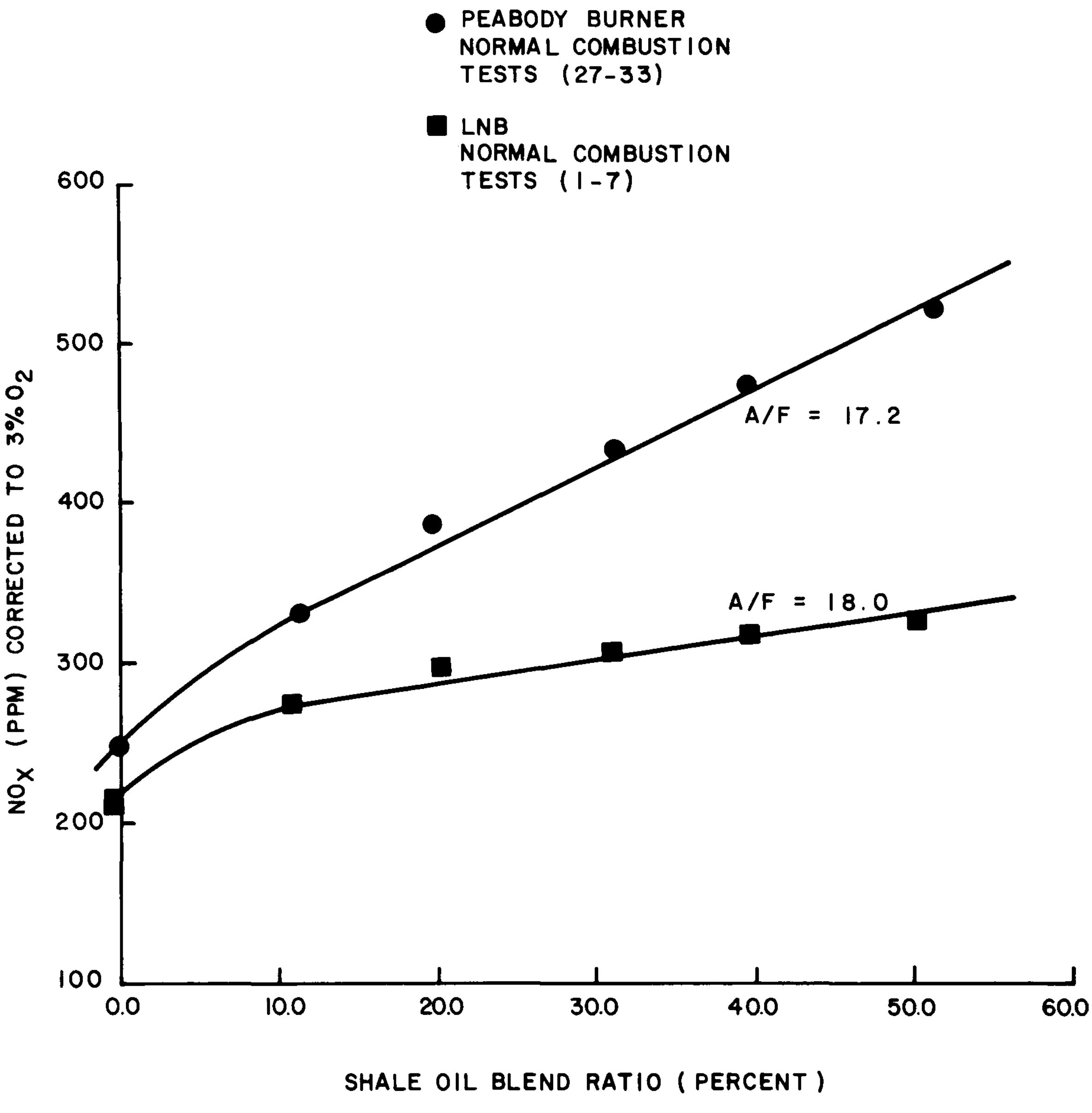

Figure 9. NOx Emission from LNB and Peabody Burner Under Normal Combustion, Using Dual Fuel System

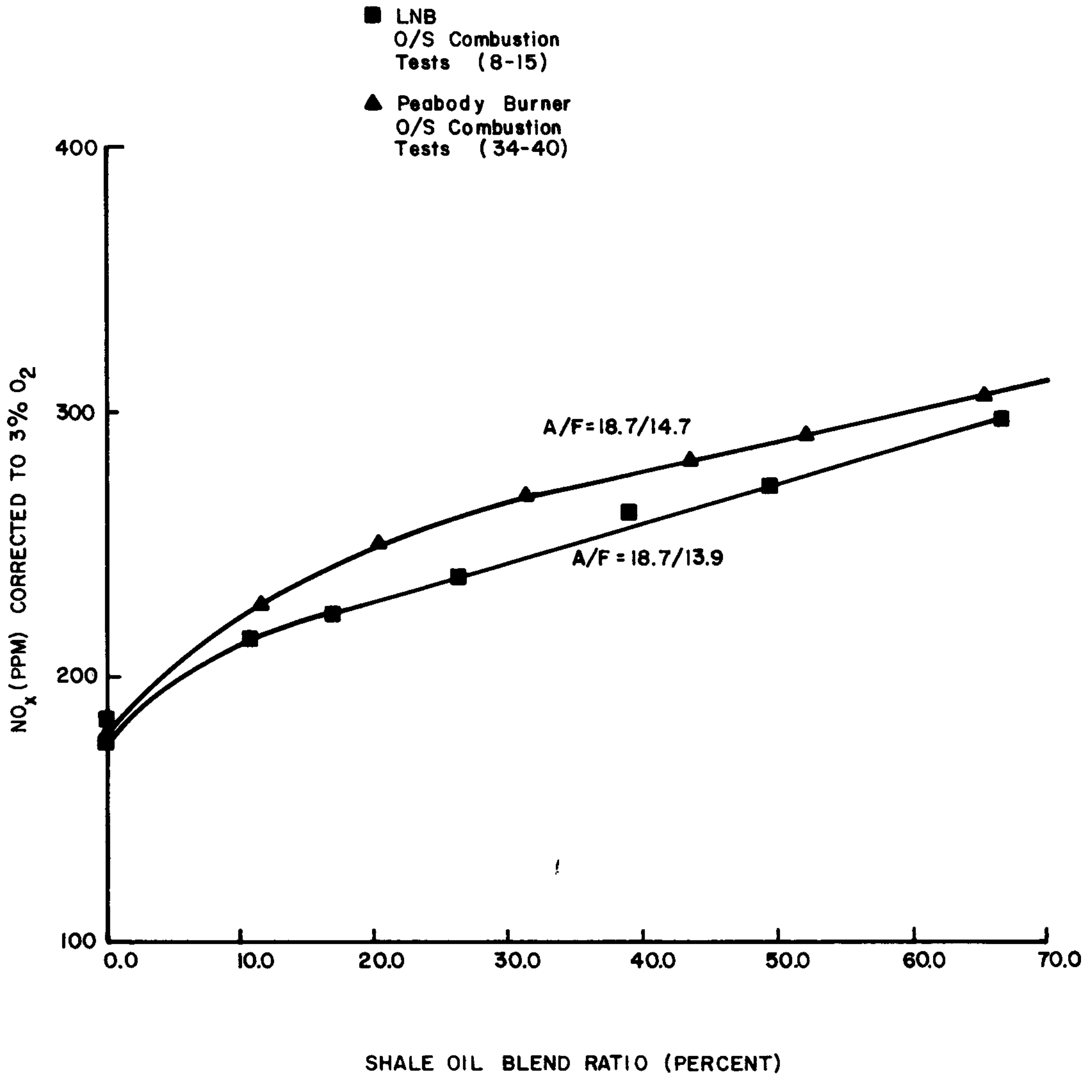

Figure 10. NOx Emission from LNB and Peabody Burner, Under Off-Stoichiometric Combustion Using Dual Fuel System

The total NOx emission from the two types of burners were comparable since the reduction in emission achieved by operating the Peabody burner fuel rich at the lower burners elevation was offset by the high emission generated by burners in the upper elevation due to its operation at normal or slightly lean stoichiometry. It appeared, from the results, that the lowest overall NOx emission levels would be achieved when dual fuel combustion was implemented using Peabody burners in the bottom row and LNB in the top row.

By operating the LNB under off-stoichiometric combustion, it was possible to burn as much as 17% crude shale oil in the boiler at full load without exceeding the local NOx emission regulations of 225 ppm (corrected to 3% O2). The corresponding maximum shale oil blend ratio achieved by the Peabody burners was limited to 12%. A maximum shale oil blend ratio of 58% was obtained at the same NOx levels when shale oil blends were burned fuel rich in the bottom row of Peabody burners followed by the combustion of natural gas in the upper burners elevation.

4.1.3 Fuel Nitrogen Content

As to be expected, NOx emission level increased with the increase in the nitrogen content of the fuel. To quantitatively evaluate the impact of fuel nitrogen on NOx formation, the conversion efficiency of fuel nitrogen into NOx was calculated and plotted as a function of fuel nitrogen content in Figure 11. The graph was developed based on test data obtained using the dual fuel combustion system where the variation in fuel nitrogen content was introduced to the bottom row of burners only. The increase in the lower burners' contribution to the total NOx emission level as a result of blending the shale oil was calculated as described in Section 3.3.2 and Appendix 1 and was correlated to the nitrogen content of fuel burned in those burners.

The data showed that the conversion efficiency of fuel nitrogen into NOx is inversely proportional to the nitrogen content of the fuel. High conversion efficiency occurred at low fuel nitrogen concentrations and low conversion efficiency occurred at high concentrations. The trends in nitrogen conversion efficiency were consistent for both types of burners. Changing burner stoichiometry from fuel lean to rich, however, substantially reduced nitrogen conversion, particularly in the case of the Peabody burner.

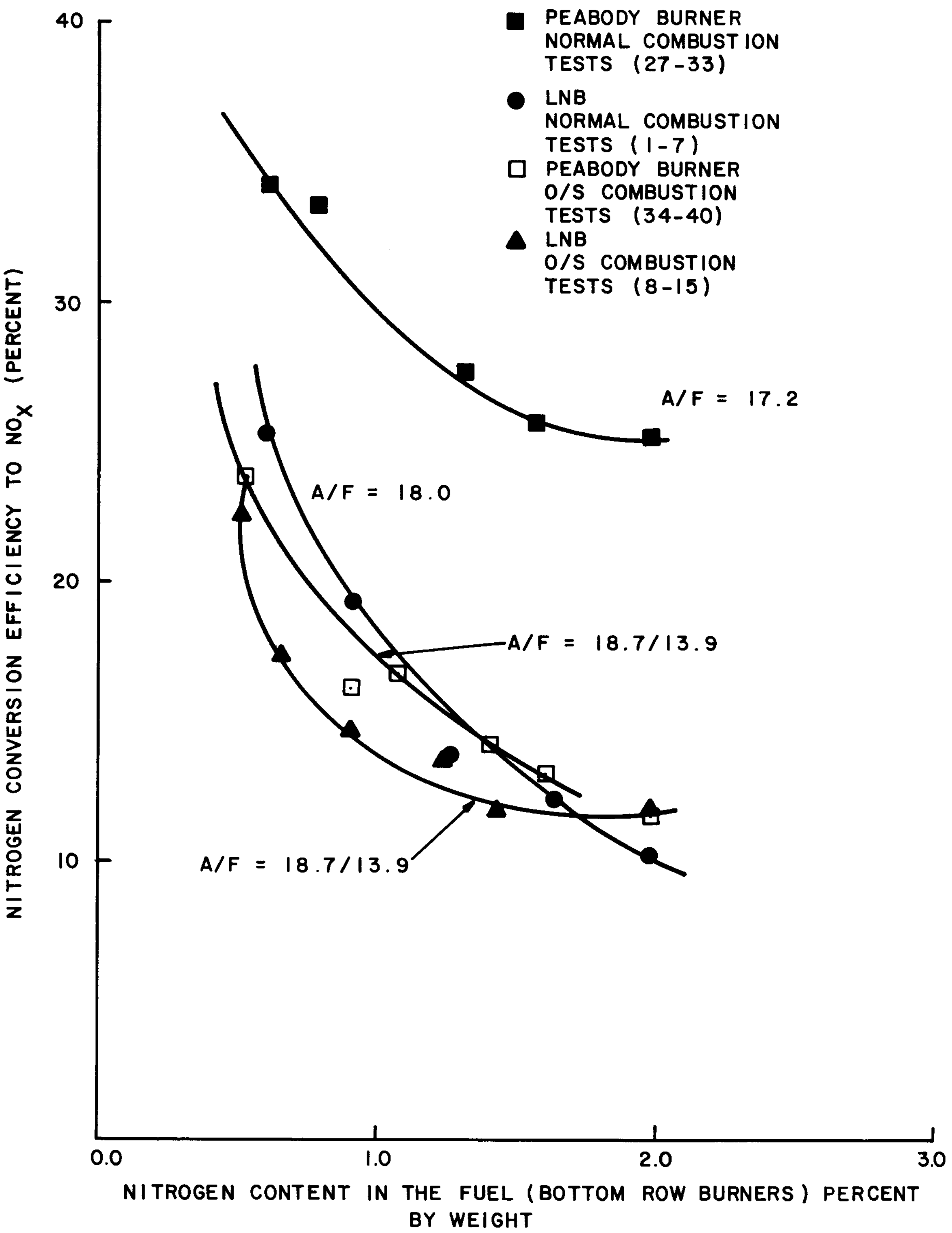

Figure 11. Fuel Nitrogen Conversion Efficiency as a Function of Nitrogen Content of the Fuel

The reduction in nitrogen conversion with fuel rich combustion was attributed primarily to the lack of oxygen within the burner's flame zone. It was postulated that nitrogen containing radicals in a reducing atmosphere are generally forced to recombine to form a more stable chemical species rather than being oxidized to NOx. The reduction in nitrogen conversion efficiency with the increase in fuel nitrogen content was not, however, readily explainable. It appeared that the phenomenon is caused by complex chemical kinetics within the flame, the details of which were felt to be beyond the scope of this study.

4.1.4 Shale Oil Blending Method

To illustrate the effect of the shale oil blending method on NOx emission, tests were conducted with the LNB where the blended shale was introduced to the bottom row of burners only in a dual fuel combustion system (Tests 1 thru 15). Additional testing was also conducted where shale oil was tank blended with low sulfur oil and the blended fuel was introduced to all six burners (Tests 16 thru 26). NOx emission levels using normal and off-stoichiometric combustion were determined for both the dual fuel combustion and tank blending systems and the emissions were compared in Figures 12 and 13.

The results indicated that the dual fuel combustion system is superior to conventional tank blending for controlling NOx emission. Under the normal mode of combustion (Figure 12), NOx emission level was reduced using the dual fuel combustion system from 420 ppm to 320 ppm. When the dual fuel combustion was combined with off-stoichiometric firing (Figure 13), the NOx reduction was improved to achieve an emission level of 260 ppm at the same shale oil blend ratio.

Examining Figure 12, it was noticeable, however, that in the region below a 12% shale oil blend ratio (a), NOx emission obtained using tank blending was lower than those obtained using a dual fuel system. The higher emission level was attributed to the fact that NOx emissions during the dual fuel combustion tests were determined for the high sale oil blend ratio first. Shale oil fuel residue left in the piping from previous testing, increased as a result, the nitrogen content of the fuel blend at the lower blend ratio and caused the noted increase in NOx emission.

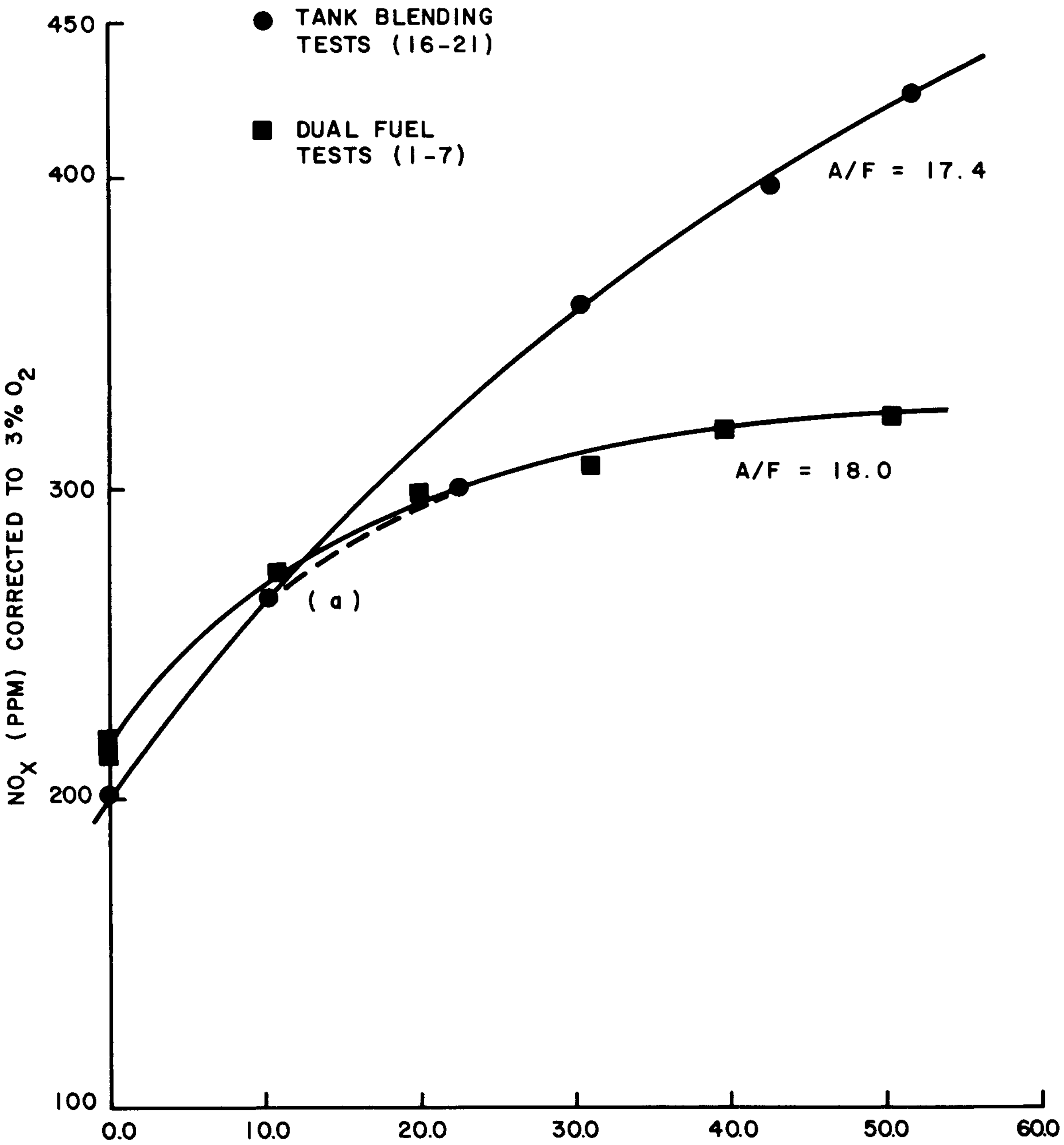

Figure 12. NOx Emission from LNB Under Normal Combustion, Using Tank Blending and Dual Fuel System

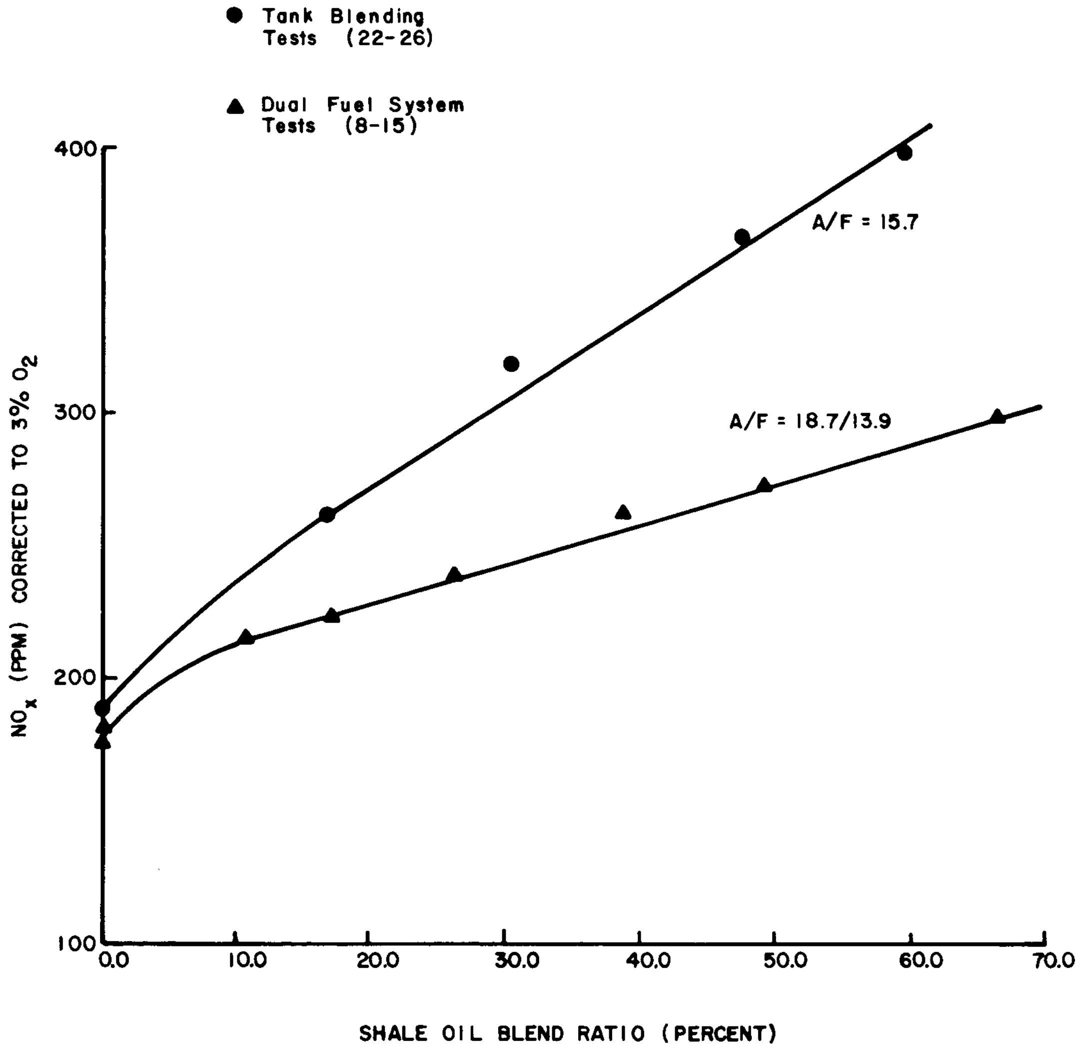

Figure 13. NOx Emission from LNB Under O/S Combustion, Using Tank Blending and Dual Fuel System

The improvement in NOx control achieved using the dual fuel combustion system was attributed to two factors. First, it has been established (Section 4.1.3) that the percent of fuel nitrogen conversion to NOx decreased as the fuel nitrogen content is increased. Therefore, concentrating the nitrogen in one location reduced the total nitrogen conversion to NOx compared with distributing the nitrogen throughout the burner system. (This assumes that the combustion conditions are the same at each burner.) In the case of off-stoichiometric firing, limiting the high nitrogen fuel to those burners operating at fuel rich conditions helped to further control fuel nitrogen conversion rate. Secondly, the level of excess oxygen is normally highest at the uppermost row of burners in a boiler. This is due to convective currents in the wind box and excess oxygen left from combustion at the lower burner levels rising through the furnace. Controlling the nitrogen content of fuel burned in the upper burners, where a high O2 environment exists, therefore further reduces NOx emission.

4.2 PARTICULATE EMISSIONS

Twenty-seven particulate tests were conducted during the program and the results are summarized in Table 7. Most of the particulate data was obtained using tank blending of low sulfur and crude shale oil. A large degree of scatter was experienced in the data and particulate emissions obtained in the morning was consistently higher (Figure 14) than that obtained in the afternoon of the same day. The change in oil temperature during the day was believed to have affected fuel viscosity and surface tension characteristics and resulted in the noted variations in emission level. Blending shale oil with low sulfur oil generally resulted, however, in a substantial increase (up to ten times) in particulate emission and the measured increase in emission level was far in excess of the increase in ash content of the fuel blends. A possible explanation to the abrupt increase in particulate emissions level, as a result of blending crude shale oil, is believed to be related to droplet burning characteristics. It was postulated that, as individual fuel droplets burn surrounded by its own diffusion flame, fuel cracking occurs in the liquid phase within the drop. The cracking process proceeds at a rate proportional to fuel boiling temperature producing initially heavy fuel residue. The formed residue in turn increases the overall boiling temperature of the fuel blends within the drop enhancing fuel cracking to proceed at a faster rate. Further fuel cracking finally produces carbonaceous and char-like particulates which are left after droplet combustion is completed. The

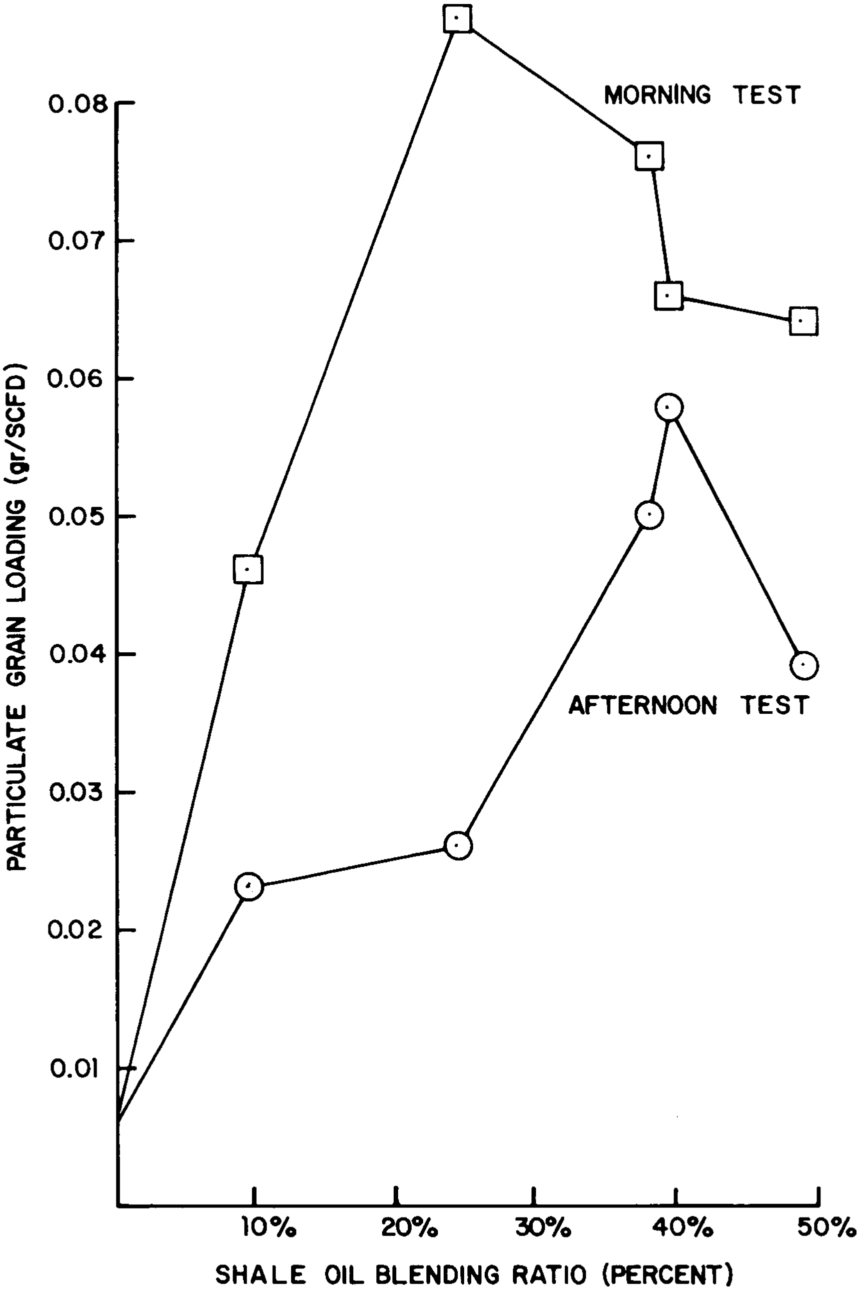

Figure 14. Variation in Particulate Emission as a Function of Time of Day

Table 7

PARTICULATE EMISSION DATA

PARTICULATE TEST NO.	DATE (1976)	GRAIN LOADING (Grains/SCFD)	MASS EMISSIONS RATE lbs/10^6 BTU	PERCENT SHALE OIL BLENDING	BLENDING METHOD
1	6/17	0.006	0.015	0.0	Tank
2	6/17	0.005	0.012	0.0	Tank
3	6/18	0.007	0.017	0.0	Tank
5	6/18	0.006	0.017	0.0	Tank
6	6/21	0.031	0.076	1.2	Tank
7	6/22	0.046	0.125	9.8	Tank
8	6/22	0.024	0.061	9.8	Tank
9	6/23	0.014	0.035	25.5	Tank
10	6/23	0.011	0.029	25.5	Tank
11	6/30	0.086	0.212	24.4	Tank
12	6/30	0.027	0.067	24.4	Tank
13	7/1	0.076	0.174	38.7	Tank
14	7/1	0.050	0.115	38.7	Tank
15	7/2	0.066	0.156	39.2	Tank
16	7/2	0.058	0.138	39.2	Tank
17	7/6	0.064	0.155	49.2	Tank
18	7/6	0.039	0.093	49.2	Tank
19	7/7	0.057	0.088	48.6	Tank
20	7/12	0.042	0.086	49.7	Dual Fuel
21	7/12	0.094	0.20	49.7	Dual Fuel
22	7/13	0.099	0.25	49.2	Dual Fuel
23	7/13	0.071	0.17	49.2	Dual Fuel
24	7/14	0.081	0.19	42.8	Dual Fuel
25	7/14	0.096	0.22	33.0	Dual Fuel
26	7/15	0.046	0.12	41.6	Dual Fuel
27	7/16	0.071	0.16	49.4	Dual Fuel

rate of particulate formation is therefore primarily dependent upon fuel evaporation characteristics and to a lesser degree, upon boiler and burner operating variables.

Comparing the evaporation characteristics of crude shale oil and low sulfur oils in Figure 15, it is evident that shale oil has a higher boiling temperature than low sulfur oil. Blending the two fuels, therefore, resulted in a high boiling point fuel blend that produced an increasingly larger proportion of particulate matter. It is also possible that fuel blending has influenced the atomization characteristics of the fuel, resulting in the formation of larger initial fuel droplets within the burner spray which could also increase the quantity of particulate matter formed. Regardless of how these various factors may have influenced particulate formation, it is clear that blending crude shale oil with light fuel distillate increased the level of particulate emissions.

Particulate size distribution analysis was conducted during the program by examining electron microscope photographs of collected particulates and calculating distribution by weight based on number count. Particulate matter was assumed to consist of spherical particles having a constant density. The weight fraction in each size range was calculated by multiplying the particulate number count by the volume of spherical particles of the given diameter, and using an assumed density of 2.2 grams/cm^3. In the case of particulate counts reported for a wide size range, an average particulate size was assumed and used in the calculation. The results, summarized in Table 8, indicated that 99+% of the particulate weight is contained in the size fraction above 10 microns.

4.3 PNA EMISSIONS

Several particulate samples were analyzed for polynuclear aromatic hydrocarbon (PNA) content. The lower limit of sensitivity for the PNA analysis was about 0.005 micrograms in the sample, generally corresponding to less than 0.05 parts per million of the total particulate solids collected on filter samples and probe wash samples. The results of the PNA analysis are presented in Table 9, where it is seen that the average PNA concentration corresponds to 6 parts per million by weight in a particulate sample corresponding to an emission level of 0.067 gr/SCFD. This would be equivalent to a PNA emissions level of 0.0000004 gr/SCFD, assuming that the PNA distribution on filter solids equals the PNA distribution on probe wash solids.

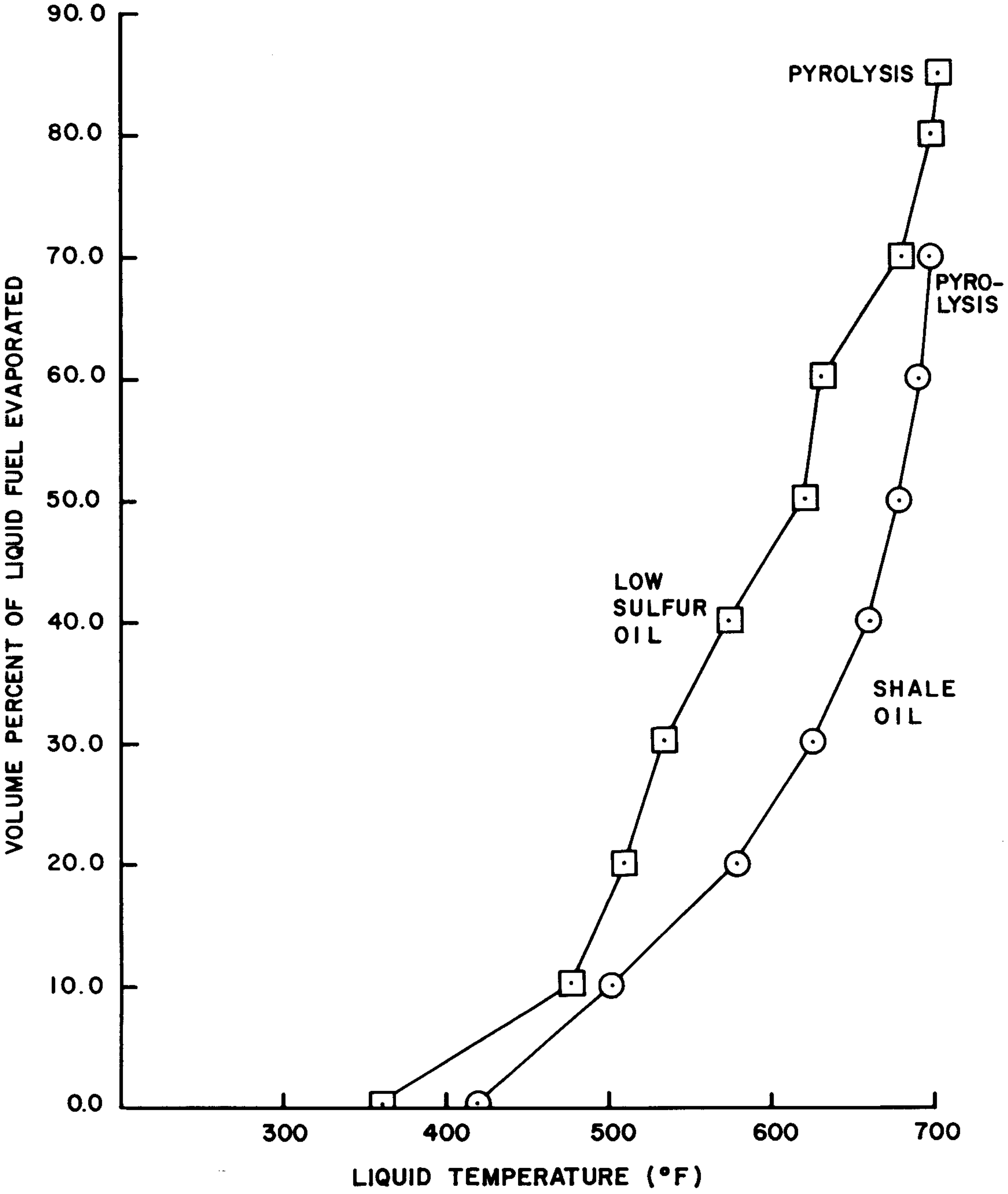

Figure 15. Evaporation Characteristics of Low Sulfur and Shale Oils

Table 8

CALCULATED PARTICLE SIZE DISTRIBUTION

Basis:
1. Particle number count.
2. Assume particles are spherical.
3. Assume particles are of equal specific gravity.

Test Date Filter Number		July 7 21		July 12 22	
Particulate Size Counted	Particulate Diameter Assumed	Calculated Weight Percent			
Microns	Microns				
1	1	0.006 wt.%		0.007 wt.%	
2	2	0.05		0.06	
3	3	0.06		0.08	
4	4	0.09		0.2	
5	5	0.1		0.3	
6	6	0.2		0.4	
7	7	0.2		0.6	
8	8	0.4		0.6	
9	9	0.1		0.9	
10	10	0.7		0.6	
11-20	15	3.6	99.3%	2.1	96.7%
21-40	30	29		17	
40	50	66		77	
		100.5(1)		99.8(1)	

(1) Due to rounding of numbers.

Table 9

POLYNUCLEAR AROMATIC HYDROCARBON EMISSIONS

Sample No.	1	2	3	4	Average
Grain Loading (gr/SCFD)	0.051	0.068	0.085	0.064	0.067
Percent Shale Oil	49.2	49.7	49.2	49.0	49.3
Low Sulfur Oil	50.8	50.3	50.8	51.0	50.7
PNA	Parts Per Million by Weight of Solids on Filter				
Benzo (a) pyrene	1	1	2		1.0
Benzo (g, h, i) Perylene	1	0.5	5		1.6
Benzo (e) pyrene	<0.4	0.5	2	0.4	0.8
Benzo (a) anthracene	1	0.5	7	3	2.9
					6.3

(6.3 ppm) (0.067 gr/SCFD) = 0.0000004 gr/SCFD

4.4 TRACE ELEMENTS

On July 22, 1976 the boiler was operated at approximately 25 percent load using pure shale oil, and the resulting flue gas (approx. 34,000 SCFM) was fed to a 10 MW size horizontal scrubber utilizing lime scrubbing reagent. The use of the scrubber was necessary since the sulfur content of the shale oil (0.67% S) was greater than the 0.5% S or equivalent allowed by the then existing air quality regulations.

Measurement of the trace element concentration of the shale oil being burned was obtained by taking three separate samples of the oil leaving the oil storage tank during an 8-hour period. These samples were combined and analyzed with the results shown in Table 10.

An estimate of the amount of trace elements being emitted into the atmosphere from the exhaust of the scrubber was obtained by sampling the exhaust gas with a small scale wet electrostatic precipitator (WEP) sampling device. The single sample was obtained over a five-hour period in order to collect a sufficient size sample to analyze. The results of this analysis were combined with the flue gas flow rate to obtain an estimate of the mass of each trace element emitted to the atmosphere per hour. This was compared to the mass of trace elements entering the boiler utilizing the shale oil analysis. A comparison of the the two mass flow rates is presented in Table 11.

While this data indicates that a large amount of the trace elements are collected either in the boiler or removed in the scrubber, it should be emphasized that it is based on only a single analysis for both the inlet and the exit. It should also be noted that the boiler was operated at an abnormally low load and hence, the amount of material deposited in the boiler might be different at higher loads and gas velocities.

Table 10

SHALE OIL TRACE ELEMENTS ANALYSIS

Element	Shale Oil Concentration (ppm) By Volume
Titanium	36
Aluminum	36
Barium	20
Magnesium	14
Fluorine	12
Calcium	12
Arsenic	9.4
Boron	6.8
Vanadium	4.8
Manganese	3.8
Nickel	2.4
Chromium	1.1
Lead	0.53
Antimony	0.53
Cadmium	0.20
Mercury	0.16
Zinc	0.074
Uranium	0.043
Beryllium	<0.02
Selenium	0.0082

Table 11

SHALE OIL TRACE ELEMENT EMISSION ESTIMATE

ELEMENT	TRACE ELEMENT FLOW RATE INTO BURNERS Thousandths of lb/hr(1)	STACK GAS TRACE ELEMENT FLOW RATE LEAVING SCRUBBER Thousandths of lb/hr(2)
Titanium	210	0.24
Aluminum	210	<4
Barium	120	15
Magnesium	81	3.6
Fluorine	74	0.35
Calcium	71	3.8
Arsenic	56	12
Boron	41	0.24
Vanadium	29	2.2
Manganese	23	3.6
Nickel	14	2.8
Chromium	6.8	<0.09
Lead	3.2	0.99
Antimony	3.2	0.16
Cadmium	1.2	0.046
Mercury	0.95	1.1 (3)
Zinc	0.44	0.95 (4)
Uranium	0.25	0.0095
Beryllium	<0.10	<0.004
Selenium	0.049	0.31 (4)

NOTES:

(1) Based on the shale oil anlysis and an average flow rate of 18.6 barrels/hr of shale oil.
(2) Based on single analysis only.
(3) Stack gas was sampled for Mercury using a gold amalgamation technique. This level of accuracy is considered good for Mercury.
(4) Zinc and Selenium were either picked up in the boiler/scrubber or the outlet sample for these elements was contaminated.

Section 5.0

CONCLUSIONS

The conclusions which can be drawn from the test data are primarily as follows:

(1) Paraho crude shale oil can be burned in a conventional utility boiler with conventional petroleum products without experiencing fuel handling, fuel mixing, combustion instability, smoke formation or boiler operational problems.

(2) Conventional off-stoichiometric combustion techniques are effective in reducing NOx emission formed by both thermal fixation of atmospheric nitrogen and conversion of organically bound nitrogen into NOx.

(3) A new technique called dual fuel combustion is demonstrated to provide effective NOx emission control capability with both normal and off-stoichiometric firing. The dual fuel combustion technique primarily reduces the conversion efficiency of organically bound nitrogen into NOx.

(4) Fuel nitrogen conversion efficiency decreases with the increase in the level of organically bound nitrogen in the fuel. Therefore, the effectiveness of the dual fuel combustion technique for NOx control is enhanced as the differential in nitrogen content of fuels introduced to the various burner elevations is increased.

(5) Further tests of burner type and combustion stoichiometries with dual fuel combustion would be needed in order to appreciate the full potential of this new combustion modification technique.

(6) Particulate emission is increased as a result of blending shale oil with light fuel distillate. It is postulated that much of the particulate increase is associated with the cracking of fuel in the liquid phase as the atomized fuel drops are burned in the furnace.

Appendix 1 - COMBUSTION CALCULATIONS

I. COMBUSTION AIR VOLUME CALCULATIONS

1. Assume in one lb of fuel there is

   C lb of Carbon
   H_2 lb of Hydrogen
   N_2 lb of Nitrogen
   S lb of Sulfur
   O_2 lb of Oxygen

2. CO_2 concentration in flue gases on dry basis (percent by Volume) is

$$\frac{31.63\ C}{V\ (\text{exhaust}) - 189.8\ H_2}$$

3. V (exhaust) = V (product of combustion)

$$+\ V\ (\text{nitrogen}) + V\ (\text{excess } O_2)$$

$$\underset{\text{at } 60F^\circ}{V\ (\text{product of combustion})} = 379.5 \left[\frac{C}{12} + \frac{H_2}{2} + \frac{N_2}{14} + \frac{S}{32}\right]$$

$$V\ (\text{nitrogen}) = V\ (\text{air}) \times .0763 \times 0.7685 \times \frac{379.5}{28}$$

$$= (.00209)\ (379.5)\ V(\text{air})$$

$$V\ (\text{excess } O_2) = V(\text{air}) \times .0763 \times 0.2315 \times \frac{379.5}{32}$$

$$- \left(\frac{32}{12} \times C + \frac{16}{2} H_2 + \frac{32}{14} N_2 + S - O_2\right) \frac{379.5}{32}$$

Therefore,

$$V\ (\text{exhaust}) = 379.5 \left[\frac{H_2}{4} + \frac{O_2}{32} + .00259\ V\ (\text{air})\right]$$

4. O_2 concentration in flue gases on dry basis (percent by volume)

$$\% O_2 = \frac{.000552\ V(air) - \left[\frac{C}{12} + \frac{H_2}{4} + \frac{N_2}{14} + \frac{S}{32} - \frac{O_2}{32}\right]}{\frac{H_2}{4} + \frac{O_2}{32} + .00259\ (V\ air)}$$

5. Sequence of calculations:

Knowing fuel ultimate analysis, perform the following steps:

(i) Use experimentally measured CO_2 to determine V (exhaust)

(ii) Use V (exhaust) to determine V(air)

(iii) Use V(air) to determine theoretical O_2 concentration in flue gas

(iv) Compare theoretical and experimental O_2 concentration.

II. CONTRIBUTION OF INDIVIDUAL BURNER TO TOTAL EMISSION AND CONVERSION EFFICIENCY OF FUEL NITROGEN TO NOx:

1. Nitrogen oxides in ppm corrected to 3% O_2 generated from the conversion of 1% by weight of fuel nitrogen into NOx

(a) Assume a fuel composition

Element	% by Wt
C	85.02
H_2	11.48
N_2	1.0
S	0.67
Ash	0.022
O_2	1.81

(b) Combustion air volume at 3% O_2

$$\% \; O_2 = \frac{.000552 \; V(air) - \left[\frac{C}{12} + \frac{H_2}{4} + \frac{N_2}{4} + \frac{S}{32} - \frac{O_2}{32}\right]}{\left[\frac{H_2}{4} + \frac{O_2}{32}\right] + .00259 \; V(air)}$$

V(air) = 212 SCF/lb of fuel.

(c) $$V \; (exhaust) = 379.5 \left[\frac{H_2}{4} + \frac{O_2}{32} + .00259 \; V(air)\right]$$

$$= 219.5 \text{ SCF/lb of fuel.}$$

(d) $$\text{Volume of } NO_2 = 379.5 \frac{N_2}{14}$$

$$= \frac{379.5 \times .01}{14} = 0.2711 \text{ SCF/lb of fuel}$$

(e) NO_x concentration in exhaust gases is:

$$\frac{0.2711}{219.5} = 1235 \text{ ppm.}$$

2. Nitrogen Conversion Efficiency

During the dual fuel combustion tests, the increase in NO_x emission level noted due to the blending of shale oil in the bottom row of burners was essentially caused by the increase in the nitrogen content of fuel burned on the bottom row. To determine the percent conversion of fuel nitrogen to NOx during both normal and off-stoichiometric firing, the following analysis is presented.

(A) NORMAL FIRING (BOTTOM ROW BLENDING)

(1) Assume NOx emission from burners in the bottom row is = (B) ppm.

(2) Assume NOx emission from burners in the top row is (T) ppm.

(3) Assume volume of products of combustion from all six burners is equal.

(4) Average NOx emissions from all six burners = $\frac{3B + 3T}{6}$

(5) Assume the NOx emissions from burners in the bottom row after shale oil blending = (B_s) then the average NOx emissions after shale oil blending is

$$\text{Average NOx} = \frac{3B_s + 3T}{6}$$

Solving for B_s, the equation becomes:

$$B_s = 2\ [\text{Average NOx}] - T$$

(6) The increase in incremental NOx emissions in the bottom burners due to shale oil blending is $\Delta NO_x = B_s - B$.

(7) The corresponding increase in incremental nitrogen content of the blended fuel

$N_2 = 1.76$ (blend ratio)

(8) Fuel nitrogen converted into NOx (percent by wt)

$$\Delta N_2 = \frac{NO_x}{1235}$$

(9) Conversion Efficiency % $= \dfrac{\Delta N_2}{N_2 \text{ x } 100}$

$$= \frac{\Delta NO_x}{1235 \text{ x } 1.76 \text{ (Blend ratio)}}$$

$$= 0.046 \; \frac{\Delta NO_x}{\text{Blend ratio}}$$

(B) OFF-STOICHIOMETRIC FIRING (BOTTOM ROW BLENDING)

(1) Make the same assumptions as under (A) from (1) thru (3)

(2) Average NOx emissions from all six burners

$= \dfrac{3B + 2T}{6}$ (No. 2 burner is out of service admitting clean combustion air)*

(3) Assume the NOx emissions level from the bottom burners after shale oil blending is B_s, then the average NOx emission level is

$$\text{average } NO_x = \frac{3B_s + 2T}{6}$$

solving for B_s gives

$$B_s = 2 \text{ (Average } NO_x) - \frac{2}{3} T$$

---

*Neglected the increase in combustion air volume due to the combustion process.

Assume that the NOx emissions level from the top burners is increased by 10% during the off-stoichiometric mode of combustion due to the air-rich environment existing in the upper row of burners.

Then $B_s = 2\ (\text{Average } NO_x) - \frac{1.1 \times 2T}{3}$

or, $B_s = 2\ (\text{Average } NO_x) - 0.73\ T$

(4) The increase in NOx emissions at the bottom burners due to shale oil blending is

$NO_x = B_s - B$

(5) Nitrogen Conversion Efficiency $= \frac{.046 \quad \Delta(NO_x)}{\text{Blending ratio}}$

Appendix 2 - EMISSION DATA OF PRELIMINARY TESTING

COMBUSTION DATA

Test No.	Date 1976	Boiler Load (mw)	Percent Shale Oil Blended	Blending Method*
1	6/17	43.5	0.0%	B/C
2	6/18	43.5	0.0%	B/C
3	6/22	45.0	1.2%	B/C
4	6/22	41.8	9.8%	B/C
5	6/23	43.9	25.5%	B/C
6	6/24	41.4	24.4%	B/C
7	7/1	43.0	38.7%	B/C
8	7/2	42.3	39.2%	B/C
9	7/6	44.2	49.2%	B/C
10	7/7	41.4	48.6%	B/C
11	7/7	43.7	48.2%	B/C
12	7/12	43.5	49.7%	A/C
13	7/12	41.3	49.7%	A/C
14	7/13	41.2	49.2%	A/C
15	7/13	41.4	49.2%	A/C
16	7/14	43.8	42.8%	A/C
17	7/14	42.5	33.0%	A/C
18	7/14	37.5	27.8%	A/C
19	7/15	38.7	50.8%	A/C
20	7/15	38.0	50.8%	A/C
21	7/15	38.1	50.8%	A/C
22	7/15	41.0	41.6%	A/C
23	7/16	43.1	0.0%	B/C
24	7/16	43.5	0.0%	B/C
25	7/16	43.0	70.8%	A/C
26	7/16	43.2	49.4%	A/C
27	7/19	42.5	71.0%	A/C
28	7/19	42.1	71.0%	A/C
29	7/19	40.2	56.6%	A/C
30	7/19	43.5	51.2%	A/C

*A/C = dual fuel system, blending in boiler after combustion.
B/C = tank blending before combustion.
**N.A. indicates that all 6 burners were in operation.

COMBUSTION DATA (Continued)

Fuel Type By Burner Row	Fuel Burn Rate Per Burner; By Row (lb/hr)	Air to Fuel Ratio By Row (lb/lb)	Burner Pattern Details**	Test No.
L.S. Oil	4041	18.1	N.A.	1
L.S. Oil	4875	16.1	#2B-O.O.S.	2
Blend.	4080	18.1	N.A.	3
Blend.	4618	16.1	#2B-O.O.S.	4
Blend.	4085	18.4	N.A.	5
Blend.	4674	16.3	#2B-O.O.S.	6
Blend.	3979	17.4	N.A.	7
Blend.	4935	15.8	#2B-O.O.S.	8
Blend.	4107	17.5	N.A.	9
Blend.	4722	16.0	#2B-O.O.S.	10
Blend.	4026	18.0	N.A.	11
Top: Shale	4008	18.0	N.A.	12
Bottom: L.S. Oil	4211	17.1	N.A.	
Top: Shale	3742	18.0	N.A.	13
Bottom: L.S. Oil	5897	17.1	#5B&R-O.O.S.	
Top: Shale	5572	13.4	#2B-O.O.S.	14
Bottom: L.S. Oil	3981	18.8	N.A.	
Top: Shale	5572	15.2	#2B&R-O.O.S.	15
Bottom: L.S. Oil	4795	17.7	N.A.	
Top: Shale	3456	21.1	N.A.	16
Bottom: L.S. Oil	4795	15.2	N.A.	
Top: Shale	2571	30.1	N.A.	17
Bottom: L.S. Oil	6228	12.7	N.A.	
Top: Shale	1979	34.4	N.A.	18
Bottom: L.S. Oil	5336	12.8	N.A.	
Top: Shale	5385	14.2	#2B-O.O.S.	19
Bottom: L.S. Oil	5414	14.1	#5B-O.O.S.	
Top: Shale	5385	17.1	#2B-O.O.S.	20
Bottom: L.S. Oil	5414	17.0	#5B&R-O.O.S.	
Top: Shale	5385	18.7	#2B&R-O.O.S.	21
Bottom: L.S. Oil	5414	18.6	#5B&R-O.O.S.	
Top: Shale	4534	16.4	#2B-O.O.S.	22
Bottom: L.S. Oil	4405	16.9	N.A.	
L.S. Oil	4142	18.4	N.A.	23
Top: L.S. Oil	2169	36.8	N.A.	24
Bottom: L.S. Oil	6115	13.1	N.A.	
Top: Nat. Gas	1710 (oil equiv.)	40.0	N.A.	25
Bottom: Shale	5597	12.3	N.A.	
Top: L.S. Oil	4251	17.1	N.A.	26
Bottom: Shale	4032	18.0	N.A.	
Top: L.S. Oil	2343	30.9	N.A.	27
Bottom: Shale	5534	13.3	N.A.	
Top: L.S. Oil	2344	38.2	N.A.	28
Bottom: Shale	5534	10.0	N.A.	
Top: L.S. Oil	4000	25.2	N.A.	29
Bottom: Shale	5245	12.4	#5B&R-O.O.S.	
Top: L.S. Oil	4022	18.7	N.A.	30
Bottom: Shale	4074	18.5	N.A.	

EMISSIONS DATA

						STACK CONDITIONS			
TEST NO.	DATE 1976	PERCENT SHALE OIL BLENDED	BLENDED FUEL NITROGEN LEVEL	NOx AT 3% OXYGEN (ppm)	PERCENT CONVERSION TO NOx*	CO_2	OXYGEN	SO_2 (ppm)	GRAIN LOADING gr/SCFD
1	6/17	0.0%	0.17%	209	8.7%	12.9%	4.3%	166	0.006
2	6/18	0.0%	0.18%	213	10.0%	11.6%	5.5%	214	0.007
3	6/22	1.2%	0.19%	257	27.6%	12.7%	4.2%	204	0.031
4	6/22	9.8%	0.33%	263	17.3%	11.6%	5.2%	175	0.046
5	6/23	25.5%	0.63%	427	29.5%	12.4%	4.5%	226	0.013
6	6/24	24.4%	0.66%	339	17.6%	11.5%	5.5%	211	0.027
7	7/1	38.7%	0.92%	393	17.2%	12.7%	3.8%	274	0.076
8	7/2	39.2%	0.94%	393	16.8%	11.5%	5.3%	238	0.058
9	7/6	49.2%	1.24%	510	20.2%	12.6%	3.9%	303	0.051
10	7/7	48.6%	1.11%	445	18.0%	11.4%	5.4%	273	0.057
11	7/7	48.2%	1.07%	469	20.4%	12.8%	3.7%	240	-
12	7/12	49.7%	1.10%	580	27.7%	13.1%	3.4%	314	0.042
13	7/12	49.7%	1.10%	634	31.5%	12.5%	4.0%	305	0.094
14	7/13	49.2%	1.09%	452	18.7%	11.5%	5.6%	277	0.099
15	7/13	49.2%	1.09%	529	24.2%	12.5%	4.1%	239	0.071
16	7/14	42.8%	0.97%	488	24.0%	12.8%	4.1%	288	0.081
17	7/14	33.0%	0.79%	455	26.2%	12.6%	4.4%	239	0.096
18	7/14	27.8%	0.70%	370	20.2%	12.0%	4.9%	-	-
19	7/15	50.8%	1.12%	449	18.1%	11.0%	6.9%	224	-
20	7/15	50.8%	1.12%	572	26.7%	10.9%	6.9%	245	-
21	7/15	50.8%	1.12%	652	32.3%	10.7%	5.0%	280	-
22	7/15	41.6%	0.95%	482	23.9%	11.4%	6.0%	260	0.046
23	7/16	0.0%	0.19%	258	27.9%	13.2%	4.7%	180	-
24	7/16	0.0%	0.19%	194	1.6%	12.4%	5.4%	169	-
25	7/16	70.8%	1.42%	254	3.5%	12.2%	4.6%	295	-
26	7/16	49.4%	1.09%	443	18.1%	12.9%	4.0%	305	0.071
27	7/19	71.0%	1.49%	352	8.5%	12.6%	5.0%	311	-
28	7/19	71.0%	1.49%	300	5.8%	12.8%	4.6%	343	-
29	7/19	56.6%	1.21%	286	6.2%	12.1%	5.5%	280	-
30	7/19	51.2%	1.13%	469	19.4%	12.7%	4.4%	280	-

*Baseline thermal NOx of 190 ppm is assumed.