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U.S. Army Toxic and Hazardous Materials Agency

PILOT-SCALE TESTING OF A FUEL OIL-EXPLOSIVES COFIRING PROCESS FOR RECOVERING ENERGY FROM WASTE EXPLOSIVES

May 1988

Prepared By:

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831

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Aberdeen Proving Ground, Maryland 21010-5104

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W. M. Bradshaw

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The U.S. Army generates and stores a significant quantity of explosives and explosive-related materials that do not meet specifications for their primary use. Current explosives disposal processes do not recover any resources from these materials. The heat of combustion of these materials is typically 9 to 15 kJ/g (4000 to 6500 BTU/lb), which is 21 to 33% of the high heating value of No. 2 fuel oil. One secondary use for explosives is to cofire them with other fuels to recover their energy content.

Bench-Scale testing has shown that cofiring is feasible and safe within certain guidelines. To further evaluate cofiring, a proof-of-principle test was conducted in a 300-kW (10^6 BTU/h) combustion chamber. The test program was discontinued before completion because of failures largely unrelated to the explosives contained in the fuel. (continued)

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This report presents the results of the proof-of-principle tests, as well as design and operational changes that would eliminate problems encountered during the course of the test program. It is clearly feasible to cofire explosives and fuel oil. However, more data are needed before the process can be tested in a production boiler, furnace, or incinerator.

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NOMENCLATURE

AEHA	Army Environmental Hygiene Agency
Comp. B	Mixture of TNT and RDX (secondary high explosive)
DRE	Destruction/removal efficiency
EPA	Environmental Protection Agency
HMX	Nitramine-based secondary high explosive
JCAP	Joint Conventional Ammunition Program
LANL	Los Alamos National Laboratory
NSPS	New Source Performance Standards
OB/OD	Open burning/open detonation
ORNL	Oak Ridge National Laboratory
P&ID	Piping and instrumentation diagram
PEP	Propellant, explosive, and pyrotechnic
RCRA	Resource Conservation and Recovery Act
RDX	Nitramine-based secondary high explosive
TNT	Trinitrotoluene (secondary high explosive)
USATHAMA	U.S. Army Toxic and Hazardous Materials Agency

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Since its inception in 1983, the supplemental fuels program has benefited from a number of contributors. I would first like to acknowledge the support of Ms. Janet Mahannah and other members of the Technology Division of the U.S. Army Toxic and Hazardous Materials Agency.

Dr. Larry Stretz, Mr. Lonnie Chapman, and others in the M-1 group at Los Alamos National Laboratory built and operated the combustor used during the proof-of-principle tests. They also provided a significant amount of design and equipment data that has been incorporated in the system described in Sect. 4.

CPT Charles Mart led the Army Environmental Hygiene Agency (AEHA) sampling crew that collected and analyzed data on particulate and organic emissions from the combustor. The information provided by AEHA shows that the explosives—fuel oil cofiring process can meet regulatory requirements.

Franklin Rinker and Keith Johnson provided invaluable assistance in designing a refractory system that can meet the severe demands of the proof-of-principle tests. Mr. Johnson provided the specifications and drawings for the refractory that are included in the Appendix.

Finally, I would like to thank the Oak Ridge National Laboratory staff members who supported this program. In particular, I would like to acknowledge Mr. Mack Lackey who provided technical direction for this program from its inception in 1983 to the conclusion of testing in 1987.

EXECUTIVE SUMMARY

The U.S. Army Toxic and Hazardous Materials Agency is developing a process to recover energy from unusable explosives and related materials. According to a 1983 study, the Army has 6.4×10^6 kg (14×10^6 lb) of unserviceable explosive materials in storage that could be recovered and used for other purposes. The Army generates an additional 1.1×10^6 kg/year (2.5×10^6 lb/year) of scrap explosives in its manufacturing processes that could also be used elsewhere.

Oak Ridge National Laboratory has conducted a series of tests to determine whether cofiring explosives and fuel oil is a safe, practical, and environmentally acceptable secondary use for scrap explosives. Laboratory tests were completed to quantify safety, compatibility, and processing requirements for cofiring explosives and fuel oil. The bench-scale tests showed that cofiring is a feasible disposal alternative.

In May 1987, cofiring was tested at the pilot scale in a 300-kW (10^6 Btu/h) combustion chamber. These tests, together known as the proof-of-principle test program, were discontinued before completion because of equipment design flaws. This report summarizes the data obtained during the course of the proof-of-principle tests and documents design and operational changes that should be made to enhance the reliability and operability of the unit.

The data obtained during the 18 tests completed in 1987 indicate that

1. explosives can be cofired using off-the-shelf equipment,
2. the process will meet present and anticipated environmental requirements,
3. the process is safe but care must be taken in selecting process equipment, and
4. the design of the proof-of-principle combustion chamber is far more complex than simply addressing the explosive-related design criteria.

The following recommendations are based on the results of the May 1987 tests, a detailed analysis of the proof-of-principle test system after the 1987 tests were discontinued, an intensive design effort to eliminate problems encountered in the 1987 tests, and an examination of the current status of the explosive disposal problem and the applicable regulations.

1. The Army still needs to find a secondary use for scrap explosives. Scrap explosives are hazardous wastes, and all of the current disposal alternatives have significant drawbacks.
2. Cofiring is a feasible alternative for disposing of explosives. The supplemental fuels program should proceed. The first step is to rebuild the proof-of-principle system and complete that test program.
3. The design and operational changes documented in Sects. 4 and 5 should be used as a basis for designing and operating the proof-of-principle combustor.
4. The specific process that will be used at the plant-scale should be evaluated in light of proposed changes to the Resource Conservation and Recovery Act (RCRA). Cofiring explosives in industrial boilers may turn the boiler into an RCRA-regulated facility. Cofiring in facilities that are already regulated by RCRA will simplify the permitting process and should reduce the operator's RCRA-related administrative work load.

PILOT-SCALE TESTING OF A FUEL OIL – EXPLOSIVES COFIRING PROCESS FOR RECOVERING ENERGY FROM WASTE EXPLOSIVES

W. M. Bradshaw

ABSTRACT

The U.S. Army generates and stores a significant quantity of explosives and explosive-related materials that do not meet specifications for their primary use. Current explosives disposal processes do not recover any resources from these materials. The heat of combustion of these materials is typically 9 to 15 kJ/g (4000 to 6500 Btu/lb), which is 21 to 33% of the high heating value of No. 2 fuel oil. One secondary use for explosives is to cofire them with other fuels to recover their energy content.

Bench-scale testing has shown that cofiring is feasible and safe within certain guidelines. To further evaluate cofiring, a proof-of-principle test was conducted in a 300-kW (10^6 Btu/h) combustion chamber. The test program was discontinued before completion because of failures largely unrelated to the explosives contained in the fuel.

This report presents the results of the proof-of-principle tests, as well as design and operational changes that would eliminate problems encountered during the course of the test program. It is clearly feasible to cofire explosives and fuel oil. However, more data are needed before the process can be tested in a production boiler, furnace, or incinerator.

1. INTRODUCTION

The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) and Oak Ridge National Laboratory (ORNL) are in the process of developing a safe, economical, and environmentally acceptable method for disposing of unserviceable energetic materials. Based on the findings of an economic evaluation and initial feasibility study conducted by ORNL in 1985, the process that is currently being developed uses waste energetic material as a supplemental fuel by cofiring it with fuel oil in an industrial boiler.[1]

ORNL and Los Alamos National Laboratory (LANL) have conducted bench-scale tests to determine the feasibility of cofiring energetic or propellant, explosive, and pyrotechnic (PEP) materials in a boiler. ORNL and LANL determined the chemical stability, handling characteristics, and reactivity of energetic-fuel mixtures in a series of laboratory tests.[2]

Based on the positive results of bench-scale testing, a proof-of-principle combustor was built and operated in 1987 at LANL. The proof-of-principle test program had to be discontinued because of operating problems that were largely unrelated to the unconventional fuel.

This report includes a summary of testing performed to date, an analysis of the 1987 proof-of-principle combustion tests, and a detailed description of the system designed by LANL, ORNL, and others that could be used to complete the proof-of-principle tests. The primary objectives of this report are to (1) document findings from the 1987 tests and (2) describe the system that has been designed to eliminate the problems encountered during the 1987 test program.

2. PROGRAM OVERVIEW

The supplemental fuels program grew out of a survey conducted by USATHAMA and ORNL in 1983 to determine whether combustible hazardous wastes being produced by the U.S. Army could be burned as a fuel supplement in industrial boilers. According to the survey, facilities that were generating combustible hazardous wastes, such as waste oils and solvents, were disposing of them adequately but not always in the most cost-effective manner.[3]

The same survey revealed that a significant quantity of waste and unserviceable energetic materials that require disposal exist. The primary sources of these materials are demilitarization of conventional munitions, production of nonconforming PEP materials, and scrap material produced while manufacturing PEP materials.

Currently, the only disposal alternatives for PEP materials are open burning/open detonation (OB/OD), and incineration.[3] Significant quantities of unserviceable PEP materials are being stockpiled because none of the disposal options is attractive. Incineration is expensive, and OB/OD operations are severely limited by environmental regulations.

In 1985, USATHAMA and ORNL explored a variety of options to dispose of PEP materials in an economical and environmentally acceptable manner. The study examined the feasibility of reducing disposal costs by recovering energy as part of the process. In addition to reducing disposal costs, energy recovery provided the potential for using the material in a combustion process that was not regulated by the Resource Conservation Recovery Act (RCRA) as a hazardous waste disposal facility.

The primary sources of PEP materials that could be cofired in a boiler are the unserviceable munitions in the Army's demilitarization account and scrap PEP material resulting from explosive manufacture. According to a 1983 study by the Joint Conventional Ammunition Program (JCAP) Demilitarization and Disposal Task Group, the demilitarization account contained ~14 Mlb of TNT, RDX,* Comp. B,† and HMX* that could be recovered and used as a supplemental fuel.[4] This number amounts to 14% of the demilitarization account (by weight) at the time of the JCAP study. Estimates indicate that a total of 1.1×10^6 kg (2.5×10^6 lb) of nonconforming TNT, RDX, and Comp B are produced by Holston, Radford, and Iowa Army Ammunition Plants each year.[5]

2.1 Current Energetic Material Disposal Alternatives

Waste or excess energetic wastes are currently disposed of by open burning, open detonation, and incineration. Although controlled incineration is a clean and effective disposal method for PEP materials, it is an energy-intensive and expensive disposal option. Radford Army Ammunition Plant now operates two incinerators that can each burn approximately 250 lb/h of PEP materials.[5] To prepare feed for these incinerators safely, the PEP materials must be ground in water to produce a slurry with a water to energetic ratio of 3:1 (on a weight basis). Incineration of this feed requires 420 lb/h of fuel oil or a fuel/PEP ratio of 1.7 (by weight).

A less expensive alternative to controlled incineration is open burning or open detonation (OB/OD). In December 1987, the EPA implemented regulations that specify permit requirements for OB/OD operations.[6] Although obtaining a permit for OB/OD is possible, there are a number of drawbacks to OB/OD. An evaluation of OB/OD must consider the EPA's RCRA permitting criteria, other environmental regulations that might apply, operational criteria for the process, and the Army's declared policy for environmental management.

2.2 Supplemental Fuels Program Objectives

To identify and develop an economical and environmentally acceptable technology for managing PEP waste materials at Army facilities, an

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*A mitramine-based secondary high explosive.

†A mixture of TNT and RDX (secondary high explosive).

economic and engineering evaluation of potential alternatives was performed. This evaluation resulted in identifying cofiring PEP materials and fuel in industrial boilers as a promising waste management technology.

To implement the supplemental fuel (cofiring) technology, several objectives were defined. The first is that the process must be practical for plant-scale operation; that is, it is most desirable to implement the process by making use of existing equipment with a minimum of modification. The primary obstacle to this objective is that existing industrial boilers are not designed to burn mixtures of oil and energetic compounds. Therefore, to meet this objective, it was determined that a combustion chamber designed to meet safety and environmental requirements would make it possible to use an existing package boiler.

In addition to the operational objective described above, it is necessary to develop a process that can be reliably and safely operated. Since energetic materials will be used, a safe process is paramount for acceptance and implementation. Additional technology development objectives are to develop a process that is capable of minimizing short and long-term environmental risks and is economical from a lifecycle standpoint.

2.3 Supplemental Fuels Development Program

As part of the design and development phase of the supplemental fuels program, a series of tests was conducted to evaluate certain aspects of cofiring PEP material in industrial boilers. These tests were designed to determine safety criteria, physical property limitations imposed by the process on PEP-fuel oil mixtures, and combustion characteristics of PEP-fuel oil mixtures.

2.3.1 Safety criteria

To fully address the safety concerns associated with cofiring PEP materials, a series of bench-scale tests was conducted to determine

1. the chemical compatibility and stability of the various mixtures used in the process, and
2. the presence of any tendency for propagation of detonation.

In summary, it was determined that the mixtures involved in the supplemental fuel process did not pose concerns with respect to chemical compatibility and stability and, at the explosive concentrations of interest, there was no tendency for propagation of detonation. A full description of these tests and results is available in Ref. 2.

2.3.2 Physical properties

In response to the program objective to use existing equipment with few modifications, it was necessary to determine the physical characteristics of the mixtures to be used. Tests were conducted to determine the viscosity, solubility, and particle size distribution of these mixtures. A significant finding of these tests was that the energetic materials are only slightly soluble in fuel oil and therefore must be fed as a fuel oil/explosive slurry to the boiler. Other tests determined the maximum particle size that could be tolerated with standard burner nozzles and allowed for the proper design of a burner gun. Again, a full accounting of these tests and results is available in Ref. 2.

2.3.3 Combustion characteristics

A design of a combustion test system was completed at the conclusion of the tests described above. This test system consisted of a 300 kW (10^6 Btu/h) combustor and was used to test the cofiring of fuel oil, solvent, and energetic materials. These tests were prematurely discontinued because of design problems; however, the preliminary results were promising for the continuation of the program, and enough information was gained to allow for the redesign of a test unit. Details of these tests are presented in Sect. 3, and a recommended redesign of the test system is presented in Sect. 4.

2.4 Future Supplemental Fuel Development Requirements

2.4.1 Proof-of-principle tests

Based on the results of the preliminary testing described in the next section, a redesign of the test system has been developed. Tests using this system will be conducted to obtain information on combustion characteristics and emissions necessary to develop design data and, most importantly, to convince potential users that the technology is safe, environmentally sound, and will result in an attractive option, both technically and economically, for managing energetic waste materials.

2.4.2 Demonstration

The proof-of-principle tests will provide information to allow for a full-scale demonstration of the technology using an existing boiler. This full-scale demonstration will result in data to confirm that the process is safe and meets environmental requirements and to develop final plant-scale optimization.

2.5 Impact of Recent Environmental Regulations on Process Selection

Environmental regulations play a key role in evaluating disposal, recycle, and recovery processes. Since deciding to pursue cofiring in industrial boilers, the EPA has proposed and enacted several changes in RCRA that directly affect this process.

In May 1987, the EPA proposed that industrial boilers and furnaces that use hazardous wastes as a fuel be regulated under the RCRA umbrella.[7] If enacted, these regulations would place rigorous monitoring and reporting requirements for a boiler used to burn mixtures of fuel oil and PEP materials. These requirements include permitting, trial burns (unless exempted under Sect. 266.34-4), and continuous monitoring of carbon monoxide and oxygen in the flue gas.

One alternative that merits further consideration is using PEP materials as a supplemental fuel for incinerators that burn explosive contaminated waste. These incinerators are often already permitted as

RCRA facilities, so the increase in monitoring and reporting requirements would be minimal. The personnel who develop, manage, evaluate, and operate these incinerators are already familiar with safety requirements for PEP processes. The energy content of the PEP material would still be recovered because it would reduce the amount of fuel oil required by the incinerator.

Several issues must be resolved before the program could be redirected toward cofiring in an incinerator. Although all installations have steam plants, some may not have incinerators suitable for this process. The process would still have to be approved by the safety community. Changing fuel would probably require a modification to any environmental permits that govern these facilities. Finally, changing direction from boiler plants to incinerators would still require the development program described in Sect. 2.4.

3. PROOF-OF-PRINCIPLE TEST PROGRAM (MAY 1987)

In 1987, a 300-kW (10^6 Btu/h) combustor was fabricated and tested at LANL. The combustion chamber is shown in Fig. 3.1. The test program was terminated before its completion for two reasons. On June 3, 1987, the blanket insulation in the reducing zone and the castable insulation in the throat was found to be in very poor condition and could not be repaired in a timely manner. Second, after shutting the system down on June 2, 1987, a small quantity of RDX that had lodged in the burner gun rapidly decomposed and severed the burner nozzle. The burner could have been repaired quickly. However, because the insulation system was no longer serviceable and the mechanism by which RDX particles remained in the burner gun after shutting the system down was not known, the tests were discontinued. A letter report, dated June 26, 1987, describes the events leading to failure and is included as Appendix A. A second letter report summarizes the findings during disassembly and cleanup and is included as Appendix B.

3.1 Test Objectives

The proof-of-principle tests were designed to evaluate the effect of process parameters such as feed rate, combustion stoichiometry, flue gas recycle, and fuel composition on combustion characteristics and emissions. A second objective of the program was to evaluate the fuel preparation and transport system.

3.1.1 Combustion performance

Flame stability and combustion efficiency are very important parameters. Parameters such as flame length, flame stability, and incidence of flameouts were evaluated. The flue gas was analyzed to determine combustion efficiency, which is a measure of energy recovery from the fuel.

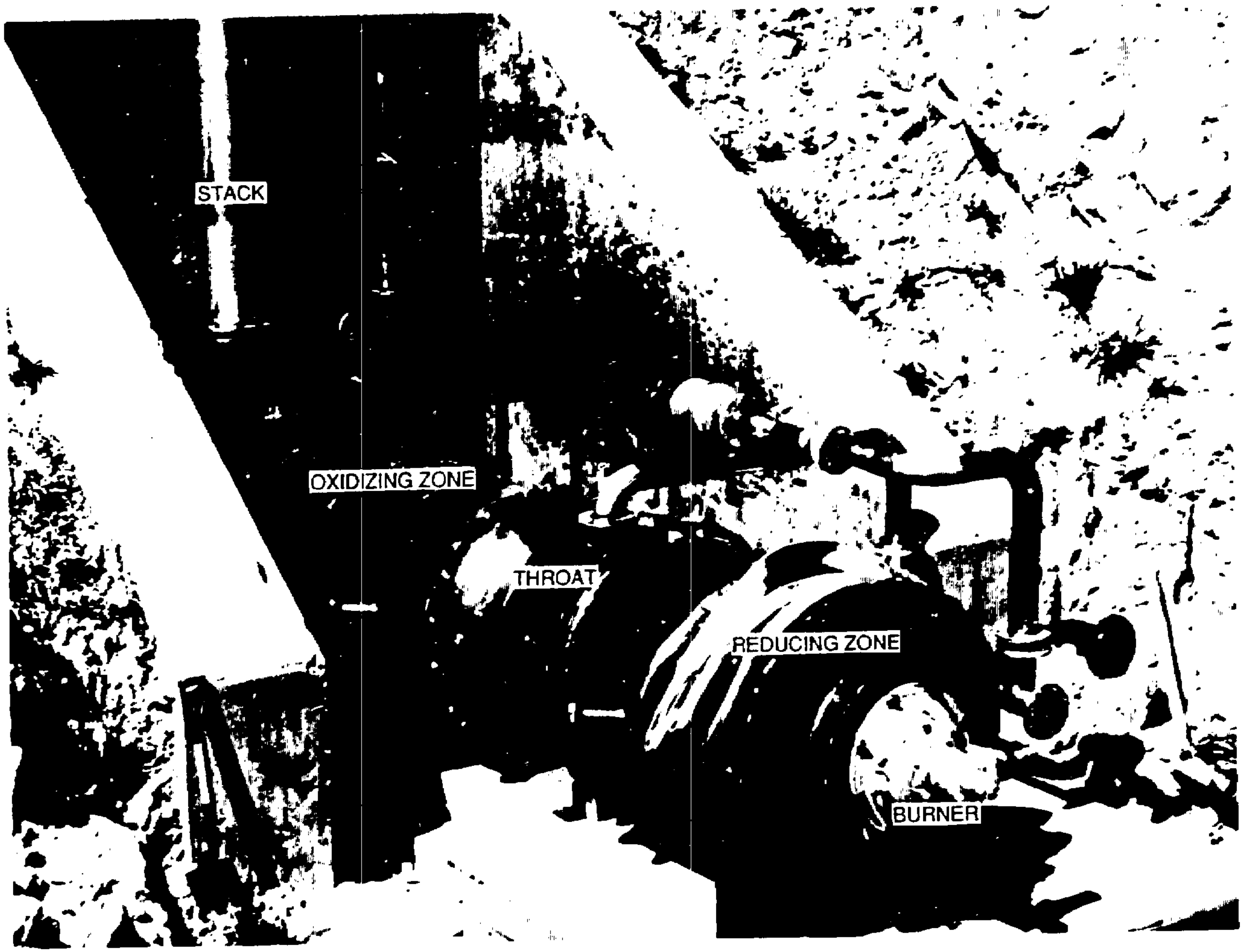

Fig. 3.1. Combustion chamber used for proof-of-principle tests

3.1.2 Emissions

As a minimum, this process would be regulated under the NSPS. NSPS has no emission limits for boilers smaller than 100 MBtu/h that would affect this process.[8] Boilers used for this process would probably be in the 20- to 50-MBtu/h range.

In all likelihood, this process would also fall under RCRA. Proposed RCRA requirements for boilers that cofire RDX and TNT include 99.99% DRE of the hazardous wastes (e.g., TNT and RDX) and an average CO emission limit of 100 ppm over any 60-min period or 500 ppm over a 10-min period (corrected to 7% O_2).[7]

3.1.3 NO_x abatement

Although NO_x emissions are not controlled under RCRA or NSPS for boilers below 100 MBtu/h, it is a very important parameter for this process. The weight fraction of nitro groups in TNT and RDX is 61 and 62%, respectively. These fuel-bound NO_2 groups could produce very high levels of NO_x. It is very likely that NO_x emissions would be a key parameter in obtaining an environmental permit for this process. One of the primary objectives of the proof-of-principle test program was to evaluate a number of techniques to reduce NO_x emissions.

3.1.4 Fuel preparation and transport

To the maximum extent possible, the fuel preparation and transport system modeled a plant-scale system. No parametric studies were planned for evaluating process equipment. A single design was evaluated during the course of testing.

3.2 Proof-of-Principle Test Results

In 1987, the proof-of-principle test program was conducted with a 300-kW (10^6 Btu/h) combustor. Although this test was discontinued before completion, significant data were obtained during the 8 d of testing. A variety of mixtures was burned, including TNT in No. 2 fuel oil and Comp. B in No. 5 fuel oil.

Figure 3.2 is a schematic diagram of the combustion system. Combustion air and fuel oil/energetic flows were metered. Gas analyzers in the stack continuously monitored CO, CO_2, O_2, and NO_x. The key features of the system were (1) two-stage combustion, which provided for substoichiometric operation in the first stage, and (2) flue gas recycle, which is a proven technique for controlling NO_x.

The fuel preparation system is shown in Fig. 3.3. Fuel mixtures were prepared as single batches before each test. Energetic materials were dissolved to their solublity limits in toluene in the Pfaudler™ tank before adding fuel oil. The recycle pump and impeller provided continuous agitation.

Eighteen tests were run between May 20 and June 2, 1987. The fuel composition, reducing and oxidizing zone temperature, air flow rate, and flue gas composition for each test are given in Table 3.1.

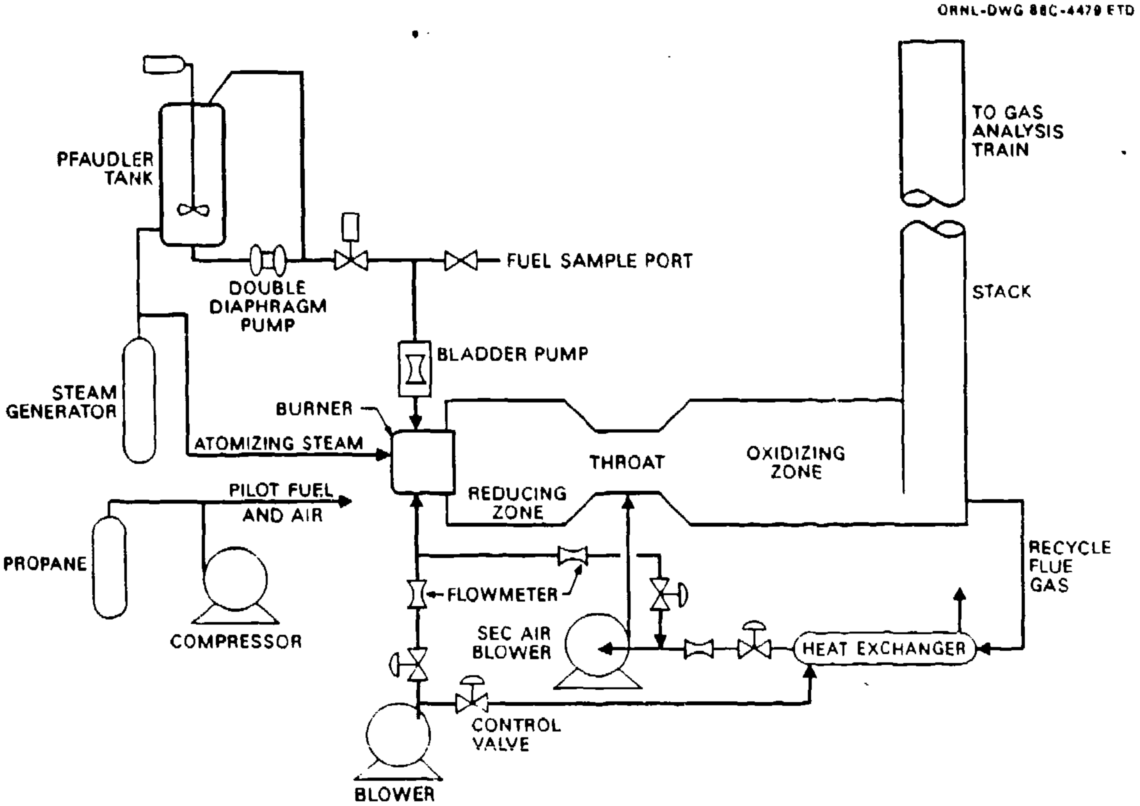

Fig. 3.2. Proof-of-principle system used for 1987 tests

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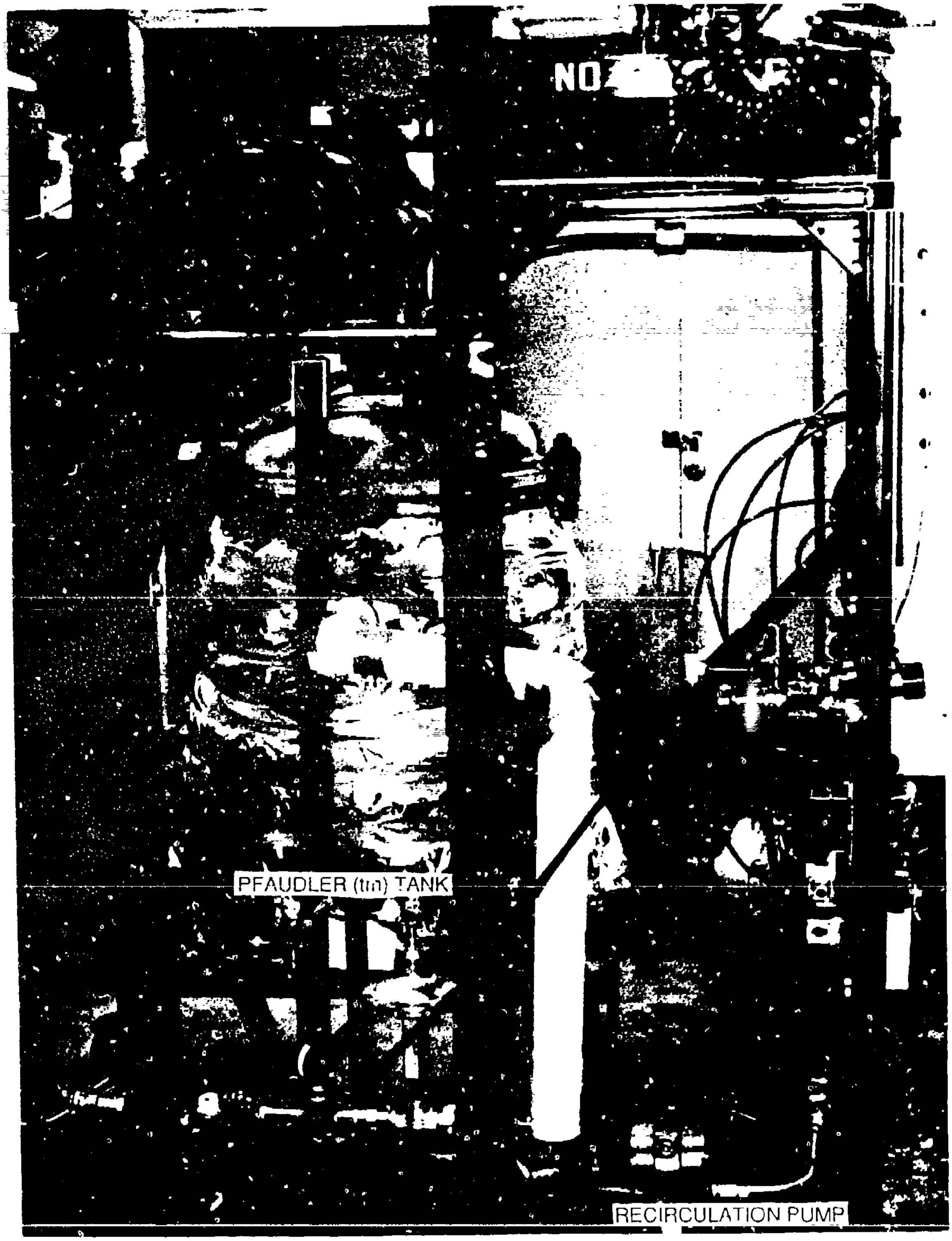

Fig. 3.3. Fuel preparation system

Table 3.1. Summary of test conditions

Run	Date	Start/end time	Fuel (mass basis)	Fuel flow (kg/min)	Air flow (kg/min)		Temperature (°C)		Gas analysis[a]		
					Red zone	Ox zone	Red zone	Ox zone	O_2 (%)	CO (ppm)	NO_x (ppm)
1	05/20/87	1030/1155	No. 2 Fuel Oil	19.1	354	0	1026	712	10.0	68	NA
2	05/20/87	1315/1400	No. 2 Fuel Oil	13.6	231	0	1072	700	9.0	31	NA
3	05/20/87	1540/1650	No. 2 Fuel Oil	14.2	73.5	103	1049	731	4.4	24	55
4	05/21/87	0950/1035	No. 2 Fuel Oil	23.7	378	234	1093	640	14.0	11	19
5	05/21/87	1110/1245	No. 2 Fuel Oil	23.1	87.1	172	969	870	4.9	19	30
6	05/21/87	1415/1510	Toluene	16.1	65.3	98.0	993	777	4.2	12	15
7	05/21/87	1535/1555	Toluene	21.8	65.3	161	1002	878	6.3	5	8
8	05/22/87	1115/1150	15% TNT, 33% Toluene, Balance No. 2 Fuel Oil	21.8	596	0	1063	696	10.0	3	NA
9	05/22/87	1425/1435	15% TNT, 33% Toluene, Balance No. 2 Fuel Oil	21.8	65.3	455	1062	767	8.0	23	689
10	5/27/88	0930/0945	40% TNT, 60% Toluene	12.0	278	0	1016	609	9.3	42	>1,000
11	05/27/87	1030/1100	No. 2 Fuel Oil	11.2	76.2	201	946	742	5.0	78	53
12	05/27/87	1100/1130	40% TNT, 60% Toluene	12.0	54.4	169	1001	671	7.2	92	2055
13	05/27/87	1130/1200	40% TNT, 60% Toluene	22.6	43.5	397	1051	708	10.0	68	1275
14	05/28/87	1650/1720	20% Comp. B, 30% Toluene, Balance No. 2 Fuel Oil	31.6	57.2	512	1091	805	9.3	28	964
15	05/29/87	1555/1745	37%, Toluene, 63% No. 5 Fuel Oil	30	62.6	623	1038	782	9.4	18	83
16	06/02/87	1035/1235	37%, Toluene, 63% No. 5 Fuel Oil	30	NA	631	NA	828	7.3	5.7	102
17	06/02/87	1500/1625	20% Comp. B, 41.1% Toluene, Balance No. 5 Fuel Oil	30	NA	623	1282	711	9.3	25	646
18	06/02/87	1840/2030	20% Comp B, 41.1% Toluene, Balance No. 5 Fuel Oil	30	NA	610	NA	724	9.2	33	583

[a] O_2 concentration is on a wet volume basis, other gas concentrations are on a dry volume basis.
[b] NA - Data not available

3.2.1 Material balance

The material balances for each test are given in Appendix C. The pilot fuel and pilot air flows were not metered, so those values were estimated from manufacturers' literature. Usually, the closure (output/input) for each element ranged from 90 to 110%.

3.2.2 Energy balance

The total energy balance is difficult to obtain. The combustor skin temperature was not measured, so closure cannot be determined. Table 3.2 gives estimates of the energy balance for three tests that cover the range of heat load and combustion stoichiometry tested. The energy balance is not critical in evaluating the proof-of-principle test data. However, because insulation failure led to the discontinuation of testing, it is very important in designing the refractory for the next proof-of-principle test system.

3.2.3 NO_x reduction

Combustion of high-nitrogen fuel will produce NO_x. A limited amount of NO_x will also result from the oxidation of nitrogen included in the combustion air. All of the NO_x measured in the stack during the proof-of-principle test program was nitric oxide (NO), a finding that agrees with thermodynamic predictions.[9,10]

Nitrogen oxides are weak acidic gases that have been linked to a number of environmental concerns, including acid rain. One abatement technique is to chemically reduce the nitrogen atom (e.g., decrease its oxidation number) by removing oxygen atoms from the molecule. Complete reduction results in elemental nitrogen and can be achieved by adjusting combustion air, controlling combustion temperature, or adding a reducing agent.

The only NO_x reduction method evaluated was substoichiometric operation in the reducing zone. Substoichiometric operation is an example of adjusting combustion air and controlling combustion temperature. Unfortunately, no tests were completed with energetic materials

Table 3.2. Energy balance for selected test conditions

Test No.	Total heat input (kW)	Flue gas (kg/h)	Enthalpy of flue gas (kW)	Shell heat loss (kW)	Heat flux from shell (kW/h)	Avg shell temperature (°C) (estimated)
10	130	323	79.4	50.4	3.50	200
7	282	281	114	167	11.7	360
15	383	749	218	165	11.5	340

at oxidizing conditions before the termination of testing. For the proof-of-principle tests, NO_x reduction can only be presented as the ratio of fuel-bound nitrogen to NO_x emitted. This ratio ranged from 23% while burning a single-phase mixture of 40% TNT in toluene (test 12) to 7% while burning a two-phase mixture of 20% Comp. B, 40% toluene, and 40% No. 5 fuel oil (test 18).

Some of the fuel-bound NO_x would have been reduced to N_2 under oxidizing conditions. Conventional boilers burning high-nitrogen fuel at oxidizing conditions typically convert 30 to 35% of the fuel-bound nitrogen to NO_x.[11] Therefore, the incremental decrease in NO_x emissions caused by substoichiometric operation is estimated to be 25 to 80%.

Flue gas recirculation was included in the test plan, but was not tested before discontinuing testing. Flue gas recirculation provides a source of combustion air that is low in oxygen, resulting in a more reducing atmosphere. In addition to providing a more reducing atmosphere, flue gas recirculation offers increased turbulence and better heat dissipation than can be achieved by limiting combustion air.

3.2.4 Observations

During the course of the test program, a number of other combustion parameters were evaluated. They include flame stability, combustion performance, and fuel preparation.

3.2.4.1 Flame stability. The flame pulsed whenever toluene was present in the fuel mixture. This was probably caused by flashing of the toluene by the atomizing steam. There did not seem to be a significant difference in pulsing when the fuel contained energetic materials in addition to toluene. The pulsing can be eliminated by using a different burner gun atomization system, as described in Sect. 4.3.5.

The flame was not stable at highly reducing conditions. The ultraviolet (UV) detector lost its signal quite often at deeply reducing conditions (<40% of stoichiometric air). Once the UV detector lost its signal, the burner would not relight until the air approached 50% of stoichiometric flow. There are several possible explanations for the instability. One is that the flame detector was covered with elemental carbon produced in the combustion process, which burned off once the air flow was increased. The view ports were always coated with soot after substoichiometric operation, so it is very probable that the flame detector was also. Another explanation is that the combustion air velocity was too low to provide a stable flame zone. Because the flame was not visible from the view port at reducing conditions, visual examination was not possible.

Flameouts are not acceptable for plant-scale operation. Three modifications would help to prevent this situation. The UV flame detector should be purged with an inert gas to reduce the soot buildup. The flame supervision system should be bypassed whenever the reducing zone temperature is above 760°C (1400°F) [as provided for in the National Fire Protection Association (NFPA) code for ovens and furnaces].[12] Finally, there is little benefit to operating at highly reducing conditions. Pohl and Sarofim demonstrated that the ratio of NO_x to fuel-bound nitrogen (for coal) is not affected by a stoichiometric ratio below 70%.[13] Scola and Santos reported no reduction in NO_x emissions between 94% and 75% of stoichiometric conditions while burning a 2% nitrogen fuel in a fluidized bed.[11]

3.2.4.2 Combustion efficiency. Boiler efficiency is a measure of the fraction of fuel completely burned to H_2O and CO_2. If all of the fuel is burned to CO_2 and H_2O, energy recovery from the fuel is maximized. Incomplete combustion results in CO, making it the principal measure of combustion efficiency.

During tests 15–18, the combustion efficiency averaged 99.98% for a mixture of 37% toluene and 63% No. 5 fuel oil and 99.92% for a mixture of 20% Comp B, 41.1% toluene, and 38.9% No. 5 fuel oil.[9] This very small loss in energy recovery is insignificant for this process.

3.2.4.3 Fuel preparation and transport. There were no significant problems with the fuel preparation system during the course of the test program. The energetic material was measured and added to the Pfaudler™ tank. Toluene was added to dissolve the energetic material. The mixture was heated for 30 to 60 min to enhance dissolution of the energetic material. The fuel oil was then added to the solvent/energetic mixture, and the impeller and recirculating pump were used to further mix the fuel.

The only notable problem with the system was discovered during cleanup. The bladder pump that delivered fuel to the burner assembly was full of RDX particles. A diagram of the pump is shown in Fig. 3.4. In all likelihood, the pump bladder was acting as a classifier whenever RDX slurries were being pumped. The problem can be eliminated by choosing a different pump design. An improved pump design is described Sect. 4.3.

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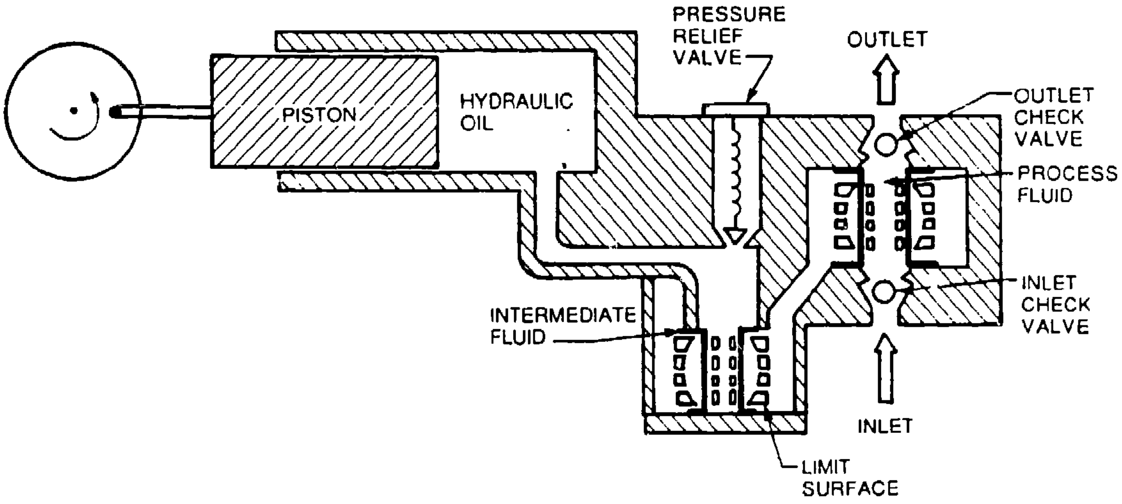

Fig. 3.4. Bladder pump used to supply fuel to burner

3.3 Discussion of Results

The proof-of-principle tests conducted in 1987 succeeded in proving the feasibility of cofiring TNT, RDX, and Comp. B with fuel oil and a solvent in an "off-the-shelf" burner. The demonstration of this process represents a major milestone in the supplemental fuels program. Moreover, a significant amount of environmental and safety data were obtained, and a number of design criteria were identified. The design implications are covered in Sect. 3.4.

3.3.1 Environmental compliance

The two regulations that are most important for this process are RCRA and NSPS. RCRA governs hazardous waste disposal facilities, while NSPS applies because changing from fuel oil to energetic mixtures is an operating change to an existing facility that will increase NO_x emissions.[9]

3.3.1.1 RCRA. The proposed RCRA regulations will bring this process under the hazardous waste umbrella even though it is carried out in a boiler.[7] The regulations proposed in May 1987 differ slightly from those that apply to hazardous waste incinerators. Specifically, no limit has been set for particulates, HCl emissions are regulated differently (but they would not apply to this process), and the trial burn may not be needed. However, the EPA plans to reissue proposed regulations in June 1988 that will include particulate standards and may require trial burns in all cases.[14] In any event, the 99.99% DRE and CO requirements described in Sect. 3.1.2 will probably apply.

The DRE for TNT exceeded 99.9996%. The DRE for RDX exceeded 99.9998%. Neither compound was detected in the flue gas. Dinitrotoluene (DNT), a potential product of incomplete combustion, was not detected in the flue gas.[9] The DREs far exceeded 99.99% required by RCRA, and the TNT did not partially decompose to form DNT.

The CO concentrations for four runs are shown in Fig. 3.5 (Ref. 7). The CO concentration averaged 25 ppm while burning toluene and No. 5 fuel oil (corrected to 7% O_2). The CO concentration averaged 83 ppm while burning toluene, Comp. B, and fuel oil (corrected to 7% O_2). The process meets the RCRA CO requirement, but is very close to the limit of 100 ppm (60 min average at 7% O_2).

Particulate emissions were measured during tests 15 and 17. The average particulate concentration while burning toluene and No. 5 fuel

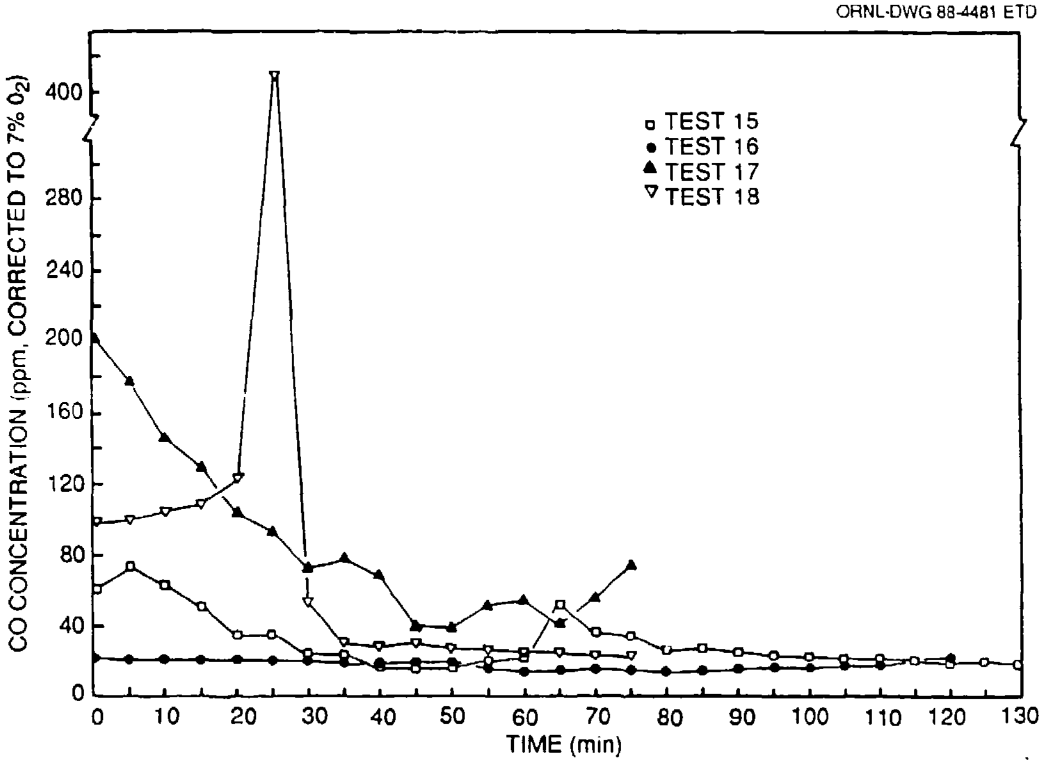

Fig. 3.5. CO concentration for tests 15-18

oil (test 15) was 172 mg/m^3 (corrected to 7% O_2).[9] The average particulate concentration while burning toluene, No. 5 fuel oil, and Comp. B (test 17) was 388 mg/m^3 (corrected to 7% O_2).[9] The RCRA standard for incinerators is 180 mg/m^3 at 7% O_2. The EPA plans to include the 180 mg/m^3 particulate standard in the June 1988 proposed regulations that cover cofiring in boilers and furnaces.[14] In any event, particulate standards can be met with off-the-shelf control equipment.

3.3.1.2 NSPS. This process would be regulated under Subpart Db, Part 60, 40 CFR.[8] There are no standards for boilers that have a heat input capacity below 100 MBtu/h. Any boiler used for this application would probably be 20 to 50 MBtu/h. If a >100 MBtu/h boiler were used, NSPS limits NO_x emissions to 0.1 lb/10^6 Btu (measured as NO_2) and particulates emissions to 0.3 or 0.4 lb/10^6 Btu (depending on the heat release rate of the unit).

During the two energetic runs that AEHA monitored, the single burner configuration used in this test did not meet the NSPS standards for >100 × 10^6 Btu/h boiler. NO_x (as NO_2) emissions averaged 1.25 lb/10^6 Btu, and particulate emissions averaged 0.4 lb/10^6 Btu.[9] However, a 100 MBtu/h boiler would have several burner guns. If a limited number of guns was used to burn energetic fuel, the NSPS regulations could be easily met.

3.3.2 Safety

LANL and ORNL conducted a number of tests to evaluate the safety of cofiring explosives in fuel oil.[2] The results of these safety tests served as a basis for designing the proof-of-principle test system.

The only safety-related incident occurred on the last evening of the test program. Upon completion of testing, every attempt was made to cool the combustor slowly to minimize damage to the castable insulation in the throat section. During the course of the cooling period, there was a popping noise and the pilot light went out. The physical condition of the equipment indicated that a small quantity of RDX inside the burner tube rapidly decomposed to smaller gaseous compounds, causing a sudden pressure rise that severed the burner assembly at the threads that join the tube and the nozzle. A section view of the burner tube assembly that shows the most likely location of RDX particles is included as Fig. 3.6.

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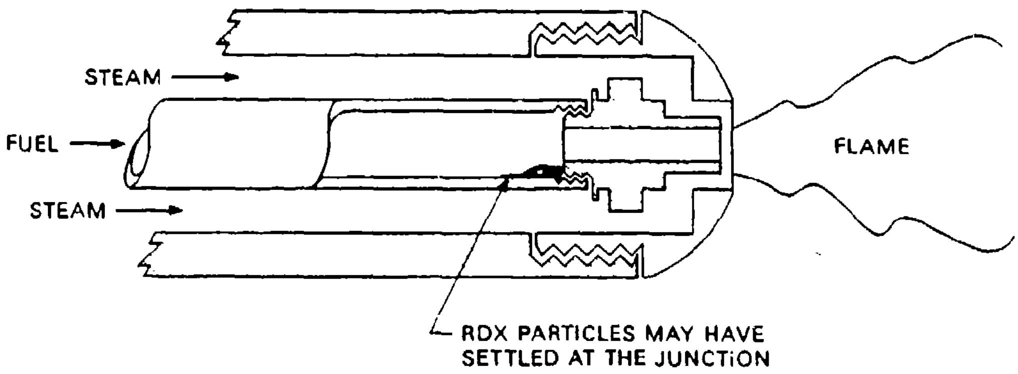

Fig. 3.6. Section view of burner tube assembly

Figure 3.7 is a photograph of the nozzle and burner tube assembly. Damage was confined to the inner tube and atomizing nozzle.

The rapid decomposition of RDX resulted from several contributing factors. Elimination of any of the factors would have prevented the problem. Moreover, the problem can be eliminated by minor changes in design.

1. At the conclusion of testing on June 2, the castable insulation was near failure. To minimize thermal stresses, the combustor was cooled slowly, resulting in slow heating of the burner assembly. RDX is unstable when subjected to slow heating.
2. As part of the slow cooling process, air flow through the burner assembly was reduced as much as possible. The air duct between the meter and burner assembly was commercial-grade plastic hose. At low flow, the hose melted, eliminating air flow to the burner assembly. The loss of air flow allowed the burner assembly to warm up to the decomposition temperature of RDX [260°C (500°F)].[15] A flexible metal hose would not have melted; it would have offered the necessary vibration damping, and overall it would have been a much more reliable choice of material.
3. The atomizing steam was shut off to further retard the cooling rate of the combustor. Shutting off the steam supply removed all cooling to the burner assembly.
4. Obviously, the root cause of the problem was that RDX particles were in the burner tube after it had been purged. The fuel lines were purged with No. 2 fuel oil before shutting down. The AEHA test protocol required a fuel sample that was routinely taken after shutting down. Because the sample port was located beyond the last valve, RDX particles in the bladder pump (see Sect. 3.2.4.3) may have migrated into the burner tube while the sample was taken. Potential solutions for this problem include moving the location of the sample port, using a full-stroke positive displacement pump, and purging the burner assembly with a solvent before shutting down.

ORNL PHOTO 8339-88

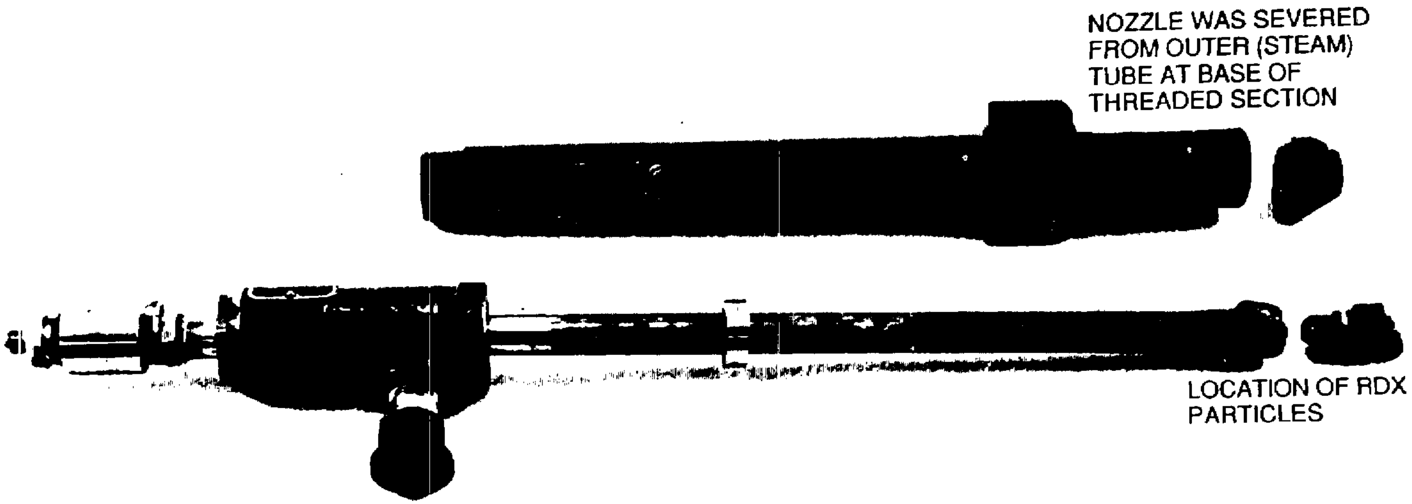

Fig. 3.7. Burner tube assembly after rapid decomposition of RDX particles in burner tube

3.4 Design and Operational Implications

Several of the "lessons learned" from the 1987 tests were incorporated in the system described in Chap. 4. The major lessons are described below.

1. A much more durable refractory system is needed because it is subjected to very severe conditions. It is thermally cycled daily, it is exposed to a highly reducing atmosphere, and it operates at a very high temperature, sometimes exceeding 1370°C (2500°F).
2. The fuel feed pump must be a full displacement device. This precaution will eliminate potential safety problems yet provide an independent mechanism to verify fuel feed rate.
3. The flame supervision system must be more reliable for this process to be practical for plant-scale operation.
4. There is no need to operate at highly reducing conditions. Deep staging results in less turbulence in the reducing zone and reduces flame stability. Furthermore, other researchers have shown that there is no correlation between the severity of reducing conditions and NO_x emissions for fuel-bound nitrogen in coal and fuel oil below 70% of stoichiometric conditions.[11,13] Finally, operating below 65% of stoichiometric air will produce elemental carbon that will coat surfaces and result in extremely high surface temperatures whenever the system is converted to oxidizing conditions.

4. PROPOSED DESIGN FOR NEXT PROOF-OF-PRINCIPLE TEST

An in-depth review of the results of the 1987 tests was conducted to determine which design modifications are necessary to ensure successful completion of the proof-of-principle test program. The design criteria, system and subsystem design, and equipment specifications are documented in this section.

4.1 Design Criteria

The test system must be capable of performing under a wide range of potential operating conditions and must be highly reliable. The criteria to meet these requirements are listed below.

4.1.1 Heat load

The basic sizing criterion for the system is heat load (expressed in British thermal units per hour or kilowatts). The heat load, fuel properties, and stoichiometric conditions determine operational parameters, such as temperature and flow rates. The system must be capable of firing rates of 150 to 750 kW (0.5 to 2.5 × 10^6 Btu/h).

4.1.2 NO_x abatement

Several NO_x reduction technologies will be available for testing: staged combustion, flue gas recycle, steam injection, and ammonia injection. The requirements for each of these technologies are as follows.

1. The reducing zone blower must provide 60 to 150% of stoichiometric air to the combustor. It must simultaneously provide the amount of air required to cool 136 kg/h (300 lb/h) of dry flue gas from 1090 to 260°C (2000 to 500°F). The oxidizing zone blower must provide up to 120% of stoichiometric air.
2. The flue gas recirculation blower must pump 136 kg/h (300 lb/h) of dry flue gas to either zone. There is no requirement to remotely redirect flow from one zone to the other. The flue gas must be cooled to 260°C (500°F) before returning to the combustor.

3. The steam supply system must be capable of providing a maximum of 1.5 kg steam/kg of fuel at the maximum heat load. The minimum steam flow is the amount required to atomize the fuel at 150 kW (500,000 Btu/h).

4.1.3 Thermal properties

The refractory system must be able to operate at highly reducing conditions at 1370°C (2500°F), with a design limit of 1650°C (3000°F). It must be capable of daily cycling and be self-supporting. The combustor must dissipate enough heat to still air at 21°C (70°F) to allow for operating at 732 kW (2.5×10^6 Btu/h) at 60% of stoichiometric oxygen in the reducing zone and 50% overall excess oxygen.

4.1.4 Instrumentation/data collection

All mass flow rates entering the combustor must be metered and recorded. Combustion air flow transducers must be mounted and plumbed for in-line verification with a manometer.

At least three thermocouples are required in each zone. The thermocouples must be capable of measuring 1650°C (3000°F) and be able to withstand a highly reducing atmosphere.

The composition of the flue gas will be continuously monitored. The NO_x, CO, CO_2, and O_2 will be monitored and recorded in the control room.

4.1.5 Operating requirements

The test program will require 5 h/d during scoping tests and 8 h/d during performance tests. The system must be capable of reaching steady state conditions within 3 h of startup.

4.2 System Design

The interfaces between the various components are shown in the process flow sheet (Fig. 4.1). A material and energy balance is included for a heat load of 732 kW (2.5×10^6 Btu/h). The physical connections between the components are shown in the piping and instrumentation diagrams (P&IDs) for the combustor and fuel preparation systems.

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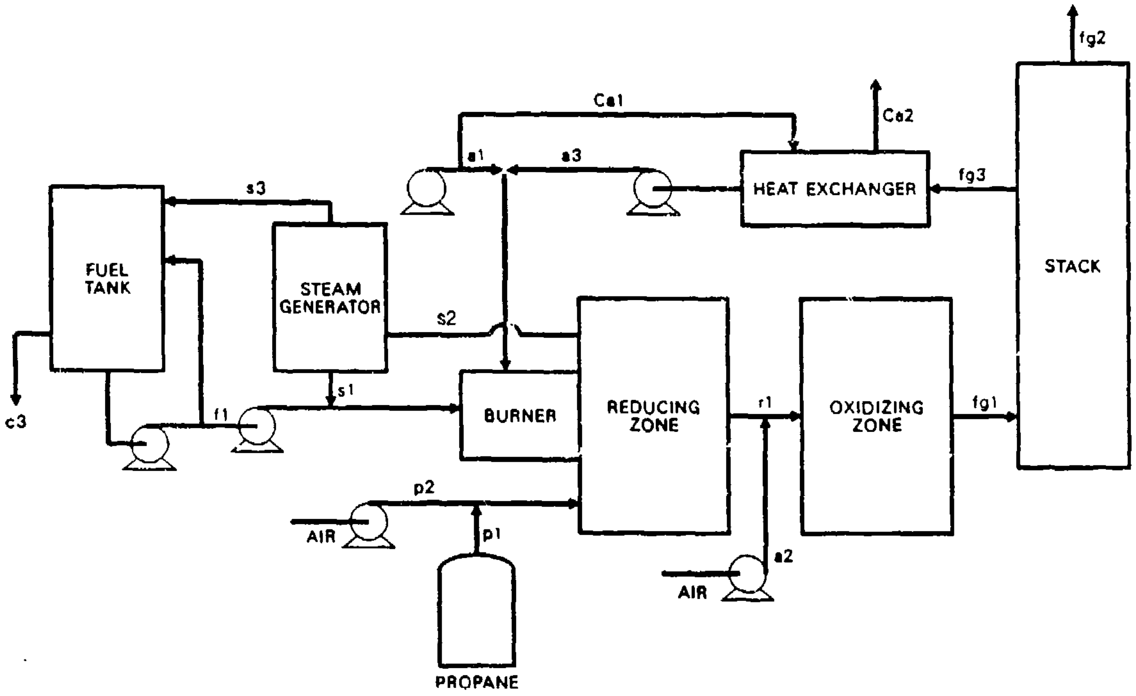

Fig. 4.1. Process flow sheet

4.2.1 Process flow sheet

Figure 4.1 and Table 4.1(a) and (b) summarize the flow sheet for 146 kW (0.5 × 10^6) and 732 kW (2.5 × 10^6 Btu/h) heat load. The proof-of-principle test includes a large number of conditions, certainly more than 20 and possibly more than 100. The process flow sheet shown in Fig. 4.1 represents the low and high end of potential heat loads to be used.

4.2.2 Material and energy balance

An analysis of the design must start with material and energy balances. The 732-kW (2.5 × 10^6 Btu/h) condition shown in Fig. 4.1 is a limiting case that can be used for sizing major components. The 732-kW (2.5 × 10^6 Btu/h) case has been selected for a detailed material and energy balance.

The material balance is summarized in Table 4.2. The corresponding flows are shown in Fig. 4.2. The detailed calculations are shown in

Table 4.1(A). Process flow sheet — 732 kW (2.5 × 10^6 Btu/h)

Stream	Material/composition		Flow rate (kg/h)	Temperature (°C)
a1 Primary air		Air	425	21
a2 Secondary air		Air	716	21
a3 Recycle flue gas	6.7%	O_2 (by volume	155	260
	82.1%	N_2 dry)		
	11.2%	CO_2		
	0.14lb	H_2O/lb dry gas		
f1 Fuel	20%	Comp. B (by wt.)	68.8	21
	30%	Toluene		
	50%	No. 5 fuel oil		
p1 Pilot fuel		Propane	0.8	21
p2 Pilot air		Air	13.6	70
s1 Atomizing Steam		H_2O	19.1	150 (saturated)
s2 Steam Injection		H_2O	83.9	150 (saturated)
s3 Steam to heat fuel tank		H_2O	8.5	150 (saturated)
c1 Condensate from fuel tank steam		H_2O	8.5	65
r1 Combustion gas from red zone	CO	14.0% (by volume)	787	1196
	H_2O	32.1%		
	N_2	52.3%		
	CO_2	1.6%		
fg1 Combustion gas from ox zone		Same as recycle flue gas	1504	1277
fg2 Flue gas		Same as recycle flue gas	1349	650
fg3 Flue gas (recycle)		Same as recyle flue gas	155	1090
ca1 Cooling air for flue gas recycle		Air	910	21
Ca2 Cooling air for flue gas recycle		Air	910	190

Table 4.1(b). Process flow sheet — 146 kW (0.5 × 10^6 Btu/h)

Stream	Material/composition	Flow rate (kg/h)	Temperature (°C)
a1 Primary air	Air	55.8	21
a2 Secondary air	Air	143	21
a3 Recycle flue gas	5.2% O_2 (by volume, 82.5% N_2 dry) 12.3% CO_2 0.149 lb H_2O/lb dry gas	156	260
f1 Fuel	20% Comp. B (by wt.) 30% Toluene 50% No. 5 fuel oil	12.9	21
p1 Pilot fuel	Propane	0.8	21
p2 Pilot air	Air	13.6	21
s1 Atomizing steam	H_2O	19.5	150 (saturated)
s2 Steam injection	H_2O	19.5	150 (saturated)
s3 Steam to heat fuel tank	H_2O	1.6	65
c1 Condensate from fuel tank steam	H_2O	1.6	65
r1 Combustion gas from red zone	CO 8.7% (by volume) H_2O 29.7% N_2 56.7% CO_2 5.6%	259	1120
fg1 Combustion gas ox zone	Same as recycle flue gas	401	1180
fg2 Flue gas	Same as recycle flue gas	245	650
fg3 Flue gas (recycle)	Same as recycle flue gas	156	1090
ca1 Cooling air for flue gas recycle	Air	910	21
Ca$_2$ Cooling air for flue gas recycle	Air	910	190

Table 4.2 Material balance for 732 kW (2.5 × 10^6 Btu/h)

Stream	Flow Rate (kg/h)
Reducing zone inputs	
Fuel	
Comp. B	13.7
No. 2 fuel oil	34.4
Toluene	20.6
Pilot fuel (propane)	0.82
Combustion air	446
Pilot air	13.8
Atomizing steam	19.1
Steam injection	83.9
Recycle flue gas	
N_2	104
O_2	10
CO_2	22
H_2O	19
Oxidizing zone inputs	
Combustion gas from reducing zone	
N_2	461
CO	123
CO_2	22
H_2O	182
Secondary air	716
Oxidizing zone output (flue gas)	
N_2	1010
O_2	96
CO_2	215
H_2O	182
Recycle flue gas	155
Flow out stack	1348

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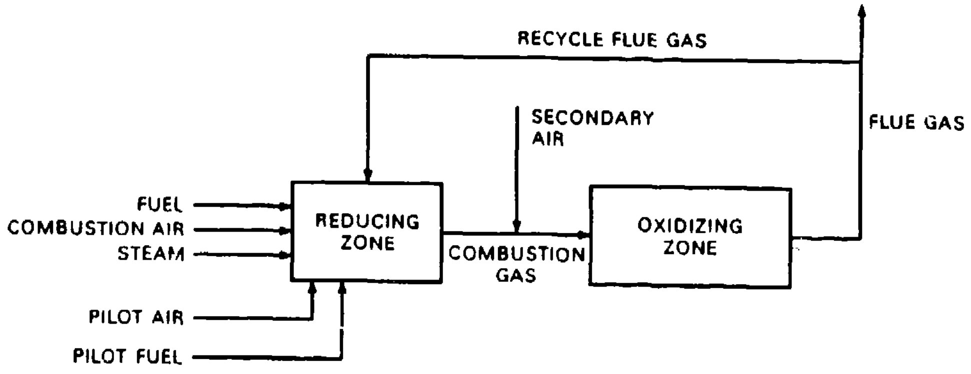

Fig. 4.2. Flows for material balance calculations

Appendix D. The energy balance is summarized in Table 4.3. Following are the assumptions used in formulating the energy balance:

1. the refractory system is as specified in Sect. 4.3.1;
2. the combustor is fabricated from carbon steel;
3. the ambient air temperature is 21°C (70°F), with no forced convection;
4. heat losses from the ends and transition section of the combustor are negligible; and
5. the order of combustion is H_2 burning to H_2O, C burning to CO, and CO burning to CO_2 (this model is explained in Sect. 5.2.1).

Table 4.3 Energy Balance for 732 kW (2.5×10^6 Btu/h)

	Temperature (°C)	Energy flow Stream (kW)
Reducing zone inputs		
Fuel	21	389 (heat of combustion)
Combustion air	21	0
Recycle fuel gas	260	24.9
Steam	151	76.2
Oxidizing zone inputs		
Combustion gases	1200	741 (sensible heat)
Air	21	0
Unburned fuel	N/A	344 (heat of combustion)
Flue gas	1280	791
Reducing zone heat loss		10.8
Oxidizing zone heat loss		31.6

4.2.3 Piping and instrumentation diagrams

The P&IDs for the combustor and the fuel preparation system are shown in Figs. 4.3(a) and (b), respectively.

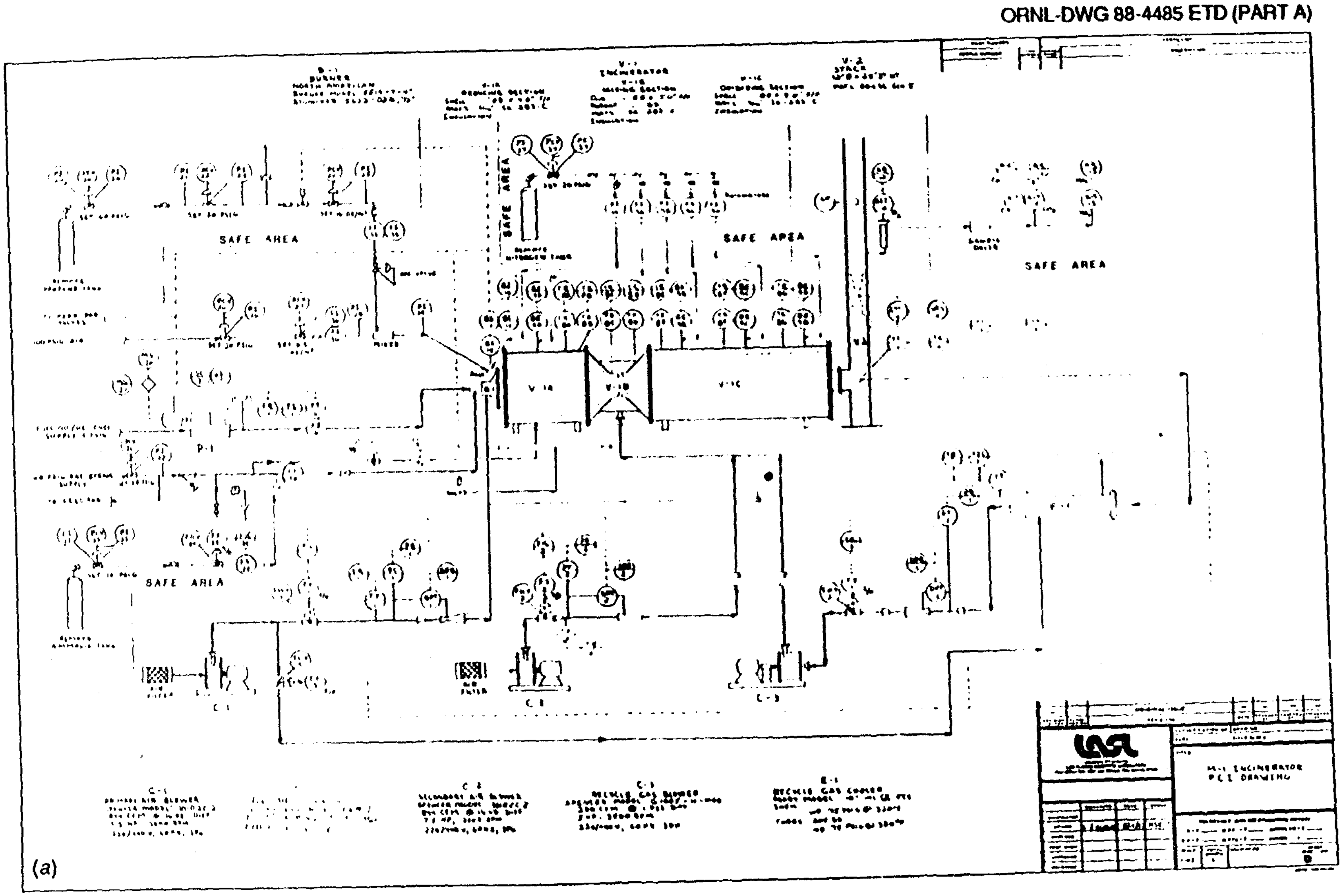

Fig. 4.3. Piping and instrumentation diagram for (*a*) the combustor and (*b*) the fuel preparation system.

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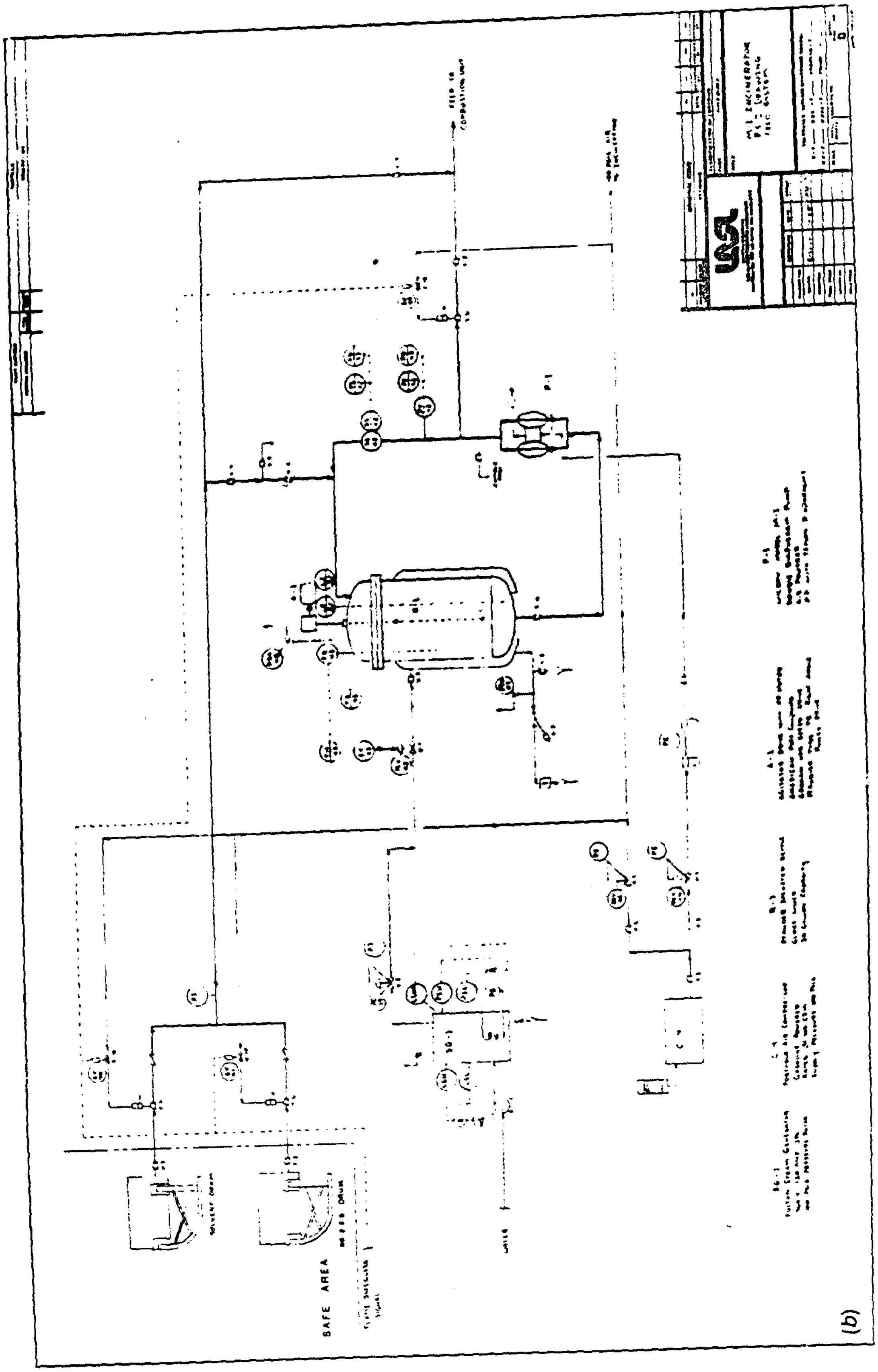

Fig. 4.3 (continued)

4.3 Component Design

The six major components are the refractory, instrumentation and controls, the combustor, the fuel preparation system, the burner assembly, and the NO_x abatement system.

4.3.1 Refractory system

The main reason for not restarting the 1987 test program was failure of the insulation used in the reducing zone and throat. Because the insulation totally failed in those areas, the combustor had to be discarded. The demands on the proof-of-principle refractory system are far greater than those placed on most refractory systems.

The 1987 system consisted of two layers of fiber blanket in the reducing and oxidizing zones that were held in place by a sprayed-on fixative. Castable insulation was used in the throat area. The fixative in the reducing zone failed, causing the top of the blanket to droop. The castable insulation cracked and fell from the throat area. Photographs of the refractory system at the conclusion of testing are included as Figs. 4.4 and 4.5.

4.3.1.1 Refractory requirements. The refractory system used in this test is subjected to extremely demanding conditions. It is thermally cycled daily, it is exposed to a highly reducing atmosphere, the hot face temperature may occasionally exceed 1370°C (2500°F), and the thermal gradient is very high. The specific requirements are listed below.

1. The system must be anchored. Any metal anchors embedded in the refractory cannot exceed 1090°C (2000°F) service temperature. A self-anchoring system is highly desirable.
2. The hot face service temperature must be 1650°C (3000°F).
3. The cold face of the refractory system must be <340°C (650°F) at maximum service temperature.
4. The hot face must have minimum open porosity and high spall resistance. Elemental carbon that is produced at reducing conditions can settle in cracks and pores and burn to CO_2 once the combustor is

PHOTO CN88-1307A

Fig. 4.4. Reducing zone blanket insulation at conclusion of testing

PHOTO CN88-1315A

Fig. 4.5. Castable insulation in throat at conclusion of testing

converted back to oxidizing conditions, resulting in very high localized temperatures.

5. A resilient backup material must accommodate thermal expansion.
6. The refractory must provide for a minimum heat loss of 3.8 kW/m^2 (1200 Btu/h/ft^2) at a hot face temperature of 1370°C (2500°F), with a carbon steel shell, no forced convection, and an ambient temperature of 21°C (70°F).

4.3.1.2 Alternatives. The alternative refractory materials considered include firebrick, fiberboard, blanket, and castable insulation. All of the alternatives evaluated required a combination of insulating materials to meet the requirements stated previously.

A high alumina firebrick with a ceramic fiber blanket backing material is the only combination of materials that met all of the requirements. Firebrick is self anchoring, it can withstand 1820°C (3300°F) on the hot face, it resists spalling, and it has minimum internal stress during thermal cycling. Fiberboards do not have the strength required for this application. Castable insulation would crack because of thermal cycling. Blanket systems are a poor choice for the hot face because they are too porous and depend on an anchoring system for structural support.

4.3.1.3 Drawings and specifications. The assembly drawings and specifications for the proposed refractory system are included in Appendix E. The specifications cover materials of construction and assembly requirements. The assembly methods called for are standard industrial practices.

4.3.1.4 Reliability. The requirements included in Sect. 4.3.1.1 can be summed up simply: "the refractory system must last for the duration of the test program." Reliability was the overriding concern in selecting materials and designing the system. Daily thermal cycling during the 60- to 90-d test program and the lack of a heat removal system, such as a water wall, result in performance requirements that exceed those of a refractory that might be used for this application at the plant-scale.

High-alumina firebrick has drawbacks in heating rate because it has a high thermal mass, it is more expensive than other brick (approximately three times the cost of other 1650°C firebrick), and it may be more expensive to install than other refractory systems. However, it is strongly recommended because it has the highest probability of lasting for the duration of the test program.

4.3.2 Instrumentation and controls

All mass flows entering and exiting the combustor, temperatures inside the combustor, and the flue gas composition must be measured and recorded in real time. Fuel and air flow must be controlled to obtain the desired heat input rates in each zone.

4.3.2.1 Fuel flow. The fuel must be metered and controlled. The primary means of measuring fuel flow is the mass flowmeter located between the positive displacement pump and burner assembly.

During the 1987 tests, the fuel mass flowmeter gave erratic readings in the field, yet it worked fine in the shop. The vibration induced by the pumps and the burner probably caused the problems. The K-flow model K-20™ flowmeter uses a quiet mode oscillation™ system to drive flow tubes at their second harmonic, thus isolating the flow measurement system from external disturbances, such as pumps.

The fuel pump is a full displacement diaphragm pump. Its volumetric pumping rate can be closely correlated to pump speed. The pump speed will be transmitted to the control room and will serve as a backup means of determining fuel flow rate.

4.3.2.2 Air flow. The combustion air flow to the system must be measured and controlled very closely to avoid overheating. High flow tubes, such as the Fluidic Techniques, Inc. model HHR-I, coupled with absolute and differential pressure transducers and a thermocouple provide the data needed to determine air flow rate. The flow is controlled with butterfly valves fitted with valve positioners to eliminate hysteresis.

During the 1987 test program, one of the differential pressure transducers was not reading correctly in the field, but tested fine in the calibration shop. Transducers are occasionally prone to error at high temperatures despite manufacturers' claims otherwise. To eliminate this problem, the transducers should be mounted several feet from the combustor behind a reflective shield to prevent heating. A manometer in parallel with each transducer provides an inexpensive and highly reliable method of checking the transducer in the field.

4.3.2.3 Temperature measurement. The temperature will be measured at two locations in the reducing zone, one location in the throat, and three locations in the oxidizing zone. Platinum/rhodium thermocouples with a platinum-rhodium alloy sheath rated at 1650°C (3000°F) are needed to withstand the high temperature and hostile atmosphere inside the combustor.

The combustor shell temperature is needed to estimate heat losses. Thermocouples attached directly to the shell or a pyrometer could be used to estimate the average shell temperature for each zone. Type K thermocouples will be used to monitor and record other temperatures, as specified in the P&IDs.

4.3.2.4 Flame supervision. The flame control system was a continual source of problems during the 1987 tests. An off-the-shelf microprocessor-based system, such as the Fireye Flame Monitor™, provides all of the necessary functions and is highly reliable. The flame supervision system would be switched out of the circuit above 760°C (1400°F) as allowed by NFPA86, Paragraph 4-6.4.2, exception 9 (Ref. 12).

4.3.2.5 Data collection and display. Programmable strip chart recorders, such as Yokogawa Corporation µR 100 series™, provide the primary means for data monitoring and collection. If readily available, a computerized data acquisition system could be used to collect data in parallel with the strip chart recorders.

The lines used to transmit data from the combustor to the control room are several hundred feet long. Although interference and attenuation were not detected in the 1987 tests, signal problems can always occur with long lines. Attenuation or interference could be eliminated with signal conditioning, improved grounding and shielding, alternate transmission methods (such as voltage to current or voltage to frequency convertors), alternate transmission media (such as fiber optics), or a combination of these techniques.

4.3.2.6 Flue gas analysis. The flue gas is continuously analyzed for O_2, CO_2, CO, and NO_x. The gas analyzers should be located as closely to the stack as possible to reduce the lag time between a change in flue gas composition and detection of the change.

4.3.2.7 Other instruments. Several other instruments are necessary to monitor flow rates and process conditions. Rotameters monitor pilot fuel, pilot combustion air, ammonia, and nitrogen purge streams. Other instruments will be used to monitor individual components. For example, a steam pressure gage will be used to monitor the performance of the steam generator. The combustion in each zone is monitored with a video camera. The principal criteria for these instruments are that they be simple, reliable, and readily available.

4.3.2.8 Reliability. The proof-of-principle combustor must be operated remotely. Therefore, it is imperative that the instrumentation be highly reliable. Unreliable instruments result in frequent interruptions, loss of data, or loss of important information needed to control the system.

The most important parameters are flow rates and the temperature in each zone of the combustor. Redundancy has been provided for the temperature measurements. Transducers measuring air flow should be mounted so that they can be checked in place and easily replaced if necessary. The fuel flow rate can be checked against pump speed.

4.3.3 Combustion chamber

The combustion chamber is shown in Fig. 4.6. The reducing zone is a cylinder with an outside diam of 1.07 m (42 in.) and a length of 1.22 m (4 ft). The oxidizing zone is the same diam and 2.74 m (9 ft) long. The transition section between the two zones reduces back mixing and

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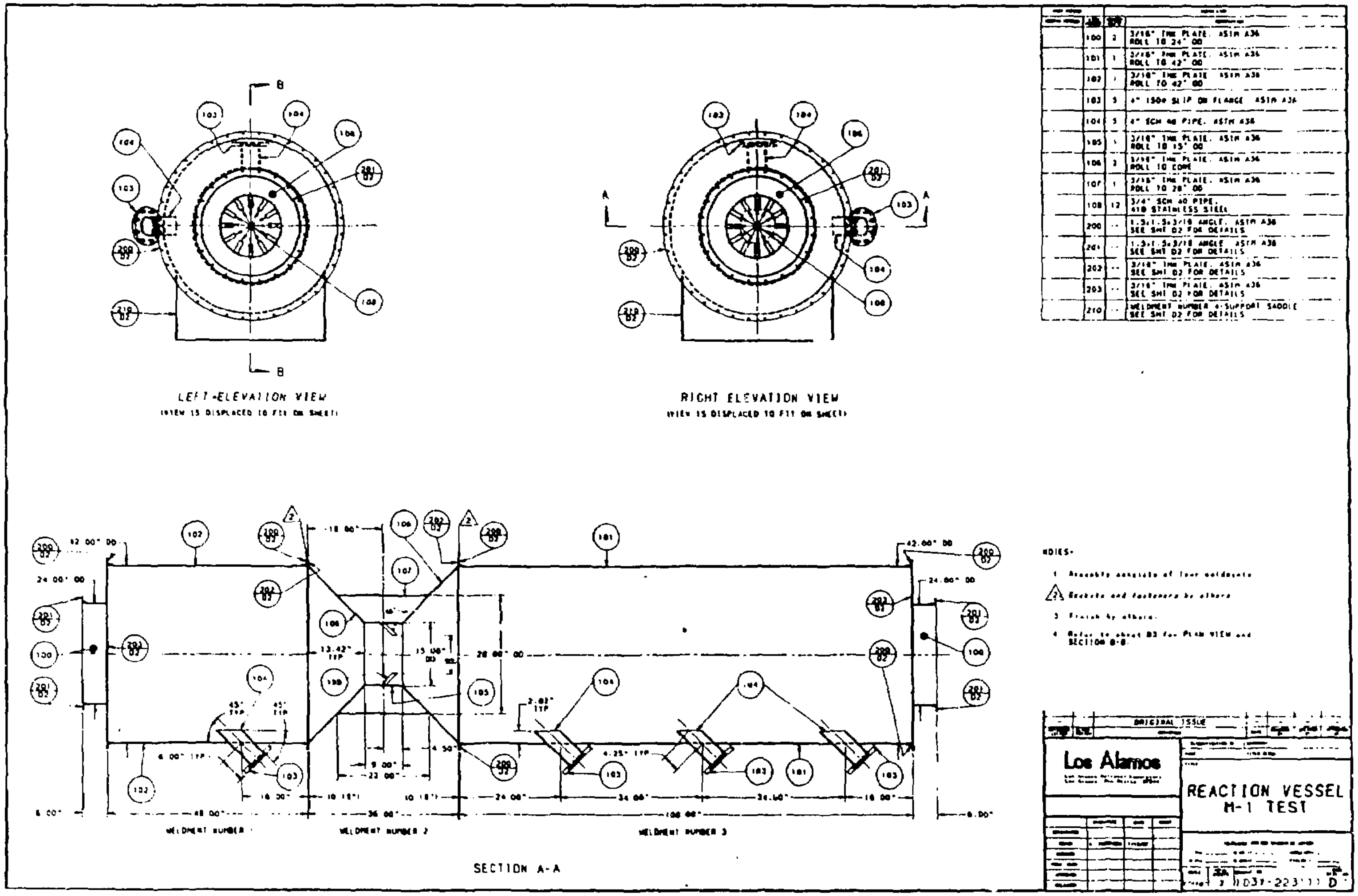

Fig. 4.6. Combustion chamber

provides a header for the secondary air. The primary purposes of the combustor shell are to prevent in-leakage of air, separate the reducing and oxidizing zones, dissipate heat, and support the refractory system.

It is virtually certain that in-leakage of air caused some local overheating in the reducing zone during the 1987 tests. A high temperature silicone gasket will provide a much better seal than the material that was used previously. The ceramic thermowells will be replaced with thermocouple sheaths that can tolerate the conditions in the combustor. The thermocouples will be sealed to the shell with flareless compression fittings. Finally, a sliding damper will be located near the top of the stack to facilitate soap bubble testing of joints if they are removed and replaced for some reason.

Any flow of secondary combustion air from the transition zone into the reducing zone will result in high local temperatures at the entrance to the throat and will bias the NO_x reduction data. Back flow may have contributed to the overheating problems at the top of the transition section when the 1987 tests concluded. The angle of the secondary air tubes has been changed from normal to the combuster axis to parallel to the inside wall between the throat section and the oxidizing zone. This modification should eliminate back mixing.

Approximately 3.1 to 3.5 kW/m^2 (1000 to 1100 $Btu/h/ft^2$) must be dissipated from the shell of the combustor. The temperature and emissivity of the shell determine the radiative heat flux. The two basic choices for construction materials are carbon steel or a stainless steel, such as 18-8. Carbon steel should not be used above 430°C (800°F), whereas 18-8 stainless steel can be used at >560°C (>1050°F).[16] The emissivity is about 0.95 for carbon steel and 0.6 for 18-8 stainless steel. The radiative heat flux is approximately

$$Q_r = \varepsilon\sigma\,(T_e^4 - T_s^4) ,$$

where

Q_r = radiative heat flux,

ε = emissivity of emitter,

σ = Boltzman's constant,

T_e = absolute temperature of emitter,

T_s = absolute temperature of surroundings.

Because T_e could be >560°C (>1050°F) for stainless steel but only 430°C (800°F) for carbon steel, more heat could be dissipated from a stainless steel shell. However, the carbon steel shell can dissipate more heat at a lower temperature. There are several reasons for using carbon steel rather than stainless.

1. The relative high thermal conductivity of the high-alumina firebrick, coupled with the requirement for a maximum temperature of 1260°C (2300°F) at the firebrick/fiber interface, requires a lower shell temperature.
2. Instruments, such as transducers and video cameras in the immediate vicinity of the combustor, are adversely affected by a high shell temperature.
3. Carbon steel is less expensive and easier to fabricate than stainless.

The shell must support the refractory system. The firebrick will weigh 432 kg/lin m (290 lb/lin ft). If the combustor is only supported at its ends (which is a worst case design), neglecting the additional stiffness provided by the transition zone and flanges, the maximum bending stress is still <4.1 MPa (600 lb/in.^{2}). This figure is well below the yield stress for steel at 371°C (700°F).

4.3.4 Fuel preparation and transport

The energetic fuel mixture is mixed in the 115-L (30-gal) Pfaudler™ tank. It is agitated with an impeller and circulated with a double diaphragm pump. The sample port and the feed line to the burner assembly are located on the discharge side of the recirculation pump. The burner feed pump is a model EKM-1 diaphragm metering pump.

4.3.4.1 Fuel mixing. During the 1987 test program, the fuel was mixed in batches in the Pfaudler™ tank. A predetermined amount of toluene and energetic material was placed in the tank. The mixture was heated until the TNT dissolved. The fuel oil was added to the tank, and the recirculation pump and impeller kept the fuel well mixed. This system worked very well.

4.3.4.2 Pumping. A bladder pump was used during the 1987 tests to deliver fuel to the burner assembly. It acted as a classifier when RDX slurries were pumped. The pump bladder was found to be filled with RDX particles during disassembly and cleanup. Trapping RDX particles in the pump is clearly an unsafe situation.

The fuel pump must meet several criteria. Safe operation requires that the pump not have any metal-to-metal pinch points. A positive displacement pump is needed to provide an independent check on fuel flow rate. Ideally, the pump would supply a constant flow to reduce flame pulsing and vibration in the flow-sensing element.

Several alternative pumps were considered for replacement of the bladder pump. The Holston Army Ammunition Plant uses a modified centrifugal pump to transfer slurries containing RDX and HMX.[17] This design has proven to be very safe, and a centrifugal pump provides a constant flow rate; however, a centrifugal pump is not a metering pump.

The U.S. Army Missile Command has purchased a modified Moyno™ pump for pumping very viscous slurries of RDX (>500,000 cp), but it has not yet been placed in service.[18] It is a positive displacement pump that provides a constant flow. LANL opposes using a Moyno™ pump because of safety problems that arose on another project using a Moyno™ pump for a similar application.

The diaphragm pump used in the recirculation line worked very well during the 1987 test program. In general, a diaphragm pump is a very good design for pumping RDX slurries. A full-stroke diaphragm pump provides a high degree of safety and is a positive displacement pump. However, the flow rate at the discharge point is not constant. A pulsation damper could be used to achieve a relatively constant flow rate.

4.3.4.3 Piping. After the system was shut down on June 2, 1987, a small quantity of RDX located at a sudden contraction near the burner tip rapidly decomposed, causing a pressure rise that severed the burner tube. The RDX particles should not have accumulated in the burner assembly. They probably accumulated during the course of testing at the sudden contraction and were not purged during the purge cycle. A second possibility is that the particles flowed from the pump to the burner tube while the fuel sample was taken (after the purge was completed).

The following design changes have been included that prevent RDX particles from accumulating in the burner system.

1. All sudden contractions, enlargements, orifices, and other abrupt changes in the inside diameter of the fuel line have been eliminated.
2. The fuel sample port has been moved to the recirculation line so samples can be taken with no flow in the line to the burner.
3. The burner feed pump is a full stroke positive displacement unit that will prevent RDX particles from accumulating in the pump cavity.
4. A solvent purge system has been included in the system to ensure that no RDX particles remain in the lines or burner assembly after shutdown. The solvent purge system is probably not a workable solution for plant-scale operation, but has been included to facilitate operation of the proof-of-principle test unit until the effectiveness of the other methods can be verified.

4.3.5 Burner assembly

During the 1987 tests, the flame pulsed whenever mixtures that contained toluene were burned. The burner assembly that was used is shown in Figs. 3.6 and 3.7. The inner tube held oil while the annular region contained steam at 150°C (300°F). The boiling point of toluene is 110°C (231°F), so a fraction of toluene was continually flashing out of solution. Flashing caused pressure surges in the oil tube, resulting in a pulsating flame. The flashing could be eliminated with air atomization. Another alternative is to use two annular regions. The outside annulus would contain atomizing steam, the inside annulus would contain water, and the inside tube would contain fuel. This alternative would thermally isolate the fuel from the atomizing steam.

4.3.6 NO_x abatement

The four methods of NO_x abatement that will be tested are staged combustion, flue gas recirculation, steam injection, and ammonia injection. Each of these methods can be tested independently or in combination with each other. Ammonia injection should be considered as the "last resort" for plant-scale operations because of the complexities it introduces in operating a production boiler.

4.4 Other Equipment Specifications

Several major equipment items are called out in the P&IDs. Manufacturers model numbers and capacities are listed in Table 4.4.

Table 4.4 Model numbers for major equipment items

Item	Manufacturer	Model	Capacity
Burner	North American	5514-7	2.8 × 10^6 Btu/h at 1 psig
Pilot	North American	4015-0-T	52,000 Btu at 3.5 in wc
Primary blower	Spencer	30102 C 2	844 scfm at 1 psi
Secondary blower	Spencer	30102 C 2	844 scfm at 1 psi
Recycle blower	Spencer	G-1005-H-MOD	200 scfm at 1 psi and 500°F
Recycle gas cooler	Perry	10-in. 141 FTS	150,000 Btu/h at ΔT_{lm}=900°F
Steam generator	Fulton		460 V, 180 A, 250 lb/h sat. steam at 70 psia

5. OPERATIONAL CONCEPTS FOR PROOF-OF-PRINCIPLE TEST PROGRAM

A critical review of the 1987 test program pointed to several problems that resulted from operational decisions. A number of instrumentation problems resulted in loss of test time until testing had to proceed without key instruments functioning properly. The scope of the test program was too ambitious for the allotted testing time. Finally, the failure of the refractory system resulted in severe damage to the reducing zone and throat sections of the combustor. Operational changes could reduce the stress on the refractory and increase system availability.

5.1 Instrument Reliability

The proof-of-principle combustor was an experimental system. Because the hazards associated with cofiring could not be quantified, the system was operated remotely whenever explosives were being burned. Successful remote operation depends on accurate and reliable instruments.

Several design changes have been made to improve reliability (see Sect. 4.3.2.8). All vital instruments will be checked daily. The combustor will not be operated unless the fuel flow and reducing zone air flows are known.

5.2 Test Program Scope

The 1987 test plan called for 255 test conditions. The length of these tests ranged from an average of 30 to 60 min during the scoping tests to 90 to 120 min during the 12 performance tests. Analysis of the 1987 test data indicates that a scaled-down test program could meet the program objectives. Testing a single-burner gun at one oxidizing condition and one or two substoichiometric conditions would be more manageable but still provide the data needed to optimize the design and operation of the demonstration-scale unit.

The key operating parameters that should be investigated in detail are fuel composition and heat load. Potential NO_x abatement requirements can be met at some ratio of energetic material to fuel oil. One key question is this: Can enough energetic material be cofired at those conditions to make the process economical? The optimal condition for other parameters, such as reducing zone temperature, moisture content, and residence time can be determined by varying the heat load and steam flow rate.

5.3 Improving Reliability of the Refractory System

The firebrick and ceramic fiber refractory system that has been designed should be very durable despite the demanding conditions. However, some operational changes could increase the reliability of the refractory system by reducing localized high temperatures and reducing thermal cycling.

5.3.1 Air leaks in reducing zone

Air leaking into the reducing zone of the combustor results in high local temperatures. Critical joints should be sealed, leak tested, and purged to ensure that air does not leak into the reducing zone.

5.3.2 Shell cooling

Most industrial boilers use a water wall system to cool the shell surrounding the combustion chamber. The water wall system would be expensive and difficult to operate for the proof-of-principle tests. An alternative to water is forced convection air cooling. Fans could be positioned to blow ambient air across the surface of the combustor. Fans are a simple and inexpensive method of providing a small amount of additional cooling if it becomes necessary.

5.3.3 Thermal cycling

The most demanding condition for the refractory system is the daily cycling. If the system could be kept hot at night, it would significantly increase the life of the refractory and would provide more test time each day because the system could be close to the operating temperature when the test crew arrives at the site.

5.3.4 Heating rate

The firebrick will limit the heating rate. A high heating rate produces a high-temperature gradient in the brick, which could cause cracking. Even if a high-temperature gradient is not a problem, the large mass and high specific heat of the brick combine to form a significant heat sink. The slow heating rate will significantly reduce the available testing time if the system is shut down nightly. This is another reason to keep the combustor hot at night.

5.4 NO_x Reduction

In addition to substoichiometric operation and flue gas recirculation, other NO_x reduction techniques are planned for the next series of tests. Specifically, they include steam injection in the reducing zone and ammonia injection in each zone. Steam and ammonia will provide a source of hydrogen, which tends to reduce NO_x to N_2.

5.4.1 Stoichiometric conditions

The primary method used to control the reducing zone temperature during the 1987 tests was adjustment of the air/fuel ratio. At substoichiometric conditions, the combustion temperature increases with increasing air flow.

The relationship between heat release and stoichiometric conditions is not linear and cannot be predicted precisely for a nonequilibrium process, such as combustion. Once the bonds holding the organic molecules together begin to break, a number of atoms, free radicals, and submolecular groups are available to react with oxygen. Hydrogen and OH radicals react quickly to form water. Elemental carbon reacts more slowly because it is a solid. Carbon will first react to form CO and then further oxidize to CO_2. To estimate heat release rates, the following model is used.

$H_2 + 1/2\ O_2 \text{ ---> } H_2O$	reaction 1
$C + 1/2\ O_2 \text{ ---> } CO$	reaction 2
$CO + 1/2\ O_2 \text{ ---> } CO_2$	reaction 3

The predicted relationship between reducing zone temperature and stoichiometric air for No. 2 fuel oil at 147 kW (500,000 Btu/h) for several ratios of steam to fuel is shown in Fig. 5.1. The hydrogen consumes the first 30% of the air. At 65%, all of the carbon has oxidized to carbon monoxide. At that point, the heat release rate increases substantially because reaction 2 produces 9.19 kJ/g carbon (3950 Btu/lb), whereas reaction 3 produces 23.56 kJ/g carbon (10130 Btu/lb). Although

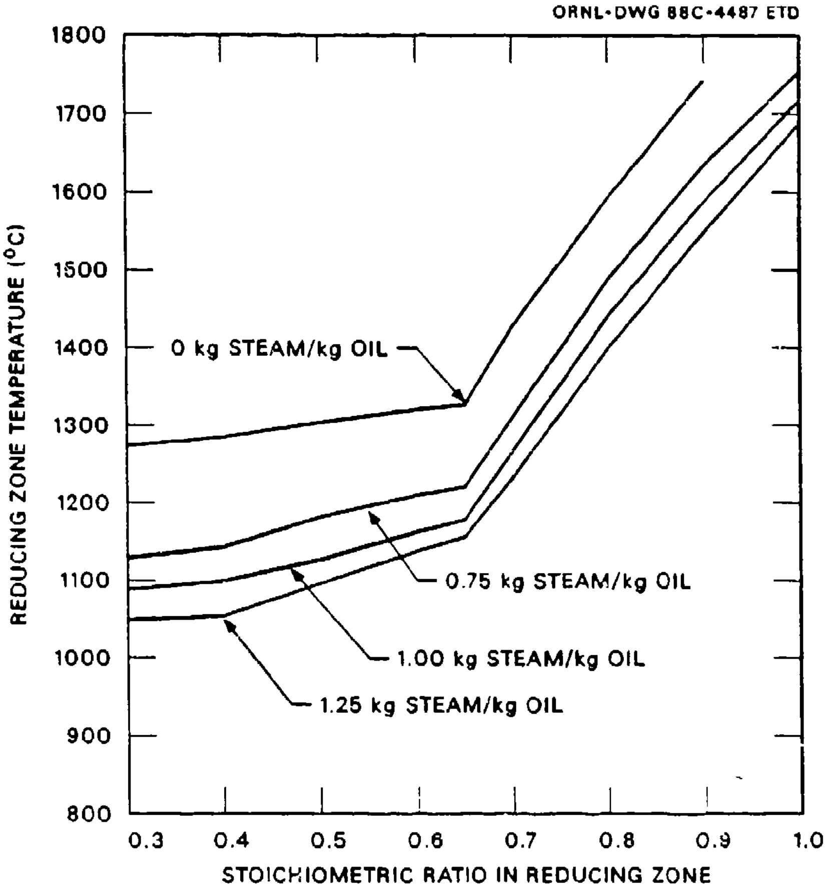

Fig. 5.1. Reducing zone temperature vs stoichiometric ratio for No. 2 fuel oil at 146 kW (0.5 × 10^6 Btu/h)

this model is a simplified one, it indicates that the reducing zone temperature will be much more sensitive to the amount of combustion air at a stoichiometric ratio >65%.

Operating below 65% of stoichiometric conditions does not substantially decrease the reducing zone temperature but does produce elemental carbon. At the conclusion of testing, the combustor must be converted from reducing to oxidizing conditions. Any elemental carbon stuck to the wall of the reducing zone begins to burn and creates very high local temperatures near the refractory. This condition can be very damaging to the refractory. The slightly lower temperatures obtainable below 65% are clearly not worth the potential damage that can be done to the refractory material by operating in this range.

5.4.2 Steam injection

Steam injection is a simple technique used in commercial incinerators to control NO_x. It is particularly attractive in this application because it could also be used to control combustion temperature. Furthermore, in the plant-scale application where energetic materials are used as a supplemental fuel in a boiler, a source of steam is readily available.

Elemental carbon reacts with steam to form hydrogen and carbon monoxide. The hydrogen then reduces NO to N_2.

$C + H_2O \longleftrightarrow CO + H_2$ (water gas reaction)

$NO + H_2 \longleftrightarrow H_2O + 1/2\ N_2$ (NO reduced by H_2)

5.4.3 Ammonia injection

Ammonia injection is another technique to reduce NO_x. At 950°C (1750°F), 90% of the NO can be removed at a NH_3/NO molar ratio of 1.6 (Ref. 19). Tests conducted by Dr. Kwak at the Tooele Army Depot indicate that 50% reduction of the NO_x can be achieved using ammonia injection while cofiring energetics and fuel oil in an APE-1236 deactivation furnace.[20] Dr. Kwak believes that a 75% reduction is theoretically possible for the APE-1236 process.

$$4\ NH_3 + 6\ NO \longleftrightarrow 5\ N_2 + 12\ H_2O \qquad \text{(NO reduced by } NH_3\text{)}$$

The proof-of-principle system design described in Chap. 4 includes ammonia injection. It is clearly feasible to use ammonia injection to control NO_x in this application. However, ammonia injection would further complicate operation of an industrial boiler. It is considered as an option for testing but would only be used if the other options cannot achieve satisfactory results.

6. CONCLUSIONS

Cofiring is a feasible method for economic disposal of unserviceable PEP materials as was demonstrated in a 300-kW (10^6 Btu/h) combustor at LANL in 1987. The 1987 tests showed that

1. energetic materials can be cofired using an off-the-shelf burner gun while meeting RCRA and NSPS requirements (for boilers <100 MBtu/h). The proposed RCRA standard for DRE is 99.99%. The DRE was >99.9996% for TNT and >99.9998% for RDX. The proposed RCRA standard for CO is 100 ppm over a 60-min period (at 7% O_2). The average CO concentration while burning a mixture containing 20% Comp. B was 83 ppm (at 7% O_2). There are no NSPS requirements for boilers <100 MBtu/h that would apply to this process.
2. cofiring energetic materials does not adversely affect flame characteristics. At oxidizing conditions, flame stability seemed to be more closely related to the presence of solvent than the presence of energetic materials.
3. substoichiometric operation provides incremental NO_x reduction as high as 80%. However, data in published literature indicate that there is no need to operate at extremely reducing conditions (e.g., <50% of stoichiometric air), which is where the proof-of-principle unit was operated.
4. cofiring can be conducted safely, but the design used for these tests was inadequate for the severe conditions and thermal stresses. The improved design and operating procedures described in Chaps. 4 and 5 will enhance the reliability and operability of the test system.
5. designing a combustion chamber to cofire energetics at reducing conditions is a more complex than designing a combustion chamber to cofire energetics per se. The integrated design of refractory, instrumentation, and control systems is key to successful operation.
6. mixtures of energetic materials, solvents, and fuel oil can be prepared by conventional processes and procedures.
7. zones where RDX particles may settle out or accumulate cannot be tolerated.

7. RECOMMENDATIONS

The need remains to develop a safe, economical, workable, and environmentally acceptable process to dispose of unserviceable PEP materials. Cofiring can meet this need, but more development work is required. The following recommendations are directed toward developing a cofiring process that meets the Army's PEP disposal requirements.

1. Continue with the proof-of-principle test program with the modifications cited in recommendations 2-4.
2. Use the information presented in Chaps. 4 and 5 in designing and operating the test system. This information is based on field experience with a cofiring process and addresses all of the known problems encountered during the 1987 proof-of-principle tests.
3. Develop a test plan that concentrates on evaluating fuel composition and heat load as the two principle parameters. Detailed tests of staged combustion and various flue gas recycle rates will not provide as much useful data per test as can be gained by concentrating on these two items.
4. Evaluate NO_x reduction with steam injection and ammonia injection in addition to staged combustion and flue gas recycle. Steam injection is simple, it provides a mechanism to prevent overheating during transient operation, and it is a proven NO_x reduction technique. Ammonia injection is not as simple for plant-scale operation in a boiler, but it is easy to test and has the potential for achieving very high NO_x removal rates.
5. Consider using energetic materials as a supplemental fuel for processes that already have a RCRA operating permit. It is virtually certain that boilers that cofire hazardous wastes will have to become RCRA-permitted facilities in the next few years. Cofiring in an incinerator that burns explosive contaminated waste reduces the administrative workload associated with operating a RCRA-permitted disposal facility. It also defuses some of the safety issues associated with introducing high explosives into an industrial boiler.

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Appendix A

LETTER REPORT ON STATUS OF PROOF-OF-PRINCIPLE TEST SYSTEM, JUNE 26, 1987

LETTER REPORT ON STATUS OF TESTING AND CONDITION OF EQUIPMENT FOR SUPPLEMENTAL FUELS TEST PROGRAM

SUMMARY

A proof-of-principle test burn of fuel oil and fuel oil/energetic material mixtures was conducted at Los Alamos National Laboratory from 5/19/87 to 6/2/87. The test program was discontinued due to structural degradation of the insulation in the reduction zone of the combustor and damage to the burner tip.

A considerable amount of data have been collected to date. The data indicate that energetic materials can be used to supplement fuel oil in industrial boilers. The Army Environmental Hygiene Agency (AEHA) obtained particulate and organic data on the flue gas for the background case (No. 5 fuel oil and toluene) and for a mixture of fuel oil, toluene, and Comp. B. However, more data is needed before proceeding with a full scale demonstration in an industrial boiler. This report describes the equipment problems as they currently exist and provides some design and operational changes to prevent the problems described from recurring.

DESCRIPTION OF EQUIPMENT

A schematic of the system is shown in figure 1. The system was designed to operate sub-stoichiometric in the reduction stage in order to reduce the NO_2 in the energetic mixture to elemental nitrogen and to control the temperature of the reducing stage. The system was started up at oxidizing conditions (typically 100% excess air in the reducing stage). The excess air was gradually reduced until the oxidizing stage reached a temperature high enough to support combustion, and the reducing zone was quickly converted to reducing conditions.

The instrumentation consisted primarily of mass flow meters, flue gas analyzers, and a thermocouple in each stage. The flow rate of fuel, total air, air supplied to the oxidization stage, and flue gas were measured with mass flow meters. The oxygen, carbon dioxide, carbon monoxide, and NO_x in the flue gas was monitored with on-line gas analyzers.

TEST SEQUENCE

The Army Environmental Hygiene Agency conducted three tests on the last day the combustor was operated. Several problems were evident at that point, but the gas temperatures and flue gas composition were near the target values at the conclusion of the last run. A chronological summary of the last several days of operation is given below.

5/27/87. Burned a HE mixture consisting of 40% TNT in toluene. The maximum temperature in the reducing stage reached 1934^{o}F at 1.1 lb/min fuel flow and 5.1 lb/min of air to the reducing stage. The flue gas exiting the oxidizing stage was 1581^{o}F.

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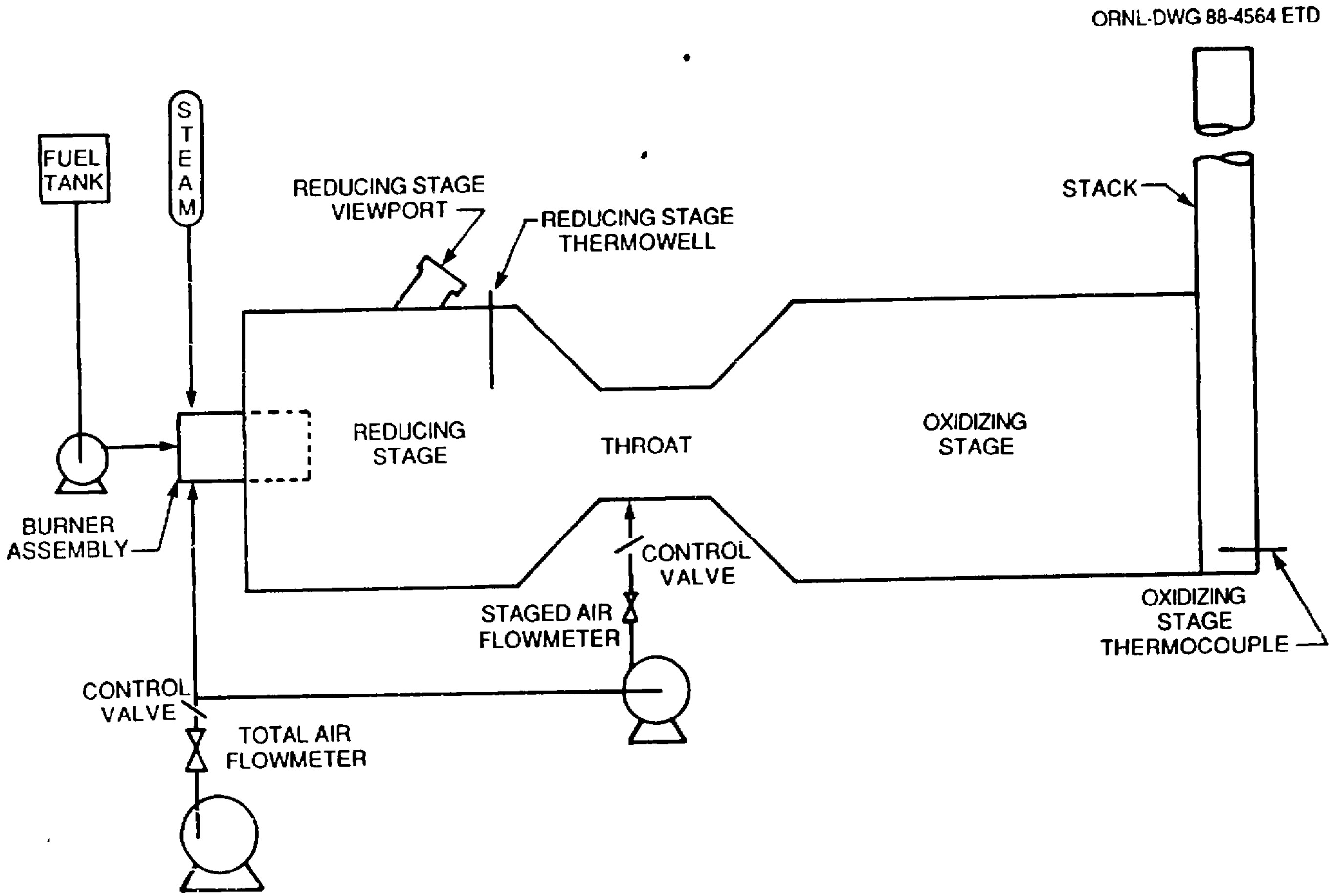

Fig. A.1. Combustor system schematic diagram

5/28/87. Burned a HE mixture consisting of 20% Comp. B, 40% toluene, and the balance No. 2 fuel oil. The maximum temperature in the reducing stage reached 2009°F at 1.2 lb/min fuel flow and 2.2 lb/min of air to the reducing stage. The flue gas exiting the oxidizing stage reached 1481°F .

5/29/87. Burned a mixture of 37% toluene and the balance No. 5 fuel oil. The oil flow meter read 1.1 lb/min, but acted erratic. A material balance yields approximately 1.1 lb/min fuel flow. The air flow to the reducing stage was 2.3 lb/min. The reduction zone temperature was 1900°F, the flue gas exiting the oxidizing stage was between 1430 and 1450°F. This was the first run for the AEHA tests.

6/1/87. Attempted to burn 37% toluene in No. 5 fuel oil. The flow meter on the oxidizing stage air line was not working. The transducer checked out fine, and the electrical line to the control room checked out. Since the problem could not be isolated, the pressure sensing lines from the oxidizing stage air venturi were rerouted to the recycle air transducer. The system was restarted with No. 2 fuel oil and operated for a short time. The reducing stage temperature was 1860°F, the flue gas temperature was 1425°F, and the air input to the reducing stage was 4.6 lb/min. The fuel flow meter was reading erratically. Since the fuel flow meter was not working properly, the oil flow was calibrated against the pump speed, resulting in a very linear curve.

Upon examining the unit after shut down, there was evidence of overheating in the reducing stage near the view port (the stainless steel bolts closest to the combustor were severely galled), and the fiberfax insulation was drooping slightly in the vicinity of the reducing stage view port.

6/2/87. Started the system up on no.2 fuel oil at oxidizing conditions with no problems. The reducing stage temperature went above 2500°F upon changing to reducing conditions burning 37% toluene in No. 5 oil. The flowmeter monitoring air entering the oxidizing zone indicated more flow than the total air meter. The flue gas composition and oxidizing zone temperatures were normal. The decision was made to operate the combustor in the most reducing conditions obtainable and to continue testing. The high temperature reading in the reducing zone was thought to be caused by a crack in the thermal well, thus allowing combustion within the thermal well. There was no explanation for the difference in flow readings between the total and staged air.

The first run was concluded at approximately 1:30 p.m. The combustor was brought back to oxidizing conditions before the second run, resulting in very high temperatures as the carbon burned out of the reducing stage. The skin of the combustor was showing signs of overheating on the top of the conical section between the reducing chamber and the throat.

The second run started at 2:45 p.m. The temperature in the reducing stage was reading below 2260°F. Every attempt was made to operate in the most reducing condition possible, resulting in the loss of the UV signal on at least one occasion. The combustor operated fairly steadily throughout the run which concluded at 4:35 p.m. At the conclusion of the run, the combustor was switched to No. 2 fuel oil and the indicated temperatures dropped drastically.

The third run started at 6:40 p.m. The reducing stage temperature was reading off scale (above 2550°F), but probably peaked only slightly above that point. The fuel flow meter, oxidizing stage temperature, and oxygen in the flue gas indicated that the fuel flow was well below the target of 1 lb/min. The pump speed was increased from 39 to 71 (arbitrary scale) to bring the fuel flow back up to the target rate.

By 7:10 p.m., the flow indication on the total air meter was creeping up, with no corresponding change in the oxidizing stage air, indicating an increase in stoichiometric air in the reducing stage. An attempt was made to decrease the total air flow. The UV signal was lost four times between 7:07 p.m. and 7:15 p.m., so the total air was set to maintain a difference in flow rates between the total air and oxidizing stage air of 0.5 (with the staged air reading higher).

At 7:25 p.m., the oil flow meter suddenly jumped from 1 lb/min to 2.2 lb/min. This change was accompanied by an immediate increase of 425°F in flue gas temperature, a decrease from 10% to 4% in oxygen in the flue gas, and an increase in CO_2, CO, and NO_x in the flue gas. All indications were that the fuel feed rate had indeed doubled. The fuel feed pump speed was decreased from 71 to 40 (arbitrary scale) and the temperatures and flue gas composition seemed to return to more normal conditions. The last half of the run was stable, with the reducing stage temperature dropping to 2240-2280°F, and the oxidizing stage temperature increasing to 1387°F.

After the third run was completed, the unit was run on No. 2 fuel oil for five minutes to purge the energetic material from the lines. After the purge was complete, the fuel flow was stopped and the unit was allowed to cool. There did not seem to be as much carbon in the reducing stage as on previous runs because the reducing stage temperature never did come up once the fuel flow was cut off.

The total air was decreased to below 10 lb/min to slow the rate of cooling. After a short time, the flue gas analyzer showed high concentrations of CO and CO_2, and low concentrations of O_2. Upon examining the combustor, it was determined that the hose that fed air to the reducing stage had failed, so the only air being fed to the stage was the pilot air. The pilot eventually went out, either because the UV detector lost its signal, or for some other reason (causing the UV detector to lose its signal). The reducing stage air hose was repaired and the combustor was shut down.

6/3/87. Upon arriving at the site, LANL personnel found damage to the burner and insulation. The decision was made to discontinue the test program until the insulation problems could be solved.

DESCRIPTION OF HARDWARE PROBLEMS

The test program was discontinued due to structural degradation of the insulation inside the combustor and due to damage to the burner tip. The two problems appear to be unrelated.

The insulation in the reducing and oxidizing zone consisted of a blanket- type material called "fiberfax". The blankets were treated with a fixative to keep them from collapsing. The insulation in the throat section consisted solely of castable insulation. The insulation in the reducing chamber collapsed, exposing the top half of the combustion chamber. The castable insulation in the throat area cracked and fell from the top half of the throat, exposing the throat area as well.

The tip of the burner was separated from the tube that carried fuel and atomizing steam to the combustion zone. The tube was swelled and split about 1/2 to 3/4 inches from the end. The remainder of the burner assembly was intact. The end of the burner tube is being examined by metallographic means to assist in analyzing the mode of failure.

POSSIBLE CAUSES OF HARDWARE PROBLEMS

The insulation probably failed because the combustor was run at a higher temperature than the insulation fixative was rated for, or it collapsed due to thermal cycling. It may have failed due to a combination of the two.

The burner tip probably failed subsequent to shut down due to rapid decomposition of a small quantity of RDX deposited in the fuel line near the burner tip. The hypothesis is that RDX remained in the fuel line after the burner was purged and shut down. The RDX was then heated slowly in the burner tip, (due to loss of air flow described above) causing it to rapidly decompose to lower molecular weight gaseous compounds. This resulted in a sudden pressure rise. Metallographic analysis is being performed to determine if the condition of the burner tip supports this hypothesis.

RECOMMENDATIONS

The testing completed to date indicates that it is feasible and safe to burn energetic materials in an industrial boiler. However, more data is needed before proceeding with a full-scale demonstration project using an existing boiler. The proof-of-principle test unit should be repaired and testing should proceed as planned prior to the problems described in this report. The following specific design and operating changes are recommended before the testing proceeds:

1. Redesign the insulation in the reducing stage and throat so that it can operate at 2500°F, with a maximum design temperature of 2700°F.

2. Make the changes necessary to operate the combustor at 1.5 - 2.0 million BTU/hr. Higher fuel feed rates will reduce the chance that RDX will settle out of the oil/toluene solution, which may have contributed to the burner failure. The atomizer nozzle should be redesigned to prevent pre-heating of the fuel/energetic mixture prior to atomizing.

3. Provide backup instrumentation so that if an instrument fails, a second instrument is in place and available to aid the operators in making decisions.

4. Provide the capability to leak check the reducing stage before starting the system up. A leak in the reducing stage will produce very high local temperatures, which could cause an insulation failure.

5. Purge the burner assembly with acetone followed by fuel oil after burning Comp. B or RDX.

Appendix B

LETTER REPORT ON DISASSEMBLY AND INSPECTION OF THE PROOF-OF-PRINCIPLE TEST SYSTEM, JULY 25, 1988

DISASSEMBLY AND INSPECTION OF THE HE/FUEL OIL COMBUSTION TEST UNIT

L. A. Stretz
Los Alamos National Laboratory
Group M-1

Introduction

A proof-of-principle combustion test on mixtures of high explosives with fuel oil or solvents was conducted in May and June of 1987. A considerable amount of data on combustibility, flame characteristics, and off-gas emissions of such mixtures was obtained during the testing. However, degradation of the combustion test unit led to termination of the testing prior to completing all desired experiments. This letter report provides information on the degradation that had occured and was identified during disassembly and inspection of the test unit. Causes of the degradation as supported by the inspection data are also discussed.

Description of Equipment

Figure 1 is a plan view of the combustion test unit, which consisted of five major sections. The sections, labeled A through E in Fig. 1 are the burner assembly, reducing chamber, transition section (throat), oxidizing chamber, and stack.

The burner assembly was of a standard industrial design and consisted of a ceramic burner block surrounding the combustion-air injection nozzle and the burner gun. This gun consisted of a fuel nozzle surrounded by an annular atomizing steam passage. Atomization of the fuel occured at the burner-gun tip.

The reducing section consisted of a cylindrical steel shell insulated with two layers of fiber-blanket insulation. The blankets were treated with a "fixative" to provide a rigid surface and allow the material to be self-supporting. A single sight-port was located on the side of the chamber. A single ceramic thermowell in the top of the chamber held a thermocouple used to monitor and control the chamber temperature.

The transition section consisted of converging and diverging conical pieces separated by a short cylindrical throat. Secondary combustion air was injected through nozzles in the throat. Insulation, a castable ceramic material, was supported by "V" anchors welded to the steel shell.

The oxidizing section was a cylindrical steel chamber insulated in the same manner as the reducing section. Three sight ports were located along the side of the chamber to allow viewing of flame patterns.

The stack consisted of an unlined stainless steel pipe and contained a flow meter and sample ports for monitoring the performance of the unit.

Disassembly and Inspection

Disassembly and inspection of the combustion test unit started at the stack and proceeded backwards toward the burner and is described as it occured.

The stack was removed from the oxidizing chamber and disassembled at the flow-meter venturi. Inspection of the main stack section, the flow venturi, and the stack base revealed all parts to be in good condition.

The oxidizing section was then removed from the transition piece. The blanket insulation was all in place and in good condition. A small amount of castable insulation in the bottom of the chamber near the transition piece had fallen from the transition section. The tip of the burner-gun assembly was also found on the floor of the oxidizing section.

Next, the transition section was separated from the reducing section and carefully inspected. A large portion of the castable insulation had cracked and pulled away from the converging conical portion of the transition section. A large piece of the insulation had fallen out of place exposing the steel shell. Melting or slagging of the castable material was also observed adjacent to the missing piece of insulation. These features can be seen in Fig. 2, which is a photograph of the inlet to the transition section taken prior to separation from the reducing section. Additional castable insulation was then removed to allow inspection of the shell and secondary air nozzles. The air nozzles were in good shape, but the shell had been severly degraded where the insulation had fallen away. This damage is evident in Fig. 3, a photo of the inside of the converging shell. Degradation was also present on the outside of the shell at this same point, as can be seen in Fig. 4.

Inspection of the reducing section revealed that the blanket insulation had dislodged and exposed essentially the entire top one-third of the cylindrical steel shell. The insulation can be seen hanging down in Figs. 2 and 5. The ceramic thermowell was also broken, as seen in Figs. 2 and 6. Figure 6 also shows scaling on the exterior of the top of the reducing section caused by overheating of the steel. Similar degradation was evident on the shell near the sight port. Evidence of melting at the exposed end of the sight-port tube was also noted, indicating very high local temperatures in this area (Fig. 5).

The burner assembly then was removed from the reducing section and inspected. The ceramic burner block was in excellent shape as was the combustion air nozzle (Fig. 7). The dark stain visible on the burner block is a residual carbonaceous deposit. Some degradation of the steel collar around the burner block was evident and probably caused by air leakage past the burner flange.

The burner gun had come apart at the liquid injection nozzle (Fig. 8). As can be seen in the closeup photo in Fig. 9, the end of the liquid-feed tube had expanded and split, disengaging the nozzle threads. The tip of the nozzle was plugged with a hard, carbonaceous material similar to that visible on the burner block. The tip of the steam-atomization nozzle was also broken at the threads. The atomization tip and liquid-injection nozzle were found in the bottom of the oxidizing section of the combustion test unit.

Inspection of other associated components of the test unit revealed little significant degradation. The only other important finding was the presence of dissolved TNT, particulate RDX, and fuel oil in the feed line at the burner nozzle, even though the line had been flushed with clean oil immediately before shutdown of the unit.

Analysis of Degradation

Four significant findings resulted from inspection of the combustion unit: failure of the castable insulation in the transition section, failure of the blanket insulation in the reducing section, high localized temperatures in the reducing and convergent portion of the transition sections, and burner-gun failure. The probable causes of each of these problems are discernable from the run history and inspection evidence.

Failure of the castable insulation in the transition section was most likely caused by thermal cycling coupled with inadequate refractory supports. The nature of the test program required that the unit be started up and shut down daily. This type of thermal cycling was almost certain to result in cracked insulation in the transition section. Had adequate supports been provided, this would have been acceptable for the needed life of the unit, since the pieces would have remained in place and the cracks closed when the unit was hot. However, the supports were not adequate and the cracked insulation separated from the shell.

The blanket insulation in the reducing section was designed to be self-supporting, with the fixative hardening the surface of the innermost layer of fiber. It appears that carbon deposited in the porous surface of the fiber blankets during operation at reducing conditions. When the atmosphere became oxidizing, such as during shutdown after fuel cutoff, the carbon burned on the surface resulting in high surface temperature and destruction of the fixative layer. The resulting loss of the self-supporting design feature led to collapse of the blankets and subsequent heat damage to the shell.

Extremely high local temperature were experienced at at least three locations. The first was at the fractured thermowell in the reducing zone. Air leakage through the broken thermowell caused a local flame in the otherwise reducing atmosphere of the chamber. This was indicated by high temperature readings on the thermocouple followed by thermocouple failure and melting of the thermocouple sheathing. The second high-temperature location was indicated by the molten surface of the castable insulation in the transition section, also probably caused by the broken thermowell. The area was directly downstream of the thermowell and air leakage through the thermowell would result in a hot flame impinging on the castable insulation. The alignment of the broken thermowell and the hot spot on the insulation can be seen in Fig. 2. The last indication of high temperature was at the junction of the reducing-chamber sight port and the chamber shell (Fig. 5). Again, the most likely cause was a combination of the failed blanket insulation and air leakage through the sight-port flange. Air entering at that location would result in a local oxidizing condition and resultant high surface temperature.

The failed burner tip occured during the last shutdown of the unit and resulted from a series of unrelated problems and actions. Shutdown procedures called for flushing the feed line with clean oil prior to cutting fuel flow to the burner, and this procedure was followed. It was necessary to sample the explosive/fuel oil mixture after fuel flow stopped, and some of the mixture leaked past a back-pressure check valve into the burner gun. Proceeding with an orderly shutdown, the combustion-air flow was reduced in an attempt to slow the cooling rate on the unit and prevent additional degradation of the insulation. The steam to the atomizing nozzle was stopped as part of normal shutdown procedures. These actions eliminated any cooling of the burner gun and contents. As the burner gun heated, the contents began to decompose thermally. The decomposition products plugged the liquid injector, which caused pressure in the feed line that ruptured and released the injector, which in turn broke the atomizer tip as the injector was propelled away from the gun. Evidence from examination of the parts is consistent with this scenario. All parts were found and failure of the tube was in the ductile mode.

Design Changes and Safety Considerations

Examination of degradation of the combustion test unit revealed that all the problems resulted from design weaknesses. These weaknesses were mainly due to the nature of the envisioned test program and funding limitations. It was accepted from the outset that thermal cycling would be severe and could lead to insulation failure, but it was believed that the unit could survive for the few weeks necessary to complete the testing program. Changes in design, including fire brick lining and enhanced insulation support coupled with controlled heatup and cooldown rates, would result in a much more reliable unit. Gasketing and leak checking would greatly reduce the air-leakage problems.

Safety considerations relate mainly to the burner-gun problem, because this is the only problem encountered involving the HE. Procedures for shutdown and personnel protection were in place that excluded access to the unit during the shutdown operation. The feed system was designed to limit the amount of fuel that could be present and react should it be initiated in some manner. Because the design and procedures existed, there was no uncontrolled hazard or personnel exposure, and damage was limited to the burner gun. This damage could have been repaired by simple replacement of the burner gun, an extremely common practice in the operation of conventional burners. This is not to say that the design was totally adequate. Changes that should be made to enhance safety and operability include a positive shutoff between the feed tank and the burner rather than a positive pressure check valve. Flushing of the lines with clean oil and/or solvent after closing the positive cutoff on the explosive/fuel oil mixture would eliminate the possibility of leaking explosive-laden fuel to the burner. A change in the shutdown procedure, possibly including a hardware interlock to preclude the shutoff of atomizing steam until the unit is cool, would provide cooling to the burner gun even though all air flow was off.

Summary

Disassembly and inspection of the HE/fuel oil combustion test unit revealed numerous problems related to weaknesses in design and operation of the unit. Many of these weaknesses were recognized and accepted prior to construction of the test unit to hold down costs and simplify operation for the proof-of-principle test program. Testing with the unit shows that combustion of HE/fuel oil mixtures through conventional burners is realistic and can be done safely. Degradation of the unit during testing has provided valuable insights into potential operational and design problems. The overall test program was limited by the early failure of insulation in the unit, but proof-of-principle was demonstrated.

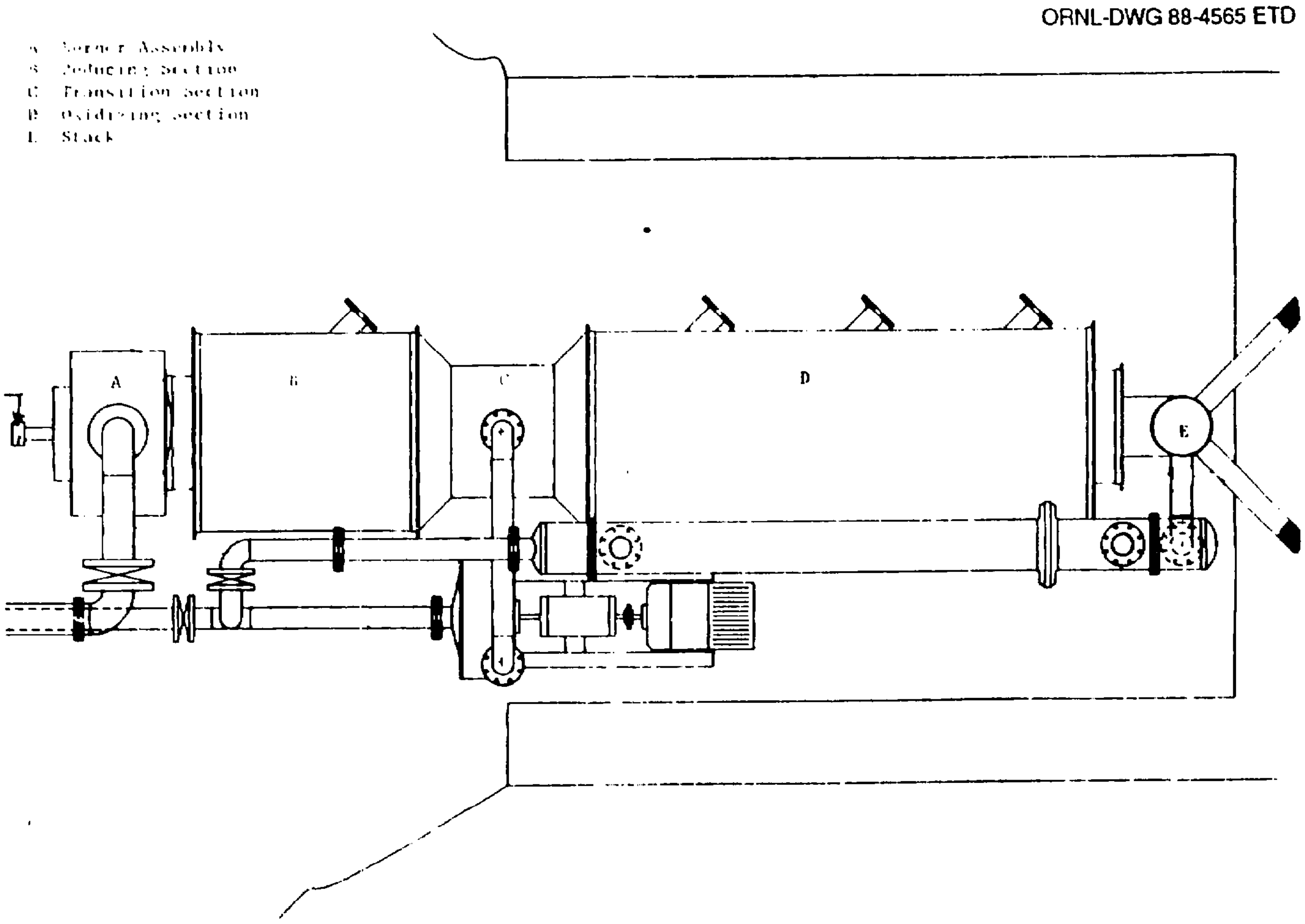

Fig. B.1. Combustion test unit layout

PHOTO CN88-1315

Fig. B.2. View through reducing section toward transition section

PHOTO CN88-1312

Fig. B.3. Transition section shell interior

PHOTO CN88-1310

Fig. B.4. Transition section shell exterior

PHOTO CN88-1307

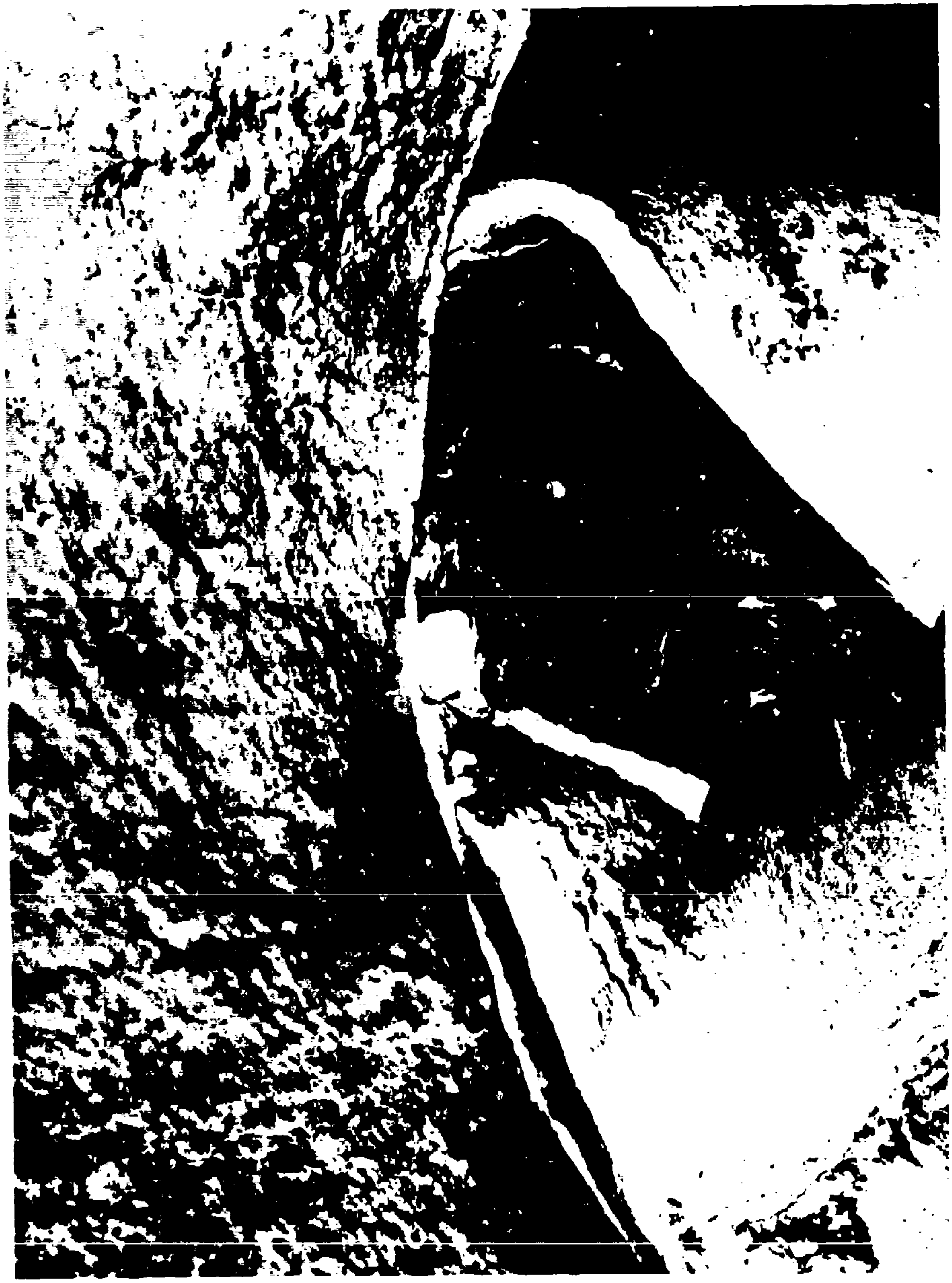

Fig. B.5. Reducing section

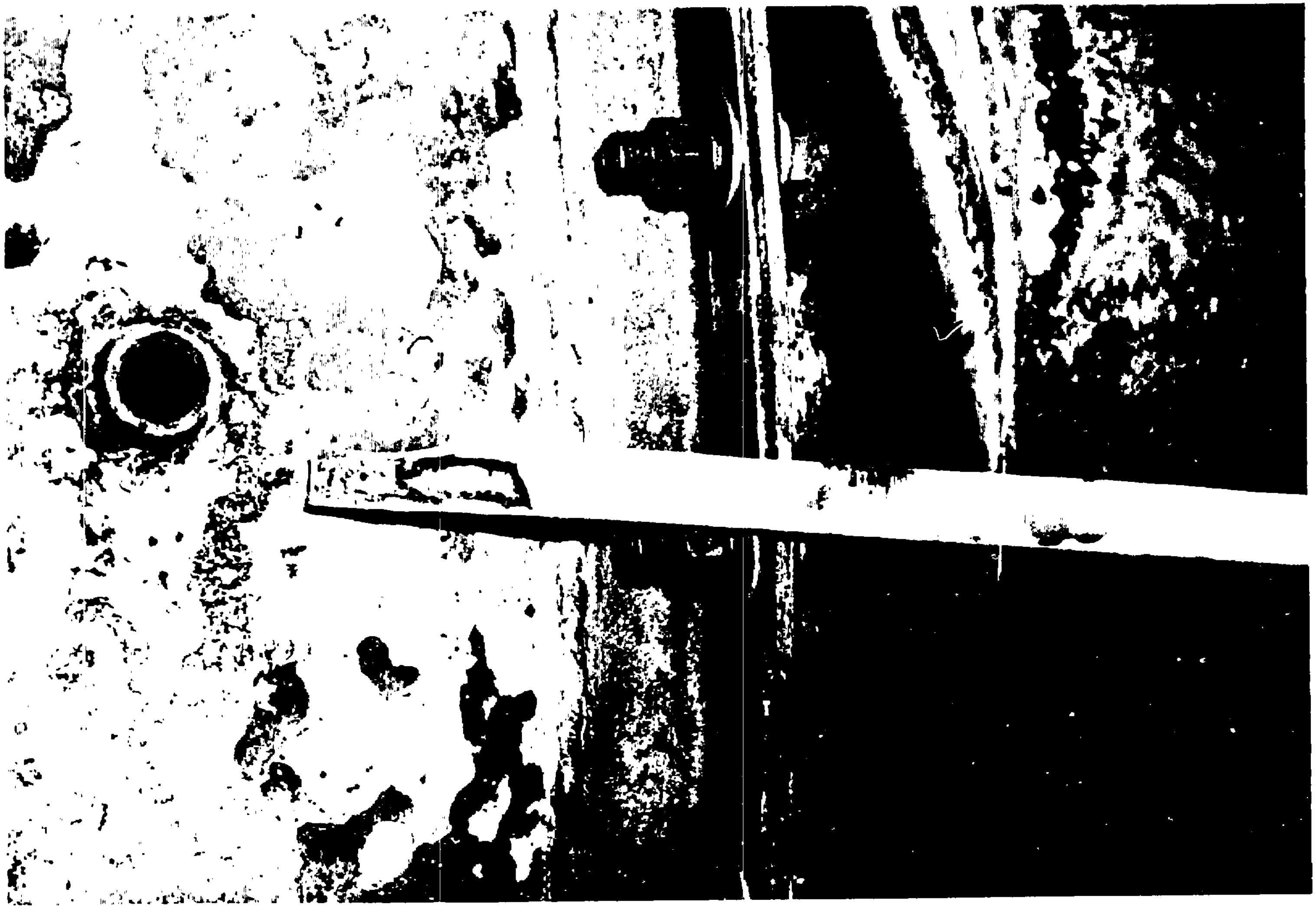

Fig. B.6. Reducing section thermowell

PHOTO CN88-1308

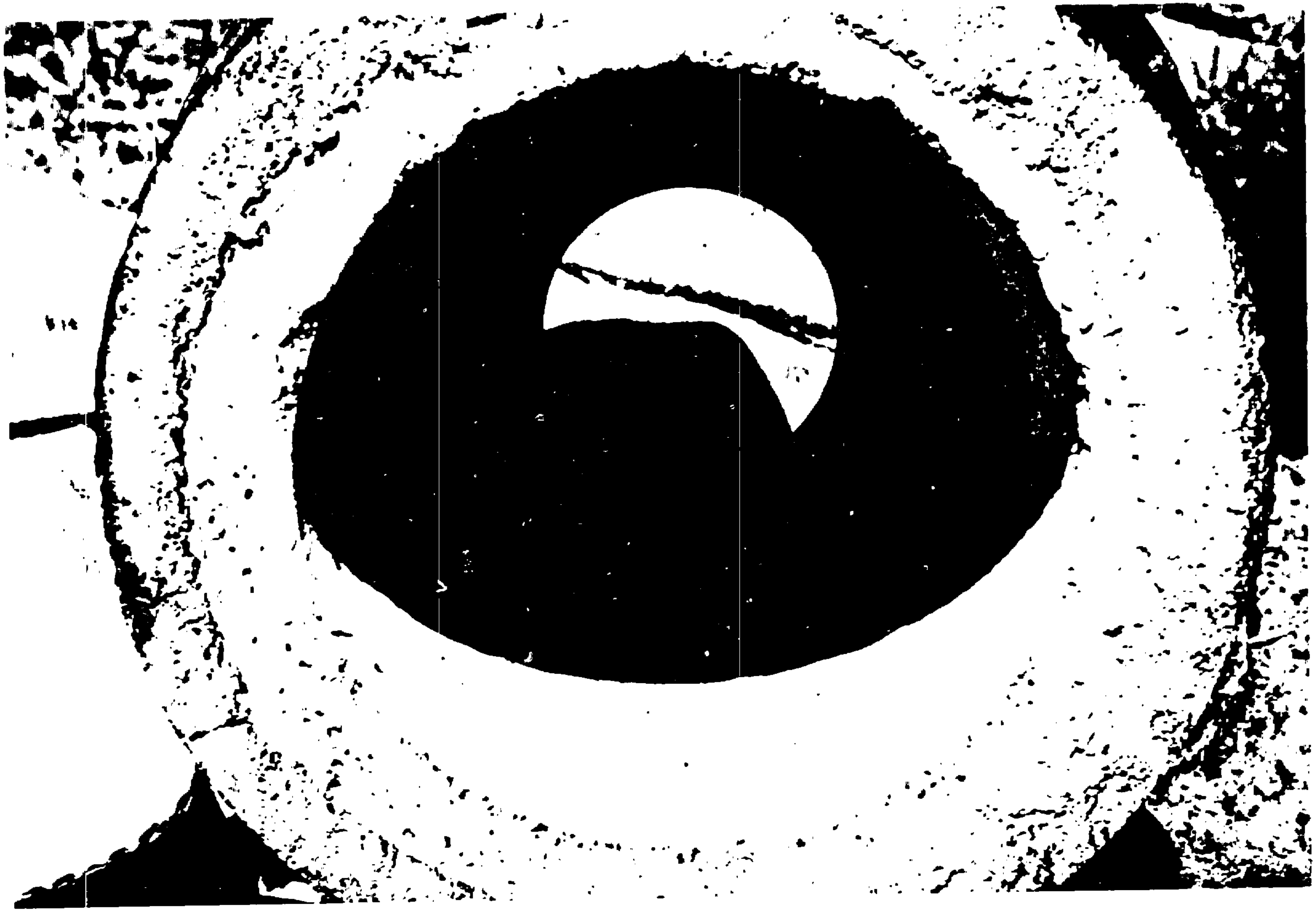

Fig. B.7. Burner block

PHOTO CN88-1313

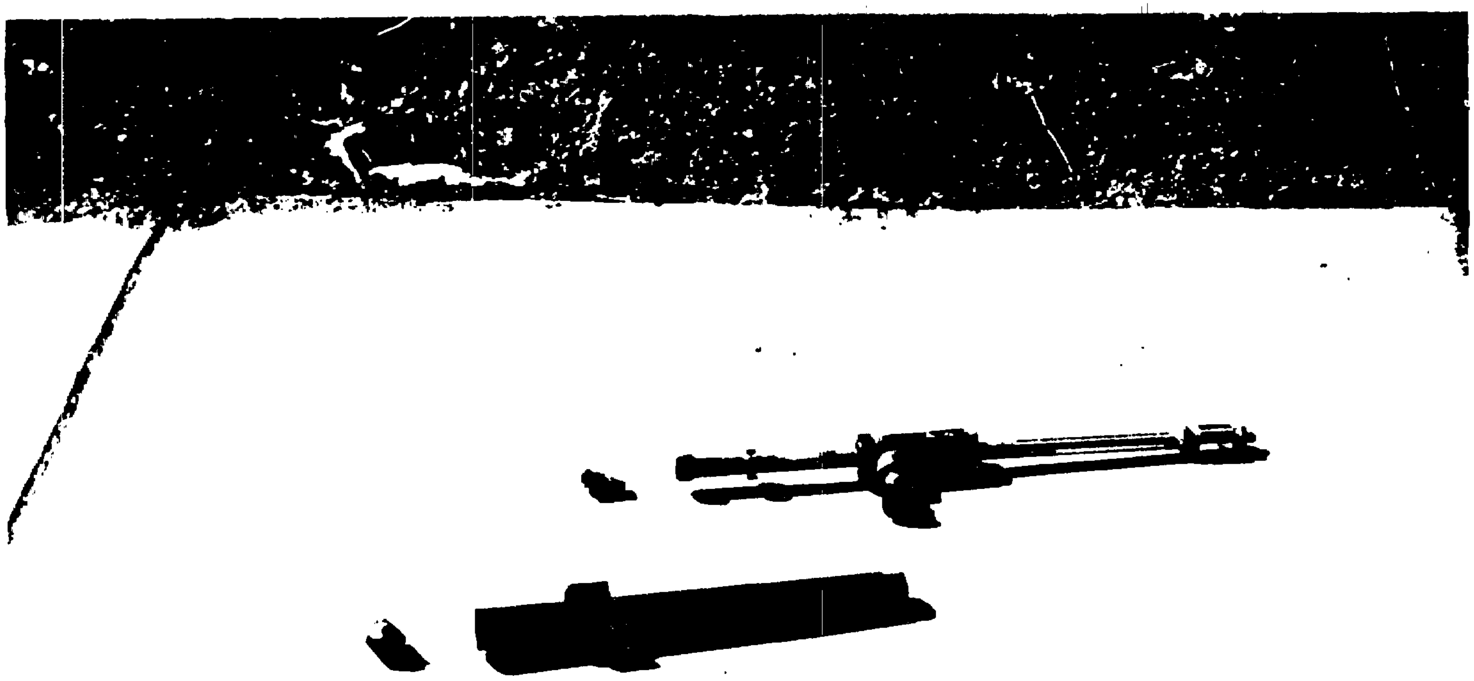

Fig. B.8. Burner gun parts

PHOTO CN88-1311

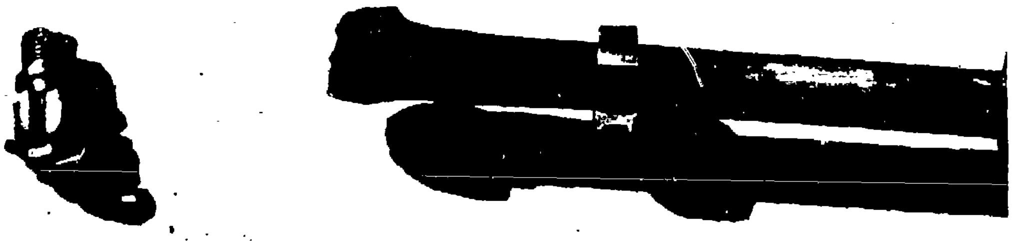

Fig. B.9. Liquid feed line and injection tip

APPENDIX C

MATERIAL BALANCES FOR 1987 PROOF-OF-PRINCIPLE TESTS

Material balances for each of the 18 tests conducted in 1987 are included in this appendix. The material balances are based on measured flow rates for fuel and combustion air. The pilot fuel, pilot air, and atomizing steam flow rates are estimated from manufacturers' literature.

The flue gas was analyzed for O_2, CO_2, CO, and NO_x. The O_2 was determined on a wet volume basis, and the other three gases were measured on a dry volume basis. The CO_2 meter was not reading accurately during the first nine tests.

The technique used to do the material balance is described below. Detailed calculations are included for test 10 as an example. Elemental input rates were determined by summing the amount of C, H, N, and O in the fuel; combustion air; pilot fuel; pilot air; and atomizing steam. The flue gas wet and dry molecular weights were estimated based on inputs. Elemental output rates were determined from the flue gas flow rate and composition. The closure is simply the ratio of output to input flow rate for each element. The humidity of the flue gas was not measured, so closure can only be specified for C, N, and O.

Elemental Material Balances for Each Test

Inputs common to all tests

Pilot fuel (propane)	0.82 kg/h
Pilot air	13.8 kg/h
Atomizing steam	19.1 kg/h

Operating data for each test are included in Table 3.1. Detailed data for tests 15-18 are available in Ref. 7. The elemental balances for each test are shown in Table C.1. The carbon balance could not be obtained for tests 1-9 because the CO_2 meter was not functioning properly.

Table C.1. Elemental material balances for each test

Test	Total elemental input (kg/h)			Total elemental output (kg/h)			Closure (output/input, %)		
	Carbon	Oxygen	Nitrogen	Carbon	Oxygen	Nitrogen	Carbon	Oxygen	Nitrogen
1	16.9	102.7	282.0	NA[a]	94.1	290.0	NA	91.6	102.9
2	12.4	74.2	188.0	NA	84.3	180.8	NA	113.7	96.2
3	12.9	61.5	224.7	NA	54.6	159.6	NA	88.8	109.1
4	21.1	163.0	480.2	NA	160.9	483.3	NA	98.7	100.6
5	20.6	78.1	200.5	NA	67.7	209.1	NA	86.8	104.3
6	15.3	58.2	135.8	NA	45.5	151.6	NA	78.1	111.7
7	20.6	72.8	183.8	NA	59.2	197.4	NA	81.4	107.4
8	18.2	160.5	468.3	NA	123.7	510.2	NA	77.1	108.9
9	18.2	142.7	409.9	NA	125.2	491.0	NA	87.7	119.8
10	9.0	88.7	224.6	9.5	83.7	229.2	105.6	94.4	102.0
11	10.3	84.9	223.5	10.7	76.6	234.9	103.4	90.2	105.1
12	9.0	74.2	182.6	8.2	66.4	168.1	90.6	89.5	92.0
13	16.4	126.7	350.4	14.3	123.7	357.7	87.0	97.6	102.1
14	24.5	155.5	448.7	19.5	162.7	462.3	79.7	104.6	103.0
15	26.9	180.1	536.7	23.0	184.9	545.1	85.4	102.6	101.6
16	26.9	178.8	532.5	24.3	166.1	508.3	90.4	92.9	95.5
17	23.3	178.2	523.8	21.1	166.4	490.6	90.3	93.4	93.7
18	23.3	175.0	513.4	22.8	174.7	526.0	97.8	99.8	102.4

[a] NA = Not available.

Because NO_x reduction is one of the prime objectives, the ratio of NO_x to fuel-bound nitrogen is given for each test that included explosives in the fuel. The combustor produced some NO_x because of oxidation of nitrogen in the combustion air. The thermal NO_x was analyzed for eight conditions under which nitrogen-free fuel was burned. The NO_x concentration, which was corrected to 7% O_2, was very constant over a wide range of operating conditions. It averaged 100 ppm with a standard deviation of 17 ppm.

The NO_x emitted while burning high-nitrogen fuel typically exceeded 1000 ppm (corrected to 7% O_2). The NO_x resulting from fuel-bound nitrogen was determined by subtracting an estimate of the thermal NO_x from the total NO_x.

$$NO_x \text{ (fuel-bound)} = NO_x \text{ (total)} - NO_x \text{ (thermal)}^{\alpha}$$

α – thermal NO_x was estimated for the combustor by analyzing tests in which no nitrogen was in the fuel.

Thermal NO_x was usually <10% of the total. Therefore, small errors in the thermal NO_x term have very little effect on the fuel-bound NO_x term.

The total NO_x emitted was corrected to 7% O_2. It was reduced by 100 ppm to account for thermal NO_x. The ratio of total NO_x to fuel-bound nitrogen and the ratio of total NO_x minus thermal NO_x (e.g., fuel-bound NO_x) to fuel-bound nitrogen are reported for each test that included explosives in the fuel (see Table C.2).

Table C.2. NO_x reduction for tests of burning nitrogen-containing fuel

Test	Flue gas composition (dry basis)		NO_x @ 7% O_2 (ppm)	Ratio of NO_x to fuel-bound N (%)	Ratio of NO_x total − NO_x thermal to fuel-bound N (%)
	O_2 (vol %)	NO_x (ppm)			
9	8.7	689	780	32.4	28.4
10	10.7	1000	1360	15.7	14.6
12	8.7	2055	2340	23.8	22.8
13	11.2	1275	1820	16.8	15.9
14	10.5	964	1290	14.5	13.3
15[a]	10.5	83	110	46.4	4.3
16[a]	8.2	102	110	52.2	5.2
17	10.4	730	960	10.6	9.3
18	10.2	583	760	10.2	8.9

[a] No explosives were fed to the burner during the run. All fuel-bound nitrogen was contained in the No. 5 fuel oil.

Sample Material Balance

Material balance for test 10.

Data Steady state condition at 9:45 a.m., 5/27/87.

Fuel composition – 40% TNT (mass basis)
60% Toluene

Fuel flow rate – 0.20 kg/m

Combustion air flow rate – 4.63 kg/m

Flue gas composition (vol %)

O_2 – 9.3% (wet basis)

CO_2 –7.9% (dry basis)

NO – 1000 ppm (dry basis)

Flue gas flow rate – 5.44 kg/m (wet)

Assumptions

Atomizing steam – 19.1 kg/h

Pilot fuel (propane) – 0.82 kg/h

Pilot air – 13.8 kg/h

Elemental Composition for Fuel

TNT ($C_7H_5N_3O_6$) Toluene (C_7H_8)

C (0.4) (84/227) + (0.6) (84/92) = 0.696

H (0.4) (5/227) + (0.6) (8/92) = 0.061

N (0.4) (42/227) + 0 = 0.074

O (0.4) (96/227) + 0 = 0.169

Elemental Composition of Pilot Fuel (C_3H_8)

C	36/44	= 0.818
H	8/44	= 0.182

Total Inputs from Fuel

	Fuel	Pilot	Total
C	(0.20 kg/m) (60 m/h) (0.696) +	(0.82 kg/h) (0.818)	= 9.02 kg/h
H	(0.20 kg/m) (60 m/h) (0.061) +	(0.82 kg/h) (0.182)	= 0.88 kg/h
N	(0.20 kg/m) (60 m/h) (0.074) +	0	= 0.89 kg/h
O	(0.20 kg/m) (60 m/h) (0.169) +	0	= 2.03 kg/h

Air Inputs

Combustion Air Pilot Air

N $[(4.63 \text{ kg/m})\ (60 \text{ min/h}) + 13.8 \text{ kg/h}]\ \left(0.767\ \frac{\text{kg } N_2}{\text{kg air}}\right) = 223.7 \text{ kg/h}$

O $[(4.63 \text{ kg/m})\ (60 \text{ min/h}) + 13.8 \text{ kg/h}]\ \left(0.233\ \frac{\text{kg } O_2}{\text{kg air}}\right) = 67.9 \text{ kg/h}$

Steam Input

H (19.1 kg/h) (2 kg H/18 kg H_2O) = 2.12 kg/h

O (19.1 kg/h) (16 kg O_2/18 kg H_2O) = 16.98 kg/h

Total Inputs (kg/h)

	Fuel	Air	Steam	Total
C	9.02 +	0 +	0 =	9.02
H	0.88 +	0 +	2.12 =	3.00
N	0.89 +	223.7 +	0 =	224.6
O	2.03 +	69.7 +	16.98 =	88.7

Flue Gas Analysis

Because the moisture content of the flue gas was not measured, the wet and dry molecular weight of the flue gas must be estimated from the inputs. This procedure introduces very little error because relatively large changes in flue gas composition result in very small changes in the molecular weight of the flue gas.

Flue Gas Flow Rate

(5.44 kg/m) (60 min/h) = 326.6 kg/h (wet)

H_2O in Flue Gas

(3.0 lb H_2/h) (18 kg H_2O/2 kg H_2) = 27.0 kg/h

Dry Flue Gas

326.6 kg/h – 27.0 kg/h = 299.6 kg/h

Estimate Flue Gas Dry Molecular Wt Based on Inputs

CO_2 (9.0 kg C/h) (1 kg mol CO_2/12 kg C) = 0.75 kg mol CO_2/h

N_2 (224.6 kg N_2/h) (1 kg mol N_2/28 kg N_2) = 8.02 kg mol N_2/h

O_2 (88.7 kg O_2/h) (1 kg mol O_2/32 kg O_2) – 0.75 kg mol CO_2/h

–(0.88 kg H_2/h) (1/2 kg mol O_2/2 kg H_2) = 1.80 kg mol O_2/h

Dry Molecular wt of Flue Gas

$$\frac{(0.75\ \text{mol CO}_2/\text{h})\ (44\ \text{kg/mol}) + (8.02\ \text{mol N}_2/\text{h})\ (28\ \text{kg/mol}) + (1.80\ \text{mole O}_2/\text{h})\ (32\ \text{kg/mole})}{0.75\ \text{mol CO}_2 + 8.02\ \text{mol N}_2 + 1.80\ \text{mol O}_2}$$

= 29.8 kg/kg mol (dry flue gas)

Wet Molecular wt of Flue Gas

H_2O in flue gas (27.0 kg/h) (1 mol/18 kg) = 1.50 kg mol/h

(299.6 kg dry flue gas/h)/29.8 kg/mol = 10.05 kg mol dry flue gas/h

$$\frac{326.6\ \text{kg wet flue gas/h}}{1.50\ \text{mol H}_2\text{O/h} + 10.05\ \text{mol dry flue gas/h}}$$

= 28.28 kg/kg mol (wet flue gas)

Outputs (volume %)

O_2 = 9.3% (wet)
CO_2 = 7.9% (dry)
NO = 0.001% (dry)

$$O_2\quad \left(\frac{326.6\ \text{kg wet flue gas/h}}{28.28\ \text{kg/mol}}\right)\left(0.093\ \frac{\text{mol O}_2}{\text{mol f.g.}}\right) = 1.07\ \text{kg mol O}_2/\text{h}$$

$$CO_2\quad (10.05\ \text{kg mol dry flue gas/h})\left(0.079\ \frac{\text{mol CO}_2}{\text{mol f.g.}}\right) = 0.79\ \text{kg mol CO}_2/\text{h}$$

$$NO\ (10.05\ \text{kg mol dry flue gas/h})\left(0.001\ \frac{\text{mol NO}}{\text{mol f.g.}}\right) = 0.01\ \text{kg mol NO/h}$$

N_2 (10.05 mol dry f.g./h) − (1.07 mol O_2/h + 0.79 mol CO_2/h + 0.01 mol NO/h) = 8.18 mol/h
H_2O = 1.50 mol/h

Elemental Analysis of Flue Gas (kg/h)

	O_2	CO_2	N_2	H_2O	NO	Total
C	0	$+\ 0.79\ \frac{12\ \text{kg C}}{\text{mol O}_2}$	+ 0	+ 0	+ 0	= 9.48 kg/h
H	0	+ 0	+ 0	$+\left(1.50\ \frac{\text{mol}}{\text{h}}\right)\left(2\ \text{kg H}_2/\text{mol}\right)$	+ 0	= 3.00 kg/h
N	0	+ 0	$+\left(8.18\ \frac{\text{mol}}{\text{h}}\right)\left(28\ \frac{\text{kg}}{\text{mol}}\right)$	+ 0	$+\left(0.01\ \frac{\text{mol}}{\text{h}}\right)\left(\frac{14\ \text{kg}}{\text{mol}}\right)$	= 229.2 kg/h
O	$\left(1.07\ \text{mol/h}\right)\left(\frac{32\ \text{kg O}_2}{\text{mol}}\right)$	$+\left(0.79\ \frac{\text{mol}}{\text{h}}\right)\left(\frac{32\ \text{kg O}_2}{\text{mol CO}_2}\right)$	+ 0	$+\left(1.50\ \frac{\text{mol}}{\text{h}}\right)\left(\frac{16\ \text{kg O}_2}{\text{mol}}\right)$	$+\left(0.01\ \frac{\text{mol}}{\text{h}}\right)\left(\frac{16\ \text{kg}}{\text{mol}}\right)$	= 83.7 kg/h

Summary of Elemental Material Balance

Element	Input (kg/h)	Output (kg/h)	Closure (output/input) (%)
C	9.02	9.48	105
H	3.00	3.00	100
N	224.6	229.2	102
O	88.7	83.7	94

NO_x Reduction

"NO_x reduction" is reported in terms of the percent of fuel-bound nitrogen converted to NO. This ratio must be adjusted for thermal NO that is produced during the combustion process.

Fuel-Bound Nitrogen

$$(0.89 \text{ kg N/h}) \left(\frac{1 \text{ mol } N_2}{14 \text{ kg}}\right) = 0.0636 \text{ kg mol N/h}$$

NO Emitted

$$\frac{0.01 \text{ kg mol NO/h}}{0.0636 \text{ mol N/h}} = 15.7\%$$

However, some of the NO results from the oxidation of nitrogen in the combustion air. Based on tests with No. 2 fuel oil and toluene, the combustor produced 100 ppm NO (adjusted to 7% O_2). When burning fuels that did not contain nitrogen at similar conditions.

NO at 7% O_2 (dry)

$$O_2 \text{ concentration is } \frac{1.07 \text{ mol } O_2/\text{h}}{10.05 \text{ mol dry flue gas/h}} = 10.65\%$$

$$NO \text{ @ } 7\% \; O_2 = (1000 \text{ ppm}) \left(\frac{21 - 7\%}{21 - 10.65\%}\right) = 1350 \text{ ppm}$$

$$NO_{thermal} + NO_{fuel} = NO_{total} \text{ (at } 7\% \; O_2)$$

So $NO_{fuel} \cong 1350 \text{ ppm} - 100 \text{ ppm} = 1250 \text{ ppm @ } 7\% \ O_2$

at 10.65% O_2, $NO_{fuel} = 1250 \text{ ppm} \left(\frac{21 - 10.65\%}{21 - 7\%}\right) = 924 \text{ ppm}$

$$NO_{fuel} = \left(924 \times 10^{-6} \frac{\text{mol NO}}{\text{mol f.g.}}\right) (10.05 \text{ mol dry flue gas/h})$$

$$= 9.29 \times 10^{-3} \text{ kg mol NO/h}$$

So $\frac{9.29 \times 10^{-3} \text{ kg mol NO/h}}{0.0636 \text{ mol N/h}}$ = 14.6% of fuel-bound Nitrogen is emitted as NO.

APPENDIX D

MATERIAL AND ENERGY BALANCES FOR THE PROPOSED PROOF-OF-PRINCIPLE TEST SYSTEM

This appendix includes the detailed calculations for the material and energy balances for the proof-of-principle system described in Chap. 4. The proof-of-principle tests would include a large number of test conditions. Each condition should be analyzed before it is included in the test plan to ensure that mass flow and thermal conditions will not exceed design limits.

There is no need to analyze hundreds of potential operating conditions at this time. Rather, the limiting cases have been analyzed to ensure that the system described in Chap. 4 is capable of operating over a wide range of conditions. Heat loads of 147 kW (0.5×10^6 Btu/h) and 732 kW (2.5×10^6 Btu/h) were chosen for detailed analysis because they represent the limits of projected mass flow rates. Because the only thermal design limitation is high temperature, the energy balance is only presented for the 2.5×10^6 Btu/h case.

The methods used here could be applied to any operating condition. Iterative calculations are required for the energy balance and the material balance at certain conditions (when flue gas recycle is included). Detailed analysis of a large number of test conditions should be performed on a computer. The computer model could follow the same logic that is presented in this appendix.

Material Balances for Process Flow Sheet

Assumptions

1. Fuel is 30% toluene, 50% No. 2 fuel oil, and 20% Comp. B.
2. Pilot is 0.82 kg/h propane, rated at 11.4 kW.
3. Adequate O_2 will be supplied to the reducing zone to burn the fuel to H_2O and CO.

Givens

1. Heat loads of interest are 147 kW (0.5×10^6 Btu/h) and 732 kW (2.5×10^6 Btu/h)
2. Total excess air is 150%
3. 136 kg/h of dry flue, gas will be recycled to the reducing zone.
4. Steam (including atomizing steam) will be 1.5 kg steam/kg fuel for both cases.

Case 1 is 147 kW (0.5×10^6 Btu/h)

Case 2 is 732 kW (2.5×10^6 Btu/h)

Fuel Data

	Composition (wt%)	High heating valve (kJ/g)
No. 2 fuel oil	86.35% C 12.72% H_2 0.82% O_2	45.35
Toluene	C_7H_8	42.43
Comp. B	60% RDX — $C_3H_6N_6O_6$ 40% TNT — $C_7H_5N_3O_6$	11.68

Elemental Composition of Fuel (basis = 1 kg)

	No. 2 fuel oil	Toluene	RDX	TNT
C	(0.50) (0.8635)	+ (0.30) $\left(\frac{84}{92}\right)$	+ (0.20) (0.60) $\left(\frac{36}{222}\right)$	+ (0.20) (0.40) $\left(\frac{84}{227}\right)$
H	(0.50) (0.1272)	+ (0.30) $\left(\frac{8}{92}\right)$	+ (0.20) (0.60) $\left(\frac{6}{222}\right)$	+ (0.20) (0.40) $\left(\frac{5}{227}\right)$
N	0	+ 0	+ (0.20) (0.60) $\left(\frac{84}{222}\right)$	+ (0.20) (0.40) $\left(\frac{42}{227}\right)$
O	(0.50) (0.0082)	+ 0	+ (0.20) (0.60) $\left(\frac{96}{222}\right)$	+ (0.20) (0.40) $\left(\frac{96}{227}\right)$

Element	Mass Fraction (%)
C	75.5
H	9.5
N	6.0
O	9.0
	100.0%

Heating Valve of Fuel

No. 2 fuel oil Toluene Comp. B

$$(0.50)(45.35) + (0.30)(42.43) + (0.20)(11.68) = 37.74\ \text{kJ/g}$$

Fuel Flow Rate

Case 1 - 146.5 kW

$$\frac{\overset{\text{Total}}{146.5\ \text{kW}} - \overset{\text{Pilot}}{11.4\ \text{kW}}}{37.74\ \text{kJ/g}} \quad \frac{1\ \text{kg}}{1000\ \text{g}} \quad \frac{3600\ \text{s}}{\text{h}} = 12.89\ \text{kg/h}$$

Case 2 - 732.5 kW

$$\frac{732.5\ \text{kW} - 11.4\ \text{kW}}{37.74\ \text{kJ/g}} \quad \frac{1\ \text{kg}}{1000\ \text{g}} \quad \frac{3600\ \text{s}}{\text{h}} = 69.87\ \text{kg/h}$$

Steam Flow Rate (Total)

Case 1

(12.89 kg/h) (1.5 kg steam/kg fuel) = 19.3 kg/h

Case 2

(69.87 kg/h) (1.5 kg steam/kg fuel) = 104.8 kg/h

O_2 Requirements

$C + O_2 \rightarrow CO_2$

$H_2 + 1/2\ O_2 \rightarrow H_2O$

Fuel — Pilot (C_3H_8)

Case 1

C $(12.89\ \text{kg/h})(0.755\ \text{kg C/kg fuel}) + (0.82\ \text{kg/h})\left(\frac{36}{44}\right) = 10.4\ \text{kg/h}$

H $(12.89\ \text{kg/h})(0.095\ \text{kg H}_2\text{/kg fuel}) + (0.82\ \text{kg/h})\left(\frac{8}{44}\right) = 1.37\ \text{kg/h}$

Case 2

C $(69.87\ \text{kg/h})(0.755\ \text{kg C/kg fuel}) + (0.82\ \text{kg/h})\left(\frac{36}{44}\right) = 53.4\ \text{kg/h}$

H $(69.87\ \text{kg/h})(0.095\ \text{kg H}_2\text{/kg fuel}) + (0.82\ \text{kg/h})\left(\frac{8}{44}\right) = 6.79\ \text{kg/h}$

O_2 Required for Reducing Zone

$C + 1/2\ O_2 \rightarrow CO$

$H_2 + 1/2\ O_2 \rightarrow H_2O$

Case 1 $(10.4\ \text{kg C/h})\left(\frac{1/2\ \text{mol O}_2}{12\ \text{kg C}}\right) + (1.37\ \text{kg H}_2\text{/h})\left(\frac{1/2\ \text{mol O}_2}{2\ \text{kg H}_2}\right) = 0.776\ \text{kg mol O}_2\text{/h}$

Case 2 $(53.4\ \text{kg C/h})\left(\frac{1/2\ \text{mol O}_2}{12\ \text{kg}}\right) + (6.79\ \text{kg H}_2\text{/h})\left(\frac{1/2\ \text{mol O}_2}{2\ \text{kg H}_2}\right) = 3.922\ \text{kg mol O}_2\text{/h}$

O_2 Required to Complete Combustion

Case 1 $0.776\ \text{kg mol O}_2\text{/h} + (10.4\ \text{kg C/h})\left(\frac{1/2\ \text{mol O}_2}{12\ \text{kg C}}\right) = 1.21\ \text{kg mol O}_2\text{/h}$

Case 2 $3.92\ \text{kg mol O}_2\text{/h} + (53.4\ \text{kg C/h})\left(\frac{1/2\ \text{mol O}_2}{12\ \text{kg C}}\right) = 6.15\ \text{kg mol O}_2\text{/h}$

O_2 Required for 50% excess air

$$\text{Case 1} \quad (1.21 \text{ kg mol } O_2/\text{h}) \frac{1.5 \text{ mol } O_2 \text{ supplied}}{\text{mol } O_2 \text{ required}} = 1.81 \text{ kg mol } O_2/\text{h}$$

$$\text{Case 2} \quad (6.15 \text{ kg mol } O_2/\text{h}) \frac{1.5 \text{ mol } O_2 \text{ supplied}}{\text{mol } O_2 \text{ required}} = 9.22 \text{ kg mol } O_2/\text{h}$$

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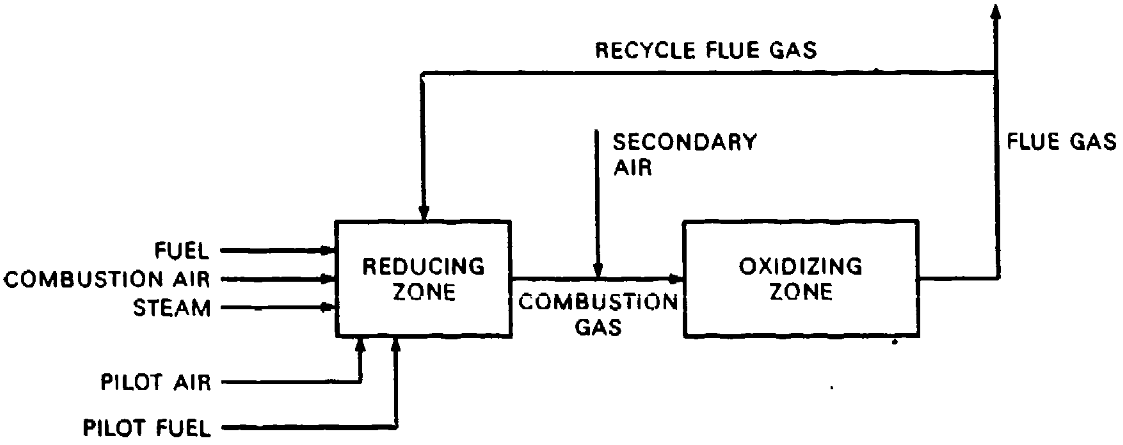


Material Balance for Dry Flue Gas

Case 1

A total of 776 g mol of O_2/h must be supplied to the reducing zone. However, the recycle flue gas composition is unknown, so an iterative process must be used to solve the problem. The last iteration is shown here.

Assume flue gas is $5.2\%\ O_2$
$82.5\%\ N_2$
$12.3\%\ CO_2$

on a dry volume basis.

Dry molecular wt of flue gas is

$$\overset{O_2}{(0.052)(32)} + \overset{N_2}{(0.825)(28)} + \overset{CO}{(0.123)(44)} = 30.2 \text{ g/mol.}$$

O_2 in recycle flue gas is

$$0.052 \left(\frac{\text{mol } O_2}{\text{mol dry f.g.}}\right)\left(\frac{136 \text{ kg dry f.g./h}}{30.20 \text{ kg/kg mol}}\right) = 0.234 \text{ kg mol } O_2\text{/h.}$$

O_2 in fuel is

$$0.09 \ \frac{\text{kg } O_2}{\text{kg fuel}} \qquad 12.89 \text{ kg fuel/h} \qquad \frac{1 \text{ mol } O_2}{32 \text{ lb}} = 0.036 \text{ kg mol/h.}$$

O_2 required in combustion air is

$$\overset{\text{Total}}{776 \text{ mol/h}} - \overset{\text{Recycle}}{234 \text{ mol/h}} - \overset{\text{Fuel}}{31 \text{ mol/h}} = 506 \text{ mol/h.}$$

N_2 in combustion air is:

$$(506 \text{ mol } O_2\text{/h}) \left(\frac{1 \text{ mol air}}{0.21 \text{ mol } O_2}\right) \left(\frac{0.79 \text{ mol } N_2}{1 \text{ mol air}}\right) = 1904 \text{ mol } N_2\text{/h.}$$

Total O_2 required at 50% excess air is 1.81 kg mole/h

$$\overset{\text{Total}}{1810 \text{ mol/h}} - \overset{\substack{\text{Reducing}\\ \text{Zone}}}{776 \text{ mol/h}} = 1034 \text{ mol/h}$$

Total N_2 in secondary air is

$$(1034 \text{ mol } O_2/\text{h}) \left(\frac{1 \text{ mol air}}{0.21 \text{ mol } O_2}\right) \left(\frac{0.79 \text{ mol } N_2}{1 \text{ mole air}}\right) = 3890 \text{ mol/h}$$

Total O_2 required at 50% excess air is 1.81 kg mol/h

O_2 in secondary air is

$$\underset{\text{Total}}{1810 \text{ mol/h}} - \underset{\text{Reducing Zone}}{776 \text{ mol/h}} = 1034 \text{ mol/h}$$

Total N_2 in secondary air is

$$(1034 \text{ mol } O_2/\text{h}) \left(\frac{1 \text{ mol air}}{0.21 \text{ mol } O_2}\right) \left(\frac{0.79 \text{ mol } N_2}{1 \text{ mol air}}\right) = 3890 \text{ mol/h}$$

Material Balance for O_2, N_2, and CO_2

O_2	supplied to reducing zone	+ 776	mol/h
O_2	consumed producing H_2O and CO	− 776	mol/h
O_2	consumed burning CO to CO_2	− 443	mol/h
O_2	supplied to oxidizing zone	+ 1034	mol/h
O_2	**leaving oxidizing zone**	**601**	**mol/h**
N_2	supplied in combustion air	1904	mol/h
N_2	supplied in secondary air	3890	mol/h
N_2	in recycle flue gas	$0.825 \left(\frac{\text{mol } N_2}{\text{mol f.g.}}\right) \left(\frac{136 \text{ kg f.g./h}}{30.2 \text{ kg/kg mol}}\right)$	
N_2	in fuel	$\left(12.89 \ \frac{\text{kg fuel}}{\text{h}}\right)\left(0.060 \ \frac{\text{kg } N_2}{\text{kg fuel}}\right) \left(\frac{1 \text{ kg mol } N_2}{28 \text{ kg}}\right)$	
	Total N_2	9.54 kg mol/h	

CO_2 produced from combustion (10.4 kg C/h)(1 mole CO_2/12 kg C)

CO_2 supplied in recycle flue gas $\left(0.123\ \frac{\text{mol } CO_2}{\text{mol f.g.}}\right)\left(\frac{136\ \text{kg f.g./h}}{30.2\ \text{kg/kg mol}}\right)$

Total CO_2 1.42 kg mol/h

Dry Flue Gas Exiting Oxidizing Zone

Compound	(kg mole/h)	Volume (%)	Recycle gas volume % (assumed)
O_2	0.60	5.2	5.2
N_2	9.54	82.5	89.5
CO_2	1.42	12.3	12.3
	11.56		

Note that the composition of the flue gas leaving the oxidizing zone matches the assumption used for the recycle flue gas. Therefore, the assumption is valid.

Case 2

Assume flue gas is (volume basis):

82.0% N_2

6.9% O_2

11.1% CO_2

Dry molecular weight of flue gas

$$\overset{N_2}{(0.820)(28)} + \overset{O_2}{(0.069)(32)} + \overset{CO_2}{(0.111)(44)} = 30.05 \text{ g/mol}$$

Elemental Flow for Recycle Flue Gas

$$O_2 \quad 0.069 \frac{\text{mol } O_2}{\text{mole dry f.g.}} \quad \frac{136 \text{ kg deg f.g./h}}{30.05 \text{ lb/mol}} = 0.312 \text{ kg mol/h}$$

$$N_2 \quad 0.820 \frac{\text{mol } N_2}{\text{mol dry f.g.}} \quad \frac{136 \text{ kg dry f.g./h}}{30.05 \text{ lb/mol}} = 3.71 \text{ kg mol/h}$$

$$CO_2 \quad 0.111 \frac{\text{mole } CO_2}{\text{mole dry f.g.}} \quad \frac{136 \text{ kg day f.g./h}}{30.05 \text{ lb/mol}} = 0.502 \text{ kg mol/h}$$

O_2 in fuel is

$$(0.09 \text{ kg } O_2/\text{kg fuel})(69.87 \text{ kg fuel/h}) \quad \frac{1 \text{ mol } O_2}{32 \text{ kg}} = 0.197 \text{ kg mole } O_2/\text{h}$$

O_2 required in combustion air is

Total	Recycle	Fuel

3920 mol/h − 312 mol/h − 197 mol/h = 3411 mol/h .

N_2 in combustion air is

$$(3.41 \text{ kg mol } O_2/\text{h})\left(\frac{1 \text{ mol air}}{0.21 \text{ mol } O_2}\right)\left(\frac{0.79 \text{ mol } N_2}{\text{mole air}}\right) = 12.83 \text{ kg mole } N_2/\text{h} .$$

Total O_2 required at 50% excess air is 9.22 kg mol/h

O_2 in secondary air is

9.22 kg mol/h − 3.92 mol/h = 5.30 kg mol/h

N_2 in secondary air is

$$(5.30 \text{ g mol/h}) \left(\frac{1 \text{ mol air}}{0.21 \text{ mol } O_2}\right)\left(\frac{0.79 \text{ mol } N_2}{\text{mole air}}\right) = 19.94 \text{ kg mol/h}.$$

Material Balances for O_2, N_2, CO_2

O_2	supplied to reducing zone	3920 mol/h
O_2	consumed producing H_2O and CO_2	-3920 mol/h
O_2	supplied to oxidizing zone	5300 mol/h
O_2	consumed burning CO to CO_2	-2225 mol/h
O_2	**existing oxidizing zone**	**3.08 kg mol/h**
N_2	supplied in combustion air	12.83 kg mol/h
N_2	supplied in secondary air	19.94 kg mol/h
N_2	in recycle fuel gas	3.71 kg mol/h
N_2	in fuel	$(67.87 \text{ kg fuel/h}) \left(0.060 \frac{\text{kg } N_2}{\text{kg fuel}}\right)\left(\frac{1 \text{ kg mol } N_2}{28 \text{ kg}}\right)$
Total N_2 exiting oxidizing zone		36.62 kg mol/h

CO_2 produced in combustion (53.4 kg C/h) $\frac{\text{1 kg mol } CO_2}{\text{12 kg C}}$

CO_2 in recycle flue gas 0.502 kg mol/h

Total CO_2 exiting oxidizing zone 4.95 kg mol/h

Dry flue gas existing oxidizing zone

Compound	Flow (kg mol/h)	Volume %	Recycle gas volume (%) (assumed)
O_2	3.08	6.9	6.9
N_2	36.62	82.0	82.0
CO_2	4.95	11.1	11.1
	44.65		

Note that the composition of dry gas exiting the oxidizing zone matches the composition assumed for the flue gas recycle.

Water Balance

Case 1

H_2O produced in combustion

$(1.37 \text{ kg } H_2/\text{h})(18 \text{ kg } H_2O/2 \text{ kg } H_2) = 12.3 \text{ kg/h}$

H_2O in steam = 19.3 kg/h

H_2O in recycle flue gas = $\underline{13.6x}$ kg/h

where x = kg H_2O/kg dry flue gas

31.6 + 136x kg/h

H_2O leaving oxidizing zone

Dry flue gas (11.56 kg mol/h) $\left(30.2 \frac{\text{kg}}{\text{kg mol}}\right) = 349.1$ kg/h

input + generation = output

31.6 + 136x = 349.1x

x = 0.148 kg H_2O/kg dry flue gas

Case 2

H_2O produced in combustion

$(6.79 \text{ kg } H_2/\text{h})(18 \text{ kg } H_2O/2 \text{ kg } H_2) = 61.1 \text{ kg/h}$

H_2O in steam = 104.8 kg/h

H_2O in recycle flue gas = $\underline{136x}$ kg/h

x = kg steam/kg dry flue gas

165.9 + 136x

H_2O leaving oxidizing zone

(44.65 kg mol/h)(30.05 kg/kg mol)x

= 1342x

input + generation = output

165.9 + 136x = 1342x

x = 0.138 kg H_2O/kg dry flue gas

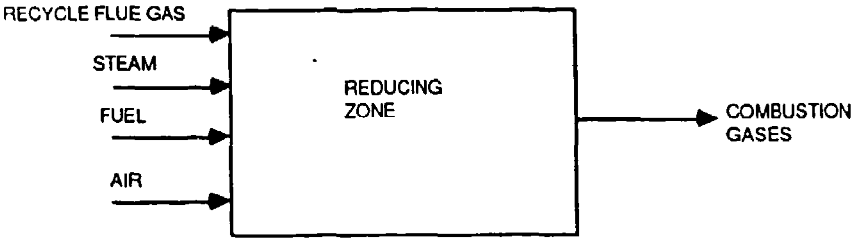
Summary

Stream	Case 1 (0.5 × 10^6 Btu/h)	Case 2 (2.5 × 10^6 Btu/h)
Fuel (kg/h)	12.89	69.87
Propane (kg/h)	0.82	0.82
Combustion air (kg mol/h)	O_2 - 0.506	O_2 - 3.411
	N_2 - 1.904	N_2 - 12.83
Total combined air (kg/h)	69.5	468.4
Steam (kg/h)	19.3	104.8
Dry recycle flue gas (kg/h)	136	136
H_2O in recycle flue gas (kg/h)	20.1	18.8
Secondary air (kg mol/h)	O_2 - 1.034	O_2 - 5.30
	N_2 - 3.890	N_2 - 19.94
Total secondary air (kg/h)	142.0	727.9
Dry flue gas exiting oxidizing zone (kg/h)	349.1	1342
Total input to combustor (kg/h)	401	1527
Total flow existing oxidizing zone (kg/h)	401	1527

Energy Balance For 730-kW (2.5 × 10^6 Btu/h) Case

The energy balance for this system is an iterative process. The results are included in this appendix and are followed by a brief summary of an iterative method that minimizes the number of calculations required.

First, consider the energy balance in the reducing zone



Reference conditions (0 enthalpy) are

21°C,

H_2O as liquid, and

all other compounds are gases.

All of the inlet streams except the recycle flue gas and steam are at ambient temperature (21°C for this case).

Energy input to the reducing zone is the sum of the energy in the recycle the gas, steam, and fuel.

Stream	Flow rate (kg/h)	Temperature (°C)	Enthalpy (MJ/kg)	Energy (kW)
Fuel	69.4	21	0	0
Air	473.1	21	0	0
Steam	103.0	151	2.66	76.05
Recycle flue gas	154.7	260	0.58	24.98

Heat of Combustion

The high heating value of the fuel is 732.5 kW. However, some of the heat is not released because of substoichiometric operation. The oxygen supplied to the reducing zone is exactly enough to burn the fuel to H_2O and CO. Therefore, the heat of combustion of CO to CO_2 is subtracted from the total to estimate heat release in the reducing zone.

$CO + 1/2\ O_2 \rightarrow CO_2$

ΔH_c = 23.56 MJ/kg C

$$(4.38 \text{ kg mol CO/h})(12 \text{ kg C/mol CO})(23.56 \text{ MJ/kg C}) \frac{1 \text{ h}}{3600\text{s}} = 344.1 \text{ kW}$$

So the heat input from the fuel is

732.5 kW – 344.1 kW = 388.4 kW

Summary of heat inputs

Fuel	388.4 kW
Recycle flue gas + steam	101.0 kW
Total	489.4 kW

As mentioned previously, this is an iterative process. The results will be presented here, with a summary of the process to follow.

Assume that the combustion exists at 1196°C. The enthalpy in the combustion gas follows:

Compound	Flow (kg/h)	ΔH_v @ 21°C (MJ/kg)	21-1196°C $\Delta H_{sensible}$ (MJ/kg)	Q (kW)
CO	122.7	NA	1.35	45.9
H_2O	182.1	2.45	2.61	256.0
N_2	460.8	NA	1.30	166.1
CO_2	22.1	NA	1.48	9.1
				477.1

489.4 kW in
477.1 kW out in combustion gas
12.29 kW loss

Heat flux through 1.067-m (42-in.) diam; 1.219-m (48-in.) long reducing zone is

$$\frac{12.29 \text{ kW}}{\pi\ (1.067 \text{ m})\ (1.219 \text{ m})} = 3.01 \text{ kW/m}^2 .$$

The inside surface of the firebrick is 0.813-m (32-in.) diam. Therefore, the heat flux, convented to the inside diameter is

$$\left(3.01\frac{kW}{m^2}\right)\left(\frac{1.067\ m}{0.813\ m}\right) = 3.95\ kW/m^2 \ ,$$

The heat transfer from the gas to the wall results from radiation and convention.

Radiation can be expressed as

$$q \cong \varepsilon_{gas} \ \sigma \ (T_g^4 - T_w^4) \ ,$$

where

q is heat flux,

E_{gas} is the gas emissivity,

σ is Boltzman's constant = 5.728 × 10^{-8} W/m² K⁴,

T_g is the gas temperature,

T_w is the inside wall temperature.

$$\varepsilon_{gas} = \varepsilon_{CO} + \varepsilon_{CO_2} + \varepsilon_{H_2O}$$

McAdams gives estimates of gas emissivities based on partial pressure, geometry, and temperature.

For the conditions in this problem:

Gas	Volume (%)	ε(@ 1196°C)
CO	14	0.06
CO_2	2	0.05
H_2O	32	0.16
		ε_{gas} = 0.27

The convective heat transfer coefficient can be estimated from the j factor equation.

$$\frac{hi}{C_pG}\left(\frac{C_p\mu}{k}\right)^{2/3}\left(\frac{\mu}{\mu w}\right)^{0.14} = j_H = 1.86\left(\frac{D}{L}\right)^{1/3}\left(\frac{DG}{\mu}\right)^{-2/3}$$

evaluation of h_i (inside heat transfer coefficient) gives

$$h_i = 1.65 \text{ W/m}^2\cdot{}^\circ\text{C}$$

$$q = \overset{\text{Radiation}}{\varepsilon_{gas}\,\sigma\,(T_g^4 - T_w^4)} + \overset{\text{Convection}}{h_i\,(T_g - T_w)}$$

Note from before that $q = 3.95 \text{ kW/m}^2$ and $T_{gas} = 1196^\circ\text{C}\ (1469^\circ\text{K})$,

if $T_w = 1176^\circ\text{C}\ (1449^\circ\text{K})$,

$$q = (0.27)\left(5.73 \times 10^{-8} \frac{\text{W}}{\text{m}^2\ \text{K}^4}\right)\left[(1469\ \text{K})^4 - (1449\ \text{K})^4\right]$$

$$+ (1.65 \text{ W/m}^2\cdot\text{K})(1469^\circ\text{C} - 1449^\circ\text{C}) \ ,$$

$$q = 3.88 \text{ kW/m}^2 \ .$$

So the inside wall of the firebrick is 1176°C.

The fire brick-Kaonool - steel refractory system was analyzed using a heat transfer program to determine heat flux through the wall as a function of inside wall temperature.

The convective heat transfer coefficient at the outside diameter was estimated from a correlation for large-diameter pipes in McAdams.

$$hc = 0.18 \frac{\text{Btu}}{\text{h}\cdot\text{ft}^{2}\cdot{}^\circ\text{F}^{1.33}} (T_{wall} - T_{amb})^{0.33}$$

The radiative heat transfer was estimated for carbon steel with the equation.

$$q_r \cong \varepsilon\,\sigma\,(T^4_{wall} - T^4_{amb})$$

For oxidized carbon steel, $\varepsilon \cong 0.95$

Both the conductive heat transfer through the wall and heat transmission from the wall to the environment must be 3.01 kW/m² (based on outside diameter).

A plot of the heat transfer rate as a function of temperature is shown in Fig. D.1. Note that at an inside wall temperature of 1175°C the heat flux is approximately 3.00 kW/m^2.

Therefore, the heat transfer rates and temperatures assumed are correct.

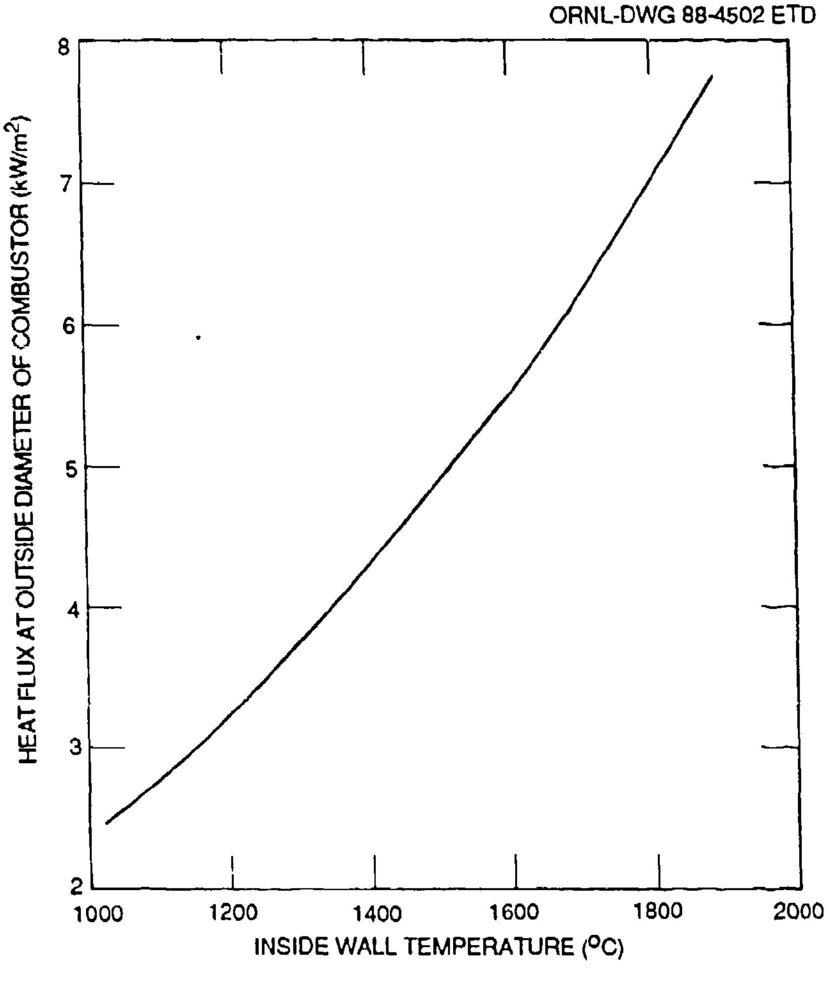
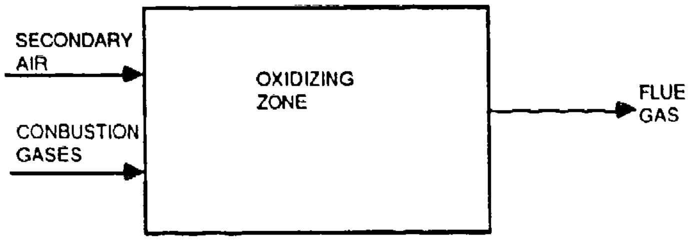


Fig. D.1. Plot of heat transfer rate as function of temperature

Now consider the oxidizing zone:



The energy input to the oxidizing zone is the heat contained in the combustion gases plus the heat of combustion for CO burning to CO_2.

From the analysis of the reducing zone, these heats are:

heat of combustion CO – CO_2	344.0 kW
heat of combustion gases at 2185°F	477.0 kW
	821 kW

The analysis is very similar to the reducing zone.

If the flue gas temperature is 1277°C, the enthalpy of the flue gas is calculated in the following way:

Compound	Flow (kg/h)	ΔH @21°C (MJ/kg)	(21–1277°C) $\Delta H_{sensible}$ (MJ/kg)	Q (kW)
CO_2	215	NA	1.59	94.7
H_2O	182	2.45	2.82	266.8
N_2	1010	NA	1.39	390.2
O_2	97	NA	1.47	39.3
				791.0

Heat loss through wall is

821.0 kW input
-791.0 kW in flue gas
30.0 kW

The oxidizing zone is 2.74 m (9 ft) long. Therefore, the heat flux at the outside diameter is

$$\frac{30.0 \text{ kW}}{\pi\ (1.067 \text{ m})\ (2.74 \text{ m})} = 3.26 \text{ kW/m}^2 .$$

At the inside face of the fire brick, the heat flux is

$$(3.26\ \text{kW/m}^2)\ \left(\frac{1.067\ \text{m}}{0.813\ \text{m}}\right) = 4.28\ \text{kW/m}^2\ .$$

The emissivity of the gas is calculated in the following way:

Compound	Volume (%)	ε
H_2O	19	0.088
CO_2	9	0.072
		0.16

If the inside face of the fire brick is 1245°C (1518 K), and the flue gas temperature is 1277°C (1550 K) then heat transfer is

$$q_r = \varepsilon\ \sigma\ (T^4_{gas} - T^4_{wall})\ \text{radiative heat transfer}$$

$$q_c = 1.65\ \text{w/m}^2{}^\circ\text{C}\ \left(T_{gas} - T_{wall}\right)\ \text{convective heat transfer}$$

$$q_r = (0.16)\ \left[5.728 \times W^{-8}\ \frac{W}{m^2\ k^4}\ \right]\ [(1550\ K)^4 - (1518\ K)^4]$$

$$q_r = 4.19\ \text{kW/m}^2$$

$$q_c = 1.65\ \text{W/m}^2\cdot{}^\circ\text{C}(1277^\circ\text{C} - 1245^\circ\text{C})$$

$$q_c = 0.053\ \text{kW/m}^2$$

$$q = q_c + q_r = 4.19\frac{kW}{m^2} + 0.05\frac{kW}{m^2} = 4.24\frac{W}{m^2}$$

This heat flux, convented to the outer wall of the combustor, is

$$\left(4.24\frac{W}{m^2}\ \right)\left(\frac{0.813\ \text{m}}{1.067\ \text{m}}\right) = 3.23\ \text{kW/m}^2\ .$$

Because the heat flux calculated from heat transfer (3.23 kW/m²) is very close to the heat flux calculated from thermodynamics (3.26 kW/m²), the inside wall temperature is 1245°C.

Note that at an inside wall temperature of 1245°C, the heat flux is 3.31 kW/m^2. Therefore, the inside wall temperature is ~1245°C.

The energy balance is obtained through many iterations. The following process will minimize iterations.

1. Determine the heat loss from the shell of the combustor as a function of shell temperature.
2. Use the heat flux and shell temperature to determine the inside surface (hot face) temperature of the fire brick as a function of heat flux. Plot this relationship as shown in Fig. D.1 (and D.2).
3. Determine the required heat loss rate as a function of flue gas temperature and plot as shown in Fig. D.2.

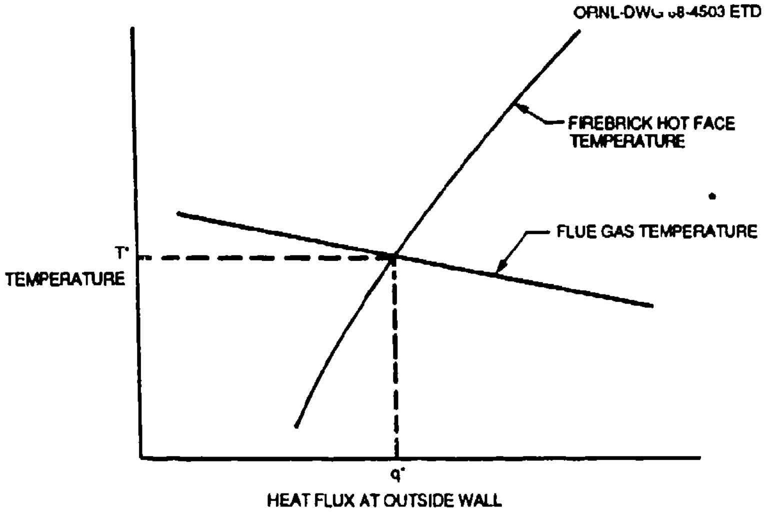


Fig. D.2. Plot of heat loss rate as function of flue gas temperature

4. The immediate observation that can be made is that the flux gas temperature must be above T* and the firebrick temperature must be below T* (heat flows from the flue gas to the fire brick at steady-state).
5. If estimates of exact flue gas and hot face temperatures are required, select a heat flux that is below q* and read the firebrick and flue gas temperatures from the graph. Use the two temperatures

to calculate the heat flux, adjust the heat flux to the outside diameter of the combustor, and determine if it matches the heat flux assumed to determine the temperature. If not, select another heat flux and repeat the process until they match.

Appendix E

DRAWINGS AND SPECIFICATIONS FOR REDESIGNED REFRACTORY SYSTEM

KEITH A. JOHNSON
Engineering Consultant
1178 Hidden Ridge Rd.
Toledo, Ohio 43615
(419)-866-6617

January 8, 1988

Mr. Bill Bradshaw;
Martin Marietta Energy Systems Inc.
P.O. Box Y
Oak Ridge, Tennessee 37831.

Dear Bill;

Enclosed is the final draft of the refractory supply and installation specification, incorporating the changes we discussed on the phone yesterday. Also enclosed is a disk on which is recorded the specification, as well as this letter. I will have a back-up copy of the spec, so if there are any changes, it will be easy for me to accomplish them.

My word processing program is "Leading Edge", copyright 1984. If you have any problems getting into the disk, that program should give complete access.

The type face used for the printing was Smith-Corona Regency 10, should you want to make corrections direct onto the master copy of the spec. This route might be most expedient for minor changes such as drawing number changes, etc.

If there are any other questions or suggestions, please contact Frank Rinker or myself and we will act on them as quickly as we can. Wishing you continued success in the new year,

Sincerely,

Keith Johnson

Keith A. Johnson.

SPECIFICATION
REFRACTORY SUPPLY AND INSTALLATION

LOS ALAMOS NATIONAL LABORATORY
COMBUSTION REACTOR VESSEL

1.0 SCOPE OF SUPPLY:

The scope of supply for the lining of the subject reactor vessel includes all labor and material to install the refractory lining in an M-1 Test Reaction Vessel to be used for the controlled burning of highly reactive combustible materials.

2.0 DESCRIPTION OF EQUIPMENT AND PROCESS:

The equipment into which the subject lining is to be installed consists of a double chamber cylindrical vessel approximately sixteen feet in length and 42 inches outside diameter. There is a 48 inch venturi section approximately 4 feet from the burner end with conical sections leading into and out of the throat.

There are also numerous probes and openings through the lining to accomodate control elements, and for the introduction of air to control the combustion reaction.

The purpose of this unit is to promote a controlled combustion reaction of highly reactive oxidizable materials. The equipment is to be used to demonstrate the feasibility of the process, and to perfect the control of the reaction.

3.0 LINING MATERIALS:

The proposed lining is to consist of the following:

3.1 HOT FACE:

4 1/2 inches of bubbled alumina high temperature insulating brick - B&W INSALCOR or an equivalent product approved by Buyer.

3.2 BACKUP:

1 inch of 6 lb/cu.ft. ceramic fiber blanket, compressed to 1/2 inch thickness - B&W KAOWOOL 2300 or an equivalent product approved by Buyer.

[redacted]

3.3 SPECIALTIES:

Suitable specialty products, chemically and physically compatible with 3.1 & 3.2 above, to enhance lining integrity. All such products are subject to Buyer's approval.

3.4 BUYER APPROVAL:

The Supplier will submit the brand names of all refractory products he intends to use in lining the vessel for the Buyer's approval at least ten days prior to commencement of refractory work.

3.5 QUANTITIES:

The Supplier will furnish all refractory material for the complete lining of the subject vessel. Material shortages or overages will be to the Suppliers Account.

4.0 INSTALLATION:

4.1 LOCATION:

Lining of the equipment is to be done in the shop of the fabricator chosen to make necessary alterations in the steel shell. Alternately, the lining may be done at a location chosen by and convenient to the refractory Installer. Transportation of the vessel shell to such site is the responsibility of the refractory installer. After completion of the lining installation, the test unit will be shipped to Los Alamos, New Mexico, for final assembly in the demonstration facility.

4.2 EQUIPMENT:

The Installer will furnish all necessary equipment, such as saws, tools, etc., which may be required to accomplish the lining task. Transportation of such equipment to the lining installation location and basic security of the equipment while there, is also the responsibility of the Installer.

4.3 SPECIAL EQUIPMENT:

The Contractor will supply a safe and convenient work area and will assure that such manipulation and moving equipment as may be necessary will be available at the lining location.

The refractory Installer shall furnish all forms and jigs necessary for cutting and installing the various lining components. The Installer must also furnish equipment to facilitate refractory transport, such as a fork lift, wheel barrows, etc.

4.4 MATERIALS:

The refractory Installer will furnish the refractory materials. It will be the Installer's responsibility to transport, inventory, and assure the safety of all refractories needed to complete the lining of the unit.

Supply of special materials which, from his experience, the refractory Installer may deem to be necessary or desirable to facilitate the installation, or to enhance lining integrity, are also the responsibility of the Installer. All such materials must be approved by the Buyer at least ten days prior to start of work.

The refractory Installer will assemble a bill of materials which will include all refractory products to be used in the lining. Such bill of materials will include piece counts of all shapes and sizes of brick and other refractory products which the contractor anticipates needing, including extras. This bill of materials will be submitted for the Buyer's approval prior to commencement of the refractory installation

4.5 WORKMANSHIP:

All refractory work will be performed in a professional workmanlike manner, conforming with recognized industry standards, and with the specific requirements set forth in section 6 of this document.

All specified dimensions must be strictly adhered to. Any deviations from specified lining construction must be preapproved by the Buyer in writing before they may be incorporated into the lining.

Prior to commencement of the installation, the Buyer and the Installer will review and agree upon all applicable criteria for acceptable workmanship.

4.6 DRAWINGS:

Four drawings have been prepared showing the configuration of the shell and the lining. The drawings are listed in section 7 of this document.

All drawings are the property of the Los Alamos National Laboratory, and must be surrendered upon request of the Buyer.

Any deviation in construction from that shown on the drawings must be pre-approved in writing by the buyer, and clearly marked on a set of master drawings kept for that purpose.

5.0 SPECIFIC INSTALLER REQUIREMENTS:

5.1 EQUIPMENT AND UTILITIES:

It will be the refractory Installer's responsibility to see that his personnel are fully equipped with the necessary tools of their trade, as well as with all necessary safety equipment, including safety glasses, gloves, hard hats, and respirators.

It is the Contractors responsibility to assure that all necessary utilities are available for the lining of the units. Selection of a refractory lining location is at the discretion of the Contractor.

5.2 PERSONNEL:

The refractory Installer will be required to man the job fully in order to complete the work in the shortest possible time. Suspension of refractory work for any reason will not be tolerated without the Buyer's specific approval.

5.3 HOUSEKEEPING:

Clean-up is part of the job. The Installer will be required to keep a safe, accessible work area, and will be expected to remove all debris and waste material in a timely fashion to a suitable site and receptical. Removal of such debris from the premises will also be the responsibility of the Contractor.

Upon completion of the lining installation, and acceptance by the Buyer, the Contractor will complete all bracing and packing necessary to assure safe transport of the unit to Los Alamos.

5.4 INSPECTION AND QUALITY CONTROL:

The Buyer will conduct on-going inspections during the progress of the installation, as well as upon completion of the lining. All work must meet the prescribed criteria outlined in section 6. Work failing to meet those criteria will be removed and replaced. All costs of such rework, including labor and material, will be to the account of the Contractor.

6.0 LINING SPECIFICATIONS:

6.1 MORTAR JOINTS:

Lining tightness is of extreme importance. All mortar joints are to be thin buttered joints of minimum thickness. In the straight barrel sections, joints will be kept to a thickness specification of 1/8 inch maximum. In miter sections, and in the cones, 3/16 inch maximum will be allowable.

All joints will be struck clean. No wash coat is permissable.

6.2 CERAMIC FIBER BLANKET:

Ceramic fiber blanket is to be installed against the shell using fiber cement to secure it in place pending installation of the hot face brick. In laying the hot face brick, the fiber is to be compressed to approximately 1/2 its nominal thickness. No studs, or other rigid hardware, are to be used to secure the ceramic fiber blanket.

6.3 HOT FACE BRICK:

The bubbled alumina brick prescribed for the lining is a high temperature, high density insulating refractory. Arch shapes are to be used in the proper proportion to assure a round interior surface.

In keying the hot face brick, no key brick less than 1/2 brick thickness should be used. All cutting shall be done with a masonry saw using a wet diamond blade.

In the cone sections, it will also be necessary to key the brick to assure lining integrity. However, due to the necessity of tapering the brick to assure a sound structure, it is recognized that some sections of brick may be less than a full half-section. Mortar joint thickness specifications as prescribed in section 6.1 will apply.

6.4 EXPANSION ALLOWANCE:

Generally, because the lining must remain as tight as possible, there has been no circumferential expansion allowed. It is expected that radial expansion will be accounted for by the crushability of the fiber back-up lining. There has, however, been longitudinal expansion allowed as shown in the included drawings, and it is imperative that this allowance be installed as shown.

6.5 LINING DIMENSIONS:

The buyer recognizes that all dimensions shown on the steel drawings may not reflect the realities found in the field. Nevertheless, it is expected that the Installer will make every effort to maintain the specified internal refractory lining dimensions.

Hot face lining roundness in the barrel sections may not vary by more than one inch as measured by crossed diameters taken at at least two points in the length of each of the barrel sections. Such points of measurement must be at least two feet apart.

The absolute diameter of the hot face refractory may not vary more than plus or minus 1/2 inch from the nominal dimension shown on the drawings.

7.0 DRAWINGS:

The following listed drawings have been prepared and are furnished with this specification for the information of the Installer. All drawings furnished are the property of Los Alamos National Laboratory and must be surrendered upon request.

Drawing No.	Title
103Y-223111 D	
Sheet 1	Reaction Vessel M-1 Test
Sheet 2	Reaction Vessel M-1 Test
Sheet 3	Reaction Vessel M-1 Test
103Y-223112	Assembly Plan View M-1 Test

ORNL-DWG 88-4607 ETD

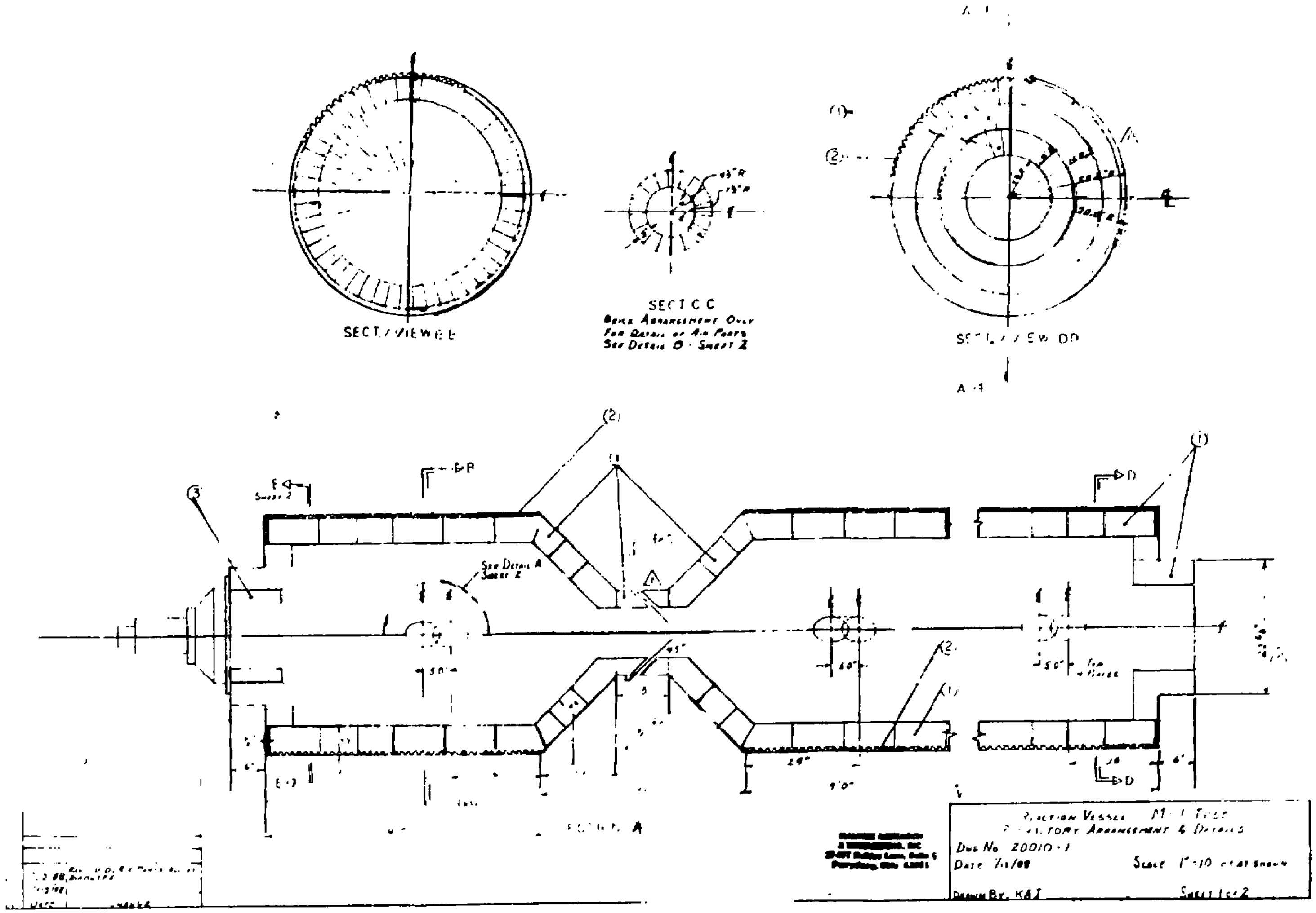


Fig. E.1. Reaction vessel M-1 test

ORNL-DWG 88-4608 ETD

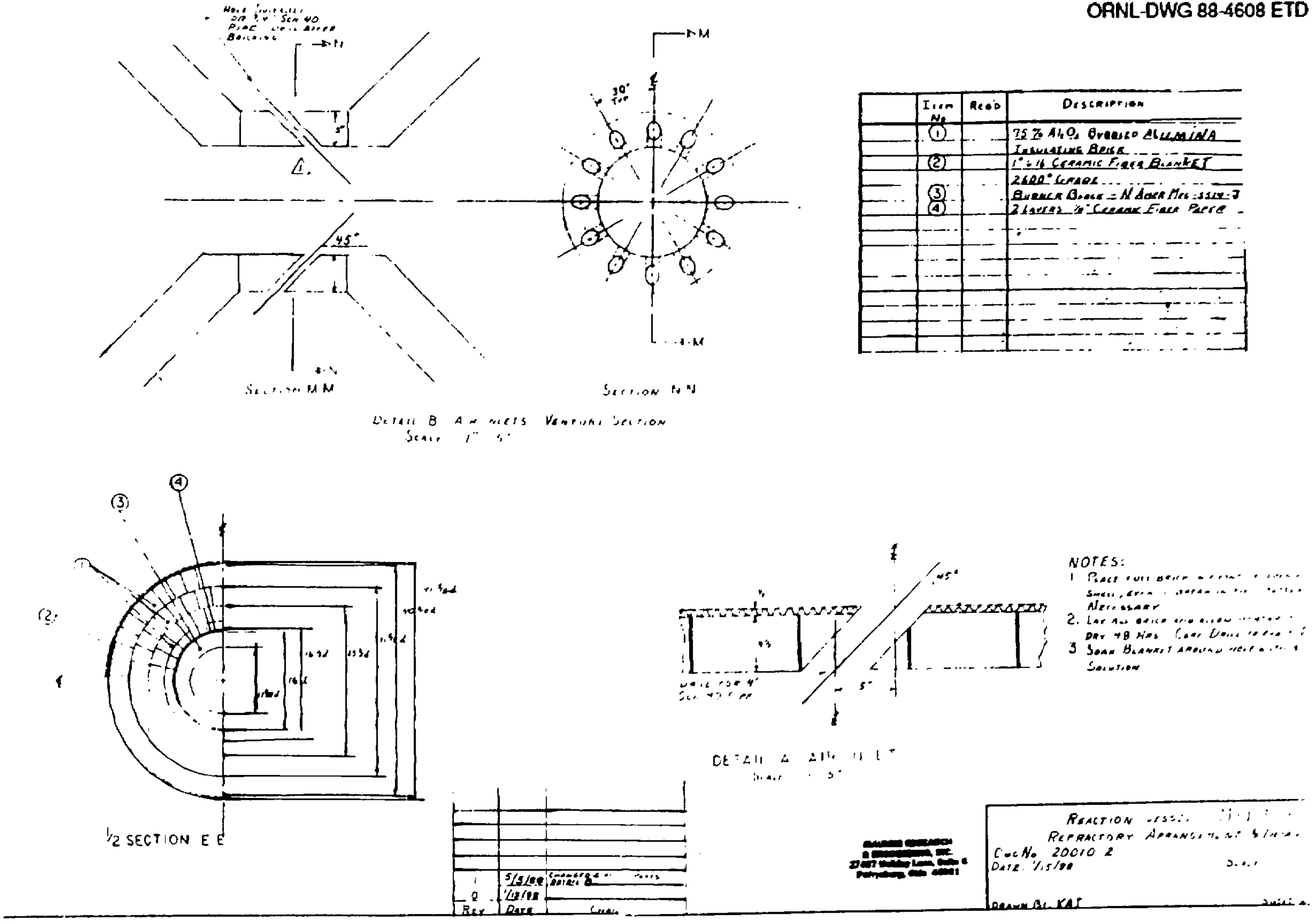


Fig. E.2. Assembly plan view M-1 test

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