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POLLUTANT CONTROL THROUGH STAGED COMBUSTION
OF PULVERIZED COAL

Phase 1

Interim Report for the
Period May-November 1975

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ABSTRACT

The factors that influence the conversion of fuel nitrogen in coal to nitrogen oxides during combustion were experimentally investigated using a unique combustion facility which is described in detail. The tests reported here constitute a prelude to an in-depth investigation on the optimum staged combustion of pulverized coal, and employed the substitution of Argon for molecular nitrogen to isolate fuel originating nitrogen oxide emissions. It was found that under practical combustion conditions fuel nitrogen conversion constituted by far the major portion of total NO_x emissions, and was only a weak function of temperature over a wide temperature range. Radical increases in fuel nitrogen conversion were, however, obtained under conditions of extremely high temperatures or under conditions where coal ignition was delayed. These phenomena are of practical interest since they indicate how both fuel composition and generalized combustion parameters are likely to affect total NO_x emissions from pulverized coal.

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1. OBJECTIVE AND SCOPE

The overall objective of this work is to define the optimum application of staged combustion as a means of lowering pollutant emissions from pulverized coal firing. The study will first investigate the formation of NO_x under classical combustion conditions (unstaged) to determine:

- What fraction of the total NO produced is the result of fuel nitrogen oxidation?
- How do fuel NO emissions depend on flame temperature, inlet and exit O_2 availability, and coal composition?

Secondly, the program will consider those questions critical to the optimum application of two stage combustion:

- How rich should the primary zone be?
- How much heat should be extracted from the primary zone?
- Where and at what temperature should the second stage air be added?

In addition to answering the above critical questions, the proposed work will provide technical insight into how the combustion/pyrolysis environment affects both the behavior of burning coal particles and the devolatilization of combustion products leaving the first (and second) stages. The results obtained can then be used to estimate the nature of problems associated with the utilization by combustion of high nitrogen Western coals, and the potential of solutions of such problems by combustion modifications.

2. SUMMARY OF PROGRESS

In this reporting period construction of the experimental pulverized coal combustor, coal feeding system and flue gas sampling and analytical system was completed and the system was shown to be operating smoothly and safely. Furnace combustion characterization tests using a Colorado bituminous coal were completed. These showed that the system exhibited the salient features of previous pilot scale and full scale pulverized coal tests as far as NO_x emissions are concerned. This means that conclusions drawn from subsequent test series should have some general applicability to combustion units of practical interest.

Because there is a scarcity of data showing the effects of operating variables on relative contributions of Fuel NO and Thermal NO to the total NO_x emissions from pulverized coal combustion, additional experiments were run to elucidate this very important point. Of specific interest is the temperature dependence of the conversion of fuel nitrogen to nitrogen oxides during pulverized coal combustion, a point which has prior to the work, evoked much speculation and controversy. The tests reported here on the combustion of coal in Argon/Oxygen mixtures resulted in a significant increase in the available data describing the conversion of coal fuel nitrogen to NO. The results are reported in detail below, but the following points are especially significant to observe and are mentioned here:

- 1) at typical combustion temperatures over 80% of the NO formed during pulverized coal combustion results from fuel nitrogen oxidation.
- 2) within a wide temperature range fuel nitrogen oxidation is not temperature dependent (as is thermal fixation) although this range may depend on coal type.

- 3) at very high temperatures fuel nitrogen oxidation suddenly increases, presumably because of radical differences in coal particle behavior.
- 4) when coal ignition is delayed allowing early mixing of secondary air, and significant slowing down of particle heating rate, fuel nitrogen conversion is markedly increased.

Future work will determine how these factors are affected by coal type, and the influence of the char burnout regime on NO_x emissions will be investigated through special tests involving coal char. This in turn will provide essential background on the role of fuel nitrogen during coal combustion under non-staged conditions, and this knowledge is critical before a detailed study of staging can be undertaken and the results understood. Present schedule anticipates that the staging test series will commence on March 1, 1976.

3. TECHNICAL PROGRESS

3.1 COMBUSTION FACILITY

3.1.1 Overview

The combustion facility was designed to meet the following criteria:

- The furnace must contain the salient features of real combustion hardware, i.e. it must be capable of burning 75%-200 mesh coal in a swirling turbulent diffusion flame with inlet air velocities near 100 ft/sec and about 600°F preheat.
- It must be large enough to allow utilization of normal screw feeding technology to deliver the coal and to insure that the flame will be self sustaining. However, it must be small enough that synthetic oxidizer atmospheres can be supplied at reasonable cost using standard pressurized cylinders.
- The facility must be flexible. In addition to a variety of pulverized coals, it should be suitable for studying the combustion of residual oils, solid (pulverized) wastes, low Btu gas, crude oil, char, oil shale, etc.
- It must be versatile so that only minor modifications are required to convert it from the classical tunnel chamber to one where the fluid dynamics are "well defined" so that the kinetically controlled NO_x chemistry can be separated from the fluid dynamics.
- It must have variable wall temperature: hot walls to simulate the environment seen by an interior burner of a multi-burner array and cooled walls to

to study particle heating effects or simulate a package boiler system.

The design described in the following sections was developed from these criteria. In concept it is somewhat similar to that used by Beer and Thring (1960) to study pulverized fuel combustion rates.

3.1.2 Furnace

The experimental furnace is illustrated in Figure 1. The vertical combustion chamber is 76" long and 6" in diameter inside. The overall outer diameter is approximately 27". In the lower half of the furnace the walls consist of an outer steel shell, $\frac{1}{4}$ " of roll board insulation, 8" of Harbison-Walker Lightweight 26 insulating castable (2600°F max. service temperature) and 2" of Harbison-Walker Castolast G 3200°F castable refractory. In the upper half of the furnace the walls consist of 6" of insulating castable and 4" of the high temperature Castolast G. This casting pattern was used so that the furnace would be capable of withstanding very hot combustion conditions (coal in argon/oxygen) and yet have minimal heat loss. As Figure 1 shows the upper portions of the inner refractory are removable so that a water cooled section of an alternate design can be installed. In future portions of the work the upper portion will be modified so that there is a well mixed zone followed by a plug flow zone.

At the full load firing rate of 85,000 Btu/hr (6.6 lbs coal/hr) the cylindrical combustion chamber provides a nominal residence time of approximately one second. This firing rate corresponds to a maximum combustion intensity of about 68,000 Btu/hr and is somewhat higher than originally planned. Initial experimentation revealed, however, that the flame was more stable and symmetric at this higher firing

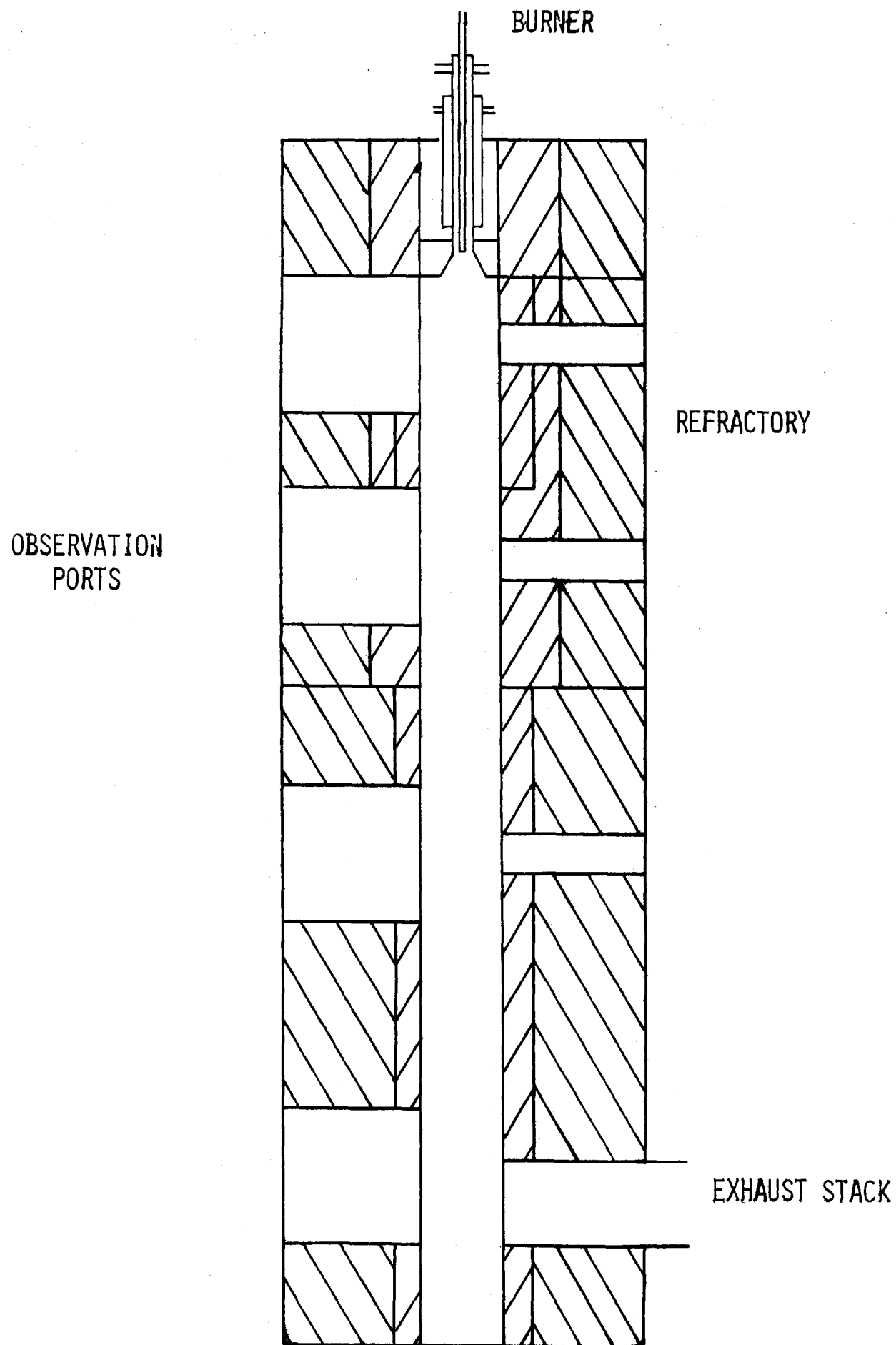


FIGURE 1. EXPERIMENTAL FURNACE

rate, probably because of a more uniform coal feed and a higher upper zone wall temperature.

There are four 6" wide x 10" long observation ports and three 2" diameter ports spaced down the length of the furnace for flame photography, visual observation, and optical wall temperature measurements.

Fuel and air enter the combustion chamber at the top via a water-cooled burner described in detail below. The combustion gases leave the furnace through a 6" diameter exhaust port and flow through approximately 40 feet of air and water double pipe heat exchangers. After the exchangers the flue has a temperature of less than 300°F and is exhausted into a fume duct.

To start the system up initially an 18" Eclipse extended pilot is used. The pilot is positioned in a horizontal portion the refractory about 5" below the top of the furnace. It normally extends approximately half way through the refractory wall and is a long, internally spark ignited pilot burner. Upon ignition it produces a long horizontal flame directly across the outlet of the main burner. When the main gas is then turned on it ignites immediately and the pilot system is turned off. Once the furnace walls are above approximately 1900°F the coal flame can be ignited directly via radiation and convection from the walls; in which case no pilot flame is required.

3.1.3 Multifuel Burner

The specially designed water-cooled burner is illustrated in Figure 2. It has separate axial and swirl air inlets and is similar to that used in previous studies by Pershing et al. (1975) The axial air enters through two ½" angled ports into

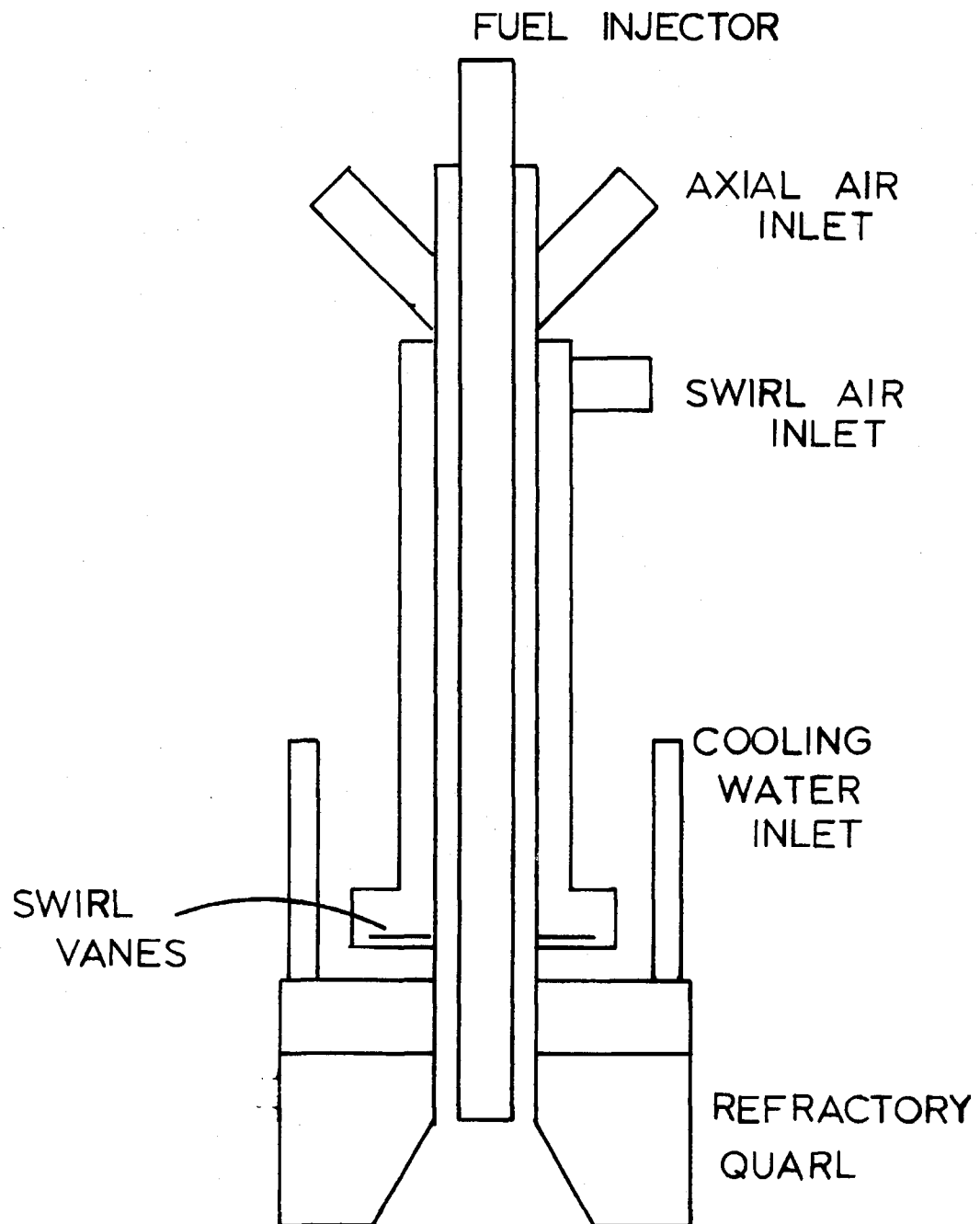


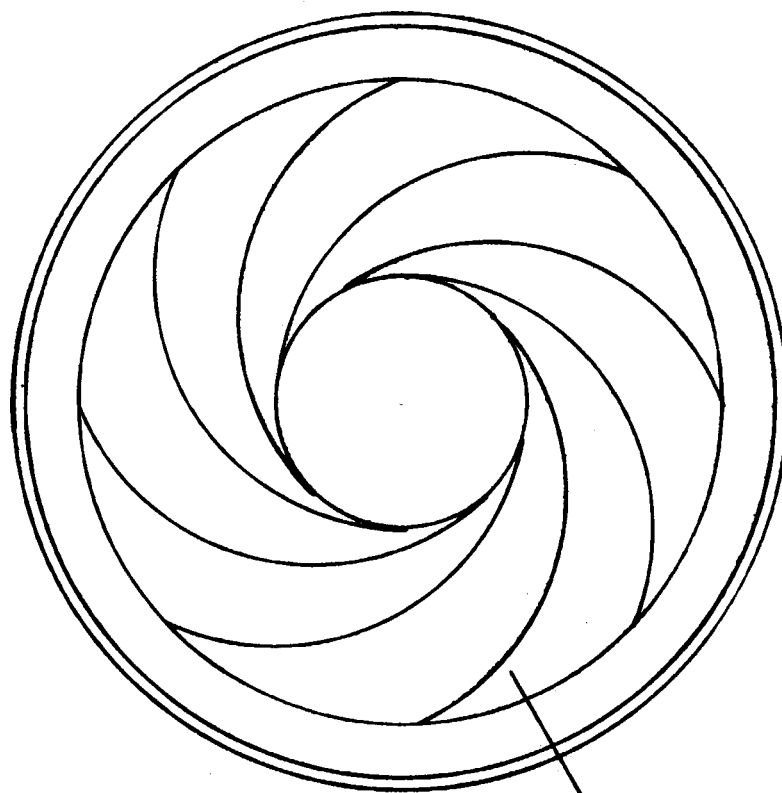
FIGURE 2. MULTI-FUEL BURNER

the center pipe. Swirl air enters a vaned swirl chamber via two tangential ports 180 degrees opposed and passes through eight 0.100" curved swirl vanes as shown in Figure 3. The inside diameter of the burner itself is 1.38", however, several burner inserts were prepared so that the secondary air velocity (axial) could be maintained at 60 ft/sec for a variety of mass flows, air preheats, etc. (Thus when the inlet air temperature was increased from 530°R to 1060°R the burner throat area was also doubled to maintain a constant velocity.) The burner throat is water cooled and the exit is fitted with a 30 degree refractory (Castolast G) quarl that has an L/D ratio of 1.

The top of the burner has a removable collar designed to accept a variety of fuel injectors for natural gas, fuel oils and pulverized coals. The coal injector used in this study is shown in Figure 4. It is a 3/4" stainless steel tube with an end plug containing three 11/64" holes angled to distribute the coal away from the axis. The injector holes are larger than those originally specified based on velocity scaling from full scale equipment. The enlargement was required to prevent plugging which probably resulted because particle size was not likewise reduced.

3.1.4 Air Supply System

The air supply system for the furnace is shown in Figure 5. Under normal operating conditions a 100 psig air compressor provides the combustion air. After being filtered and partially dried, the air goes through two high volume regulators where the pressure is stepped down to approximately 30 psig. For special tests the air is enriched or replaced with varying amounts of carbon dioxide (CO₂), argon (Ar), and/or oxygen (O₂) all of which are supplied from 250 cubic feet high pressure cylinders. In each case there is an appropriate



8 VANES
1/8" THICK
0.100" TALL

FIGURE 3. BURNER SWIRL VANES

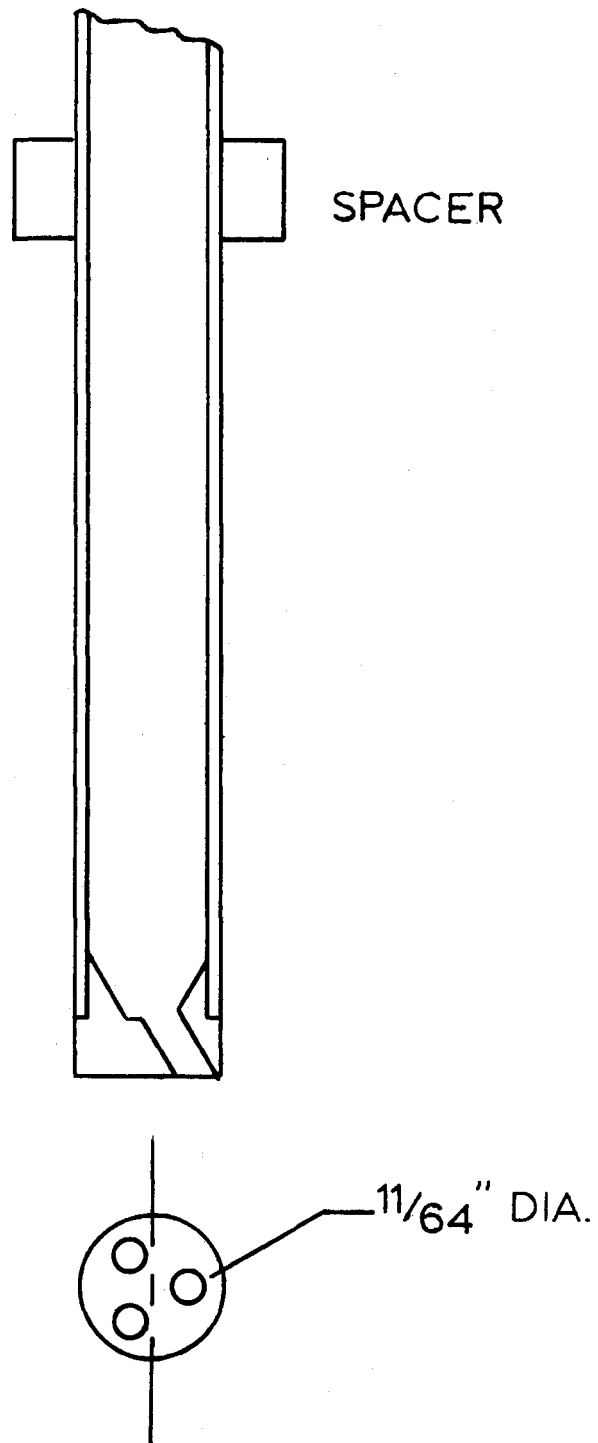


FIGURE 4. COAL INJECTOR

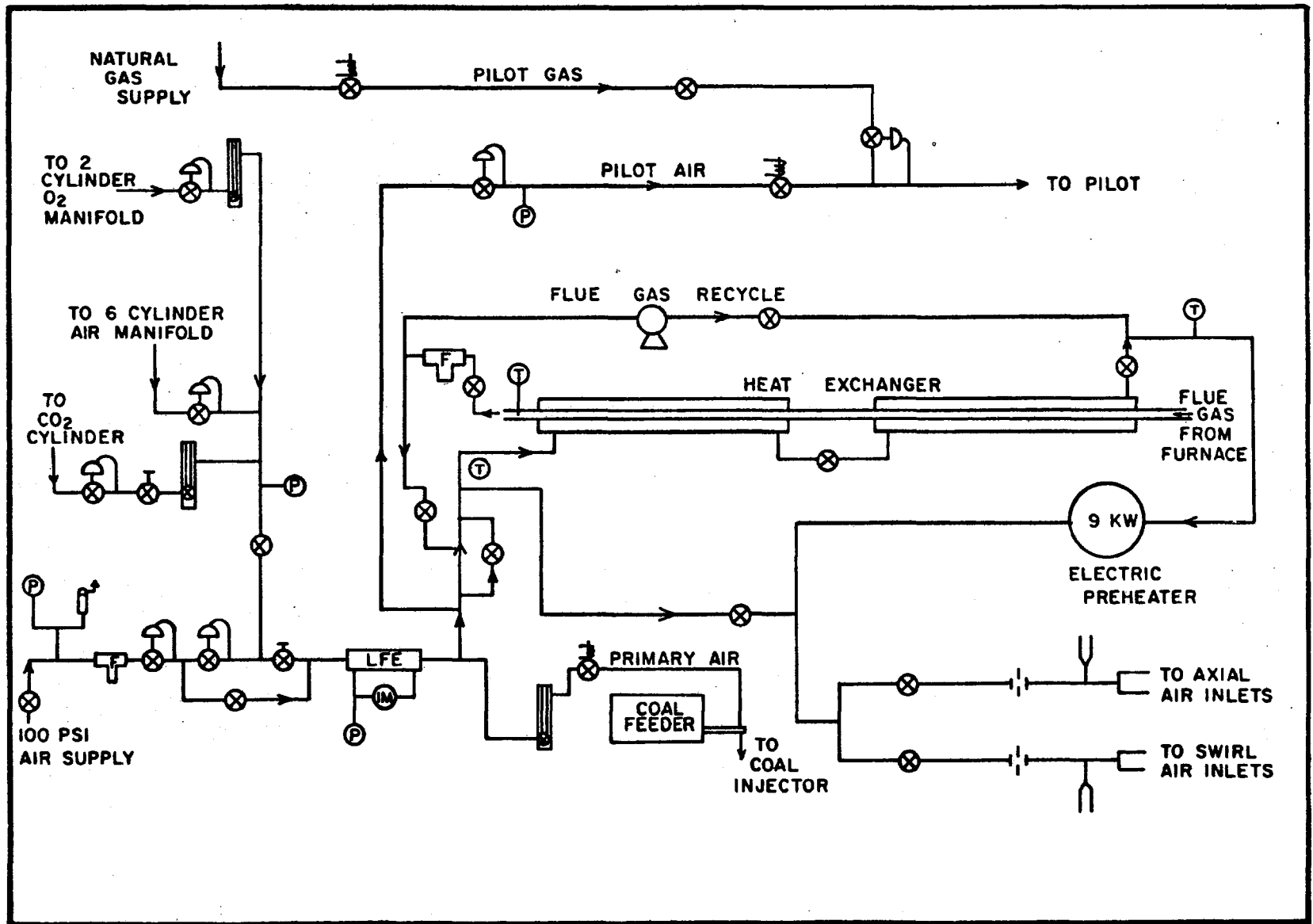


FIGURE 5. AIR SUPPLY SYSTEM

two-stage high volume regulator to step the pressure down to approximately 50 psig and a needle valve for fine control.

Once the pressure has been reduced the air (or artificial oxidizer mixture) goes through a 3/4" micro-needle valve for total flow control and a laminar flow element. The pressure drop across the laminar flow element is measured by a 10" H₂O inclined manometer. In this way a relatively accurate measurement of the inlet oxidized flow is obtained. Next the air is split into three separate streams: the pilot air, the primary air and the secondary air. On startup the pilot air goes through a regulator to step the pressure down to 10" H₂O and then to an Eclipse blast pilot mixer where it is combined with the pilot gas stream. Once the main flame has been ignited, the pilot air is shut off.

The primary air stream is used to transport the coal from the screw feeder to the burner. The flow is controlled by a needle valve and is metered with a calibrated rotameter. The primary air system also contains a solenoid valve which closes automatically after a flame-out. At present the primary air is not preheated prior to the burner.

After the pilot and primary air streams are split off the remaining flow goes to the preheating system. Here the temperature is raised from 70°F to the desired level. This is accomplished by first passing it through the shell side of a double pipe heat exchanger. (The inner pipe contains the hot combustion gases from the furnace.) In this exchanger the air is preheated to approximately 300°F. The final preheating and temperature control is accomplished with a 9 Kw Chromalox circulation heater. The heater was constructed with a 304 stainless steel shell and incoloy elements so preheats up to 1000°F can be obtained.

When desired, filtered flue gas can be recycled from the outlet of the heat exchanger ($\sim 200^{\circ}\text{F}$) and added into the secondary air stream via an ejector prior to the heat exchanger or via a pump just prior to the electric preheater. In both cases the recirculated gases go through the electric preheater and enter the burner at the same temperature as the secondary air. Recirculation of flue gases is common industrial practice, and has been shown to be an effective NO_x abatement measure for gas fired flames.

Once the secondary air has the desired temperature and composition it is split into axial and swirl air streams. The flow in each line is controlled with a high temperature globe valve and metered with a calibrated orifice. Two 0.036" exposed bead iron-constantan thermocouples just prior to the burner inlets are used both for measuring the temperature of each stream and for the input to the proportional temperature controller on the electric preheater.

3.1.5 Fuel-Delivery System

The composition of the coal used for this study is given in Table 1. The Colorado coal contains approximately 39% volatile matter, 53% fixed carbon and 9% ash. It was pulverized to 70% through 200 mesh and is the same coal used by Armento (1975) in his study of effects of design and operating variables on NO_x in a pilot scale coal-fired furnace.

The coal delivery system was designed to be totally enclosed to minimize dust and safety problems. First the coal is loaded into small steel barrels (18" dia x 36" high) outside the facility. The barrels are then closed, brought inside and positioned above the feeder. After the appropriate connections are tightened, gate valves on the bottom of the barrels are opened and the coal flows into the feeder hopper.

Table 1. Colorado Coal Analysis¹

Proximate

% Volatile	38.5
Fixed Carbon	52.6
Ash	8.9
% Total Moisture	3.3
Btu/lb, Dry	12,980

Ultimate, Dry %

C	73.1
H	5.1
N	1.2
S	1.1
Ash	9.8
O (diff.)	9.7

¹From Armento (1975)

The coal feed rate itself is controlled with a mechanical variable speed drive. A tee was attached to the end of the discharge cylinder so that the metering auger delivers the coal stream directly into the primary air flow.

Flow problems were minimized by mounting the entire feeding system directly above the burner. Based on past experience and visual observation of the flow from the feeder, it was initially felt that coal pulsing was going to be a major problem. In an attempt to overcome this a variety of in-line mixing schemes were tried. Ultimately, however, the best approach proved to be a direct, vertical connection from the feeder to the fuel injector (no mixing device) and operation of the feeder at maximum rpm.

Natural gas is used for bringing the furnace up to temperature and maintaining thermal equilibrium when coal is not being fired. In order to obtain a stable lite-off on coal it is necessary that the wall temperature in the upper section of the furnace be above about 1900°F.

3.1.6 Safety/Control System

The furnace is equipped with an electrical interlock safety system to insure both safe startup and proper shutdown in case of a variety of operational problems. The system was designed so that the facility could be operated without an attendant for long periods of time (nights, weekends, etc.) and thereby maintain thermal equilibrium. It monitors the outlet temperature and flow of the various cooling loops to insure system integrity. In the event of a poor or unstable flame for any reason it automatically shuts off all fuel flow. The system also monitors the inlet air and in the event of a compressor failure shuts down both the furnace and electric air preheater (to protect the incoloy elements

from overheating.)

Before power is available for startup and operation the following electrical switches must be closed:

- Low pressure limit switch on the combustion air
- Remote shutdown toggle switch
- High temperature limit on the burner cooling water
- High temperature limit on the window cooling water
- Flow switch on the main cooling water
- Main power switch
- High temperature limit with sensor positioned above burner
- High temperature limit on flue cooling water

Once these switches are all closed (as indicated by a series of green lights on the control panel) startup can be initiated. The natural gas system consists of the following control components.

- Total gas solenoid valve (Maxon) which requires manual opening after it is activated electronically
- Pilot gas ball valve
- Pilot air solenoid valve-interlocked with the ignition transformer so that ignition cannot be attempted without pilot air flow.
- Main gas control valve
- Main gas solenoid valve
- Ignition switch and high voltage transformer.

The coal delivery system has a similar set of control components.

- Main coal feeder switch

- Primary air solenoid valve
- Coal feeder start relay and push-button

For both fuels, the systems are designed so that in the event of a shutdown for any reason, the operator must manually either reopen the gas valve or push the feeder start button again before the fuel flow will begin.

The coal, main gas, and pilot gas flames are all monitored by a Honeywell ultraviolet flame detector. In the event of a flame-out (or very poor flame) this flame detector shuts the system down. (During startup the UV sensor system is by-passed electronically.)

3.1.7 Analytical System

The analytical system was designed so that continuous monitoring of NO, NO₂, CO, CO₂, O₂, and SO₂ could be achieved. Future work will involve, in addition, measurement of NH₃, XN, and solids loading and composition. Figure 6 shows a schematic of the sampling and analysis system. The flue gas is withdrawn from the stack through a 3/8" water-cooled stainless steel probe. During the initial shakedown testing the water-cooled stainless steel probe was compared with both cooled and uncooled quartz probes. No difference in the measured NO was noted, even with CO and unburned carbon present. It should be noted, however, that the flue gas has cooled to below 1000°F at the point of sampling and there is always at least 0.5% oxygen present in the sample.

Sample conditioning consists of a refrigerated dryer (water condenser), two glass wool filters, a 60μ stainless steel filter (50°F), a stainless/teflon sampling pump and a 7μ stainless filter. All sample lines are 1/4" teflon and all fittings 3/6 stainless steel.

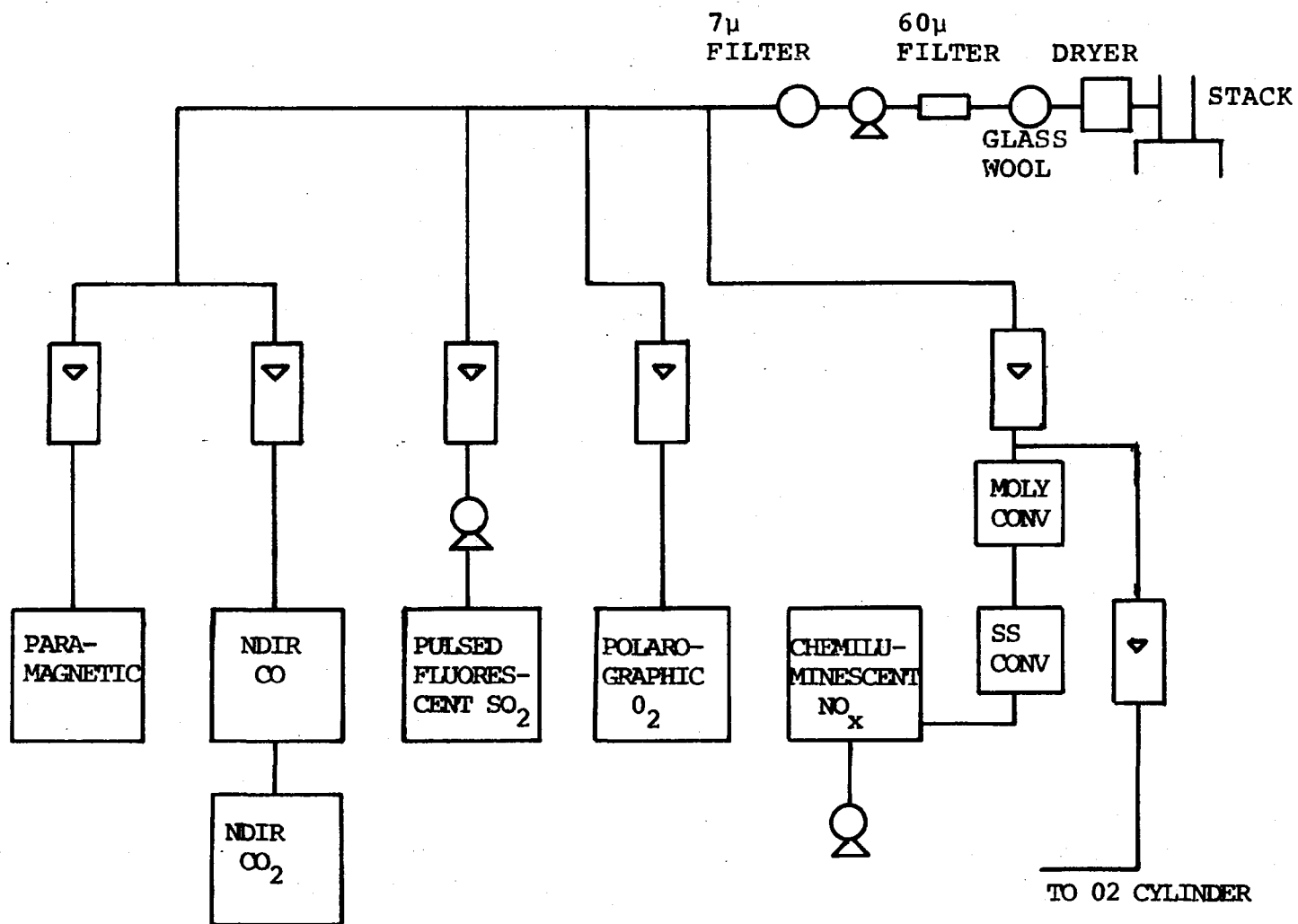


FIGURE 6. ANALYTICAL SYSTEM

The analysis system consists of the following equipment;

- Beckman Model F3 Paramagnetic Oxygen Analyzer
- Beckman Model 864 Nondispersive Infrared CO Analyzer
- Beckman Model 864 Nondispersive Infrared CO₂ Analyzer
- Thermo Electron Model 40 Pulsed Fluorescent SO₂ Analyzer
- Beckman Model 715 Polarographic Oxygen Analyzer
- Thermo Electron Model 10AR Chemiluminescent NO-NO_x Analyzer with Model 300 Molybdenum Convectector.

All instruments are calibrated with zero and span gas at least every three hours.

Future efforts will involve design of a direct water spray quenched probe for sampling gases and particulate matter from hot furnace environments. Such a probe has been used successfully by researchers at the Massachusetts Institute of Technology (Bittner et al. 1975) and Brigham Young University. (Horton et al. 1975)

3.2 EXPERIMENTAL RESULTS

3.2.1 Definition of Terms

Before considering the actual experimental results it is important to explicitly define the terminology used. The NO emission data are presented as parts per million (ppm) NO, by volume, dry, reduced to stoichiometric (zero percent excess air). Primary air is that air used to transport the pulverized coal. Primary percentage refers to the percent of the stoichiometric air which is used as primary air. In general 19% of the stoichiometric air requirement (15% of the total air at 25% excess air) was used to carry the coal.

Secondary air is that air not premixed with the coal prior to the burner. As previously described it enters through axial ports or tangential swirl vanes. The percent swirl is defined as the ratio of the volumetric flow of air introduced through the swirl vanes to the total secondary air volumetric flow rate (swirl plus axial) times 100%.

Air preheat refers to the temperature of the secondary air. The primary air is not preheated prior to the burner.

The secondary air velocity is the axial velocity component of the total secondary air in the burner throat. Note that the axial velocity does not vary with the swirl percentage because it is based on the total secondary air going through the burner throat.

3.2.2 Baseline Characterization

The purpose of the initial experimental testing was to characterize the performance of the total combustion system on one particular coal, a Colorado bituminous. Figure 7 shows the effect of excess air on NO emissions under "normal" operating conditions:

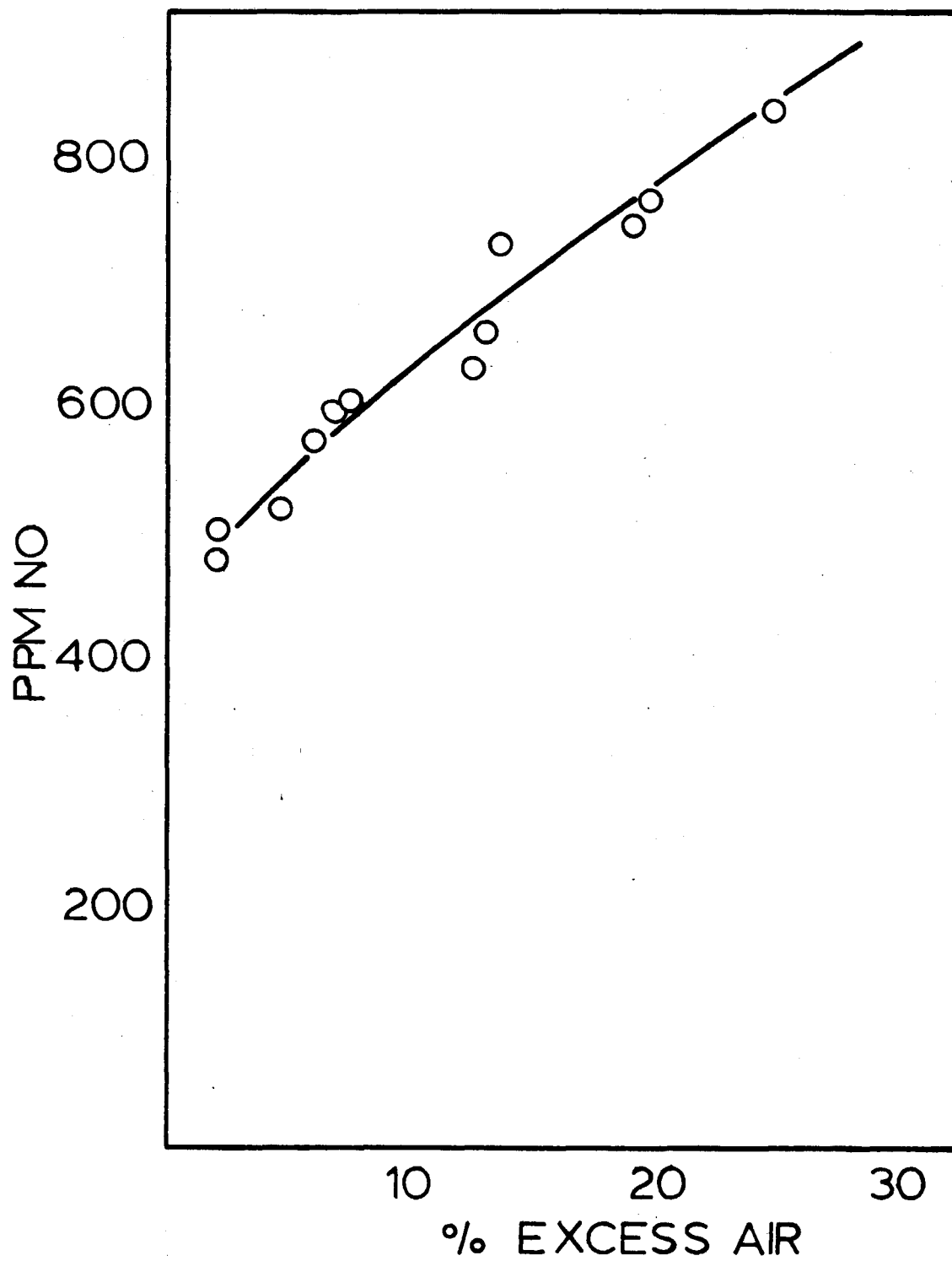


FIGURE 7. BASELINE DATA - EXCESS AIR

- full load - 6.6 lbs coal/hr
- 35% swirl
- 510°F secondary preheat
- 19% primary percentage
- 60 ft/sec secondary air velocity

Three sets of data were taken over a thirty-one day period to provide a measure of the reproducibility of the data.

CO emissions were also measured during these tests and in general they were at or below the detection limit of the analyzer (400 ppm). The low CO levels and the good agreement obtained between the O₂ and CO₂ analysis indicate that the coal was in fact being completely burned under these conditions. Below about 7% excess air, however, the CO emissions start to increase-dramatically and by 2% excess air there was approximately 0.5% CO in the flue.

Figure 8 shows the same data reported with that of other investigators. (Note that the NO in this plot is converted to a 3% O₂ basis since this is the usual point of reference for field testing results.) Armento (1975) examined the identical Colorado coal in a cylindrical, refractory lined pilot furnace with a single burner firing at about 5,000,000 Btu/hr. His results show the same increase in NO with increasing excess air although the absolute level is somewhat higher. McCann et al. (1970) tested a Pittsburgh-seam coal in a four burner water wall unit at 6,600,00 Btu/hr and found similar but lower results. Crawford et al. (1975a, 1975b) tested five full scale wall-fired utility boilers in the field and found the results shown. Thus it appears that the data obtained in the work reported herein on a 85,000 Btu/hr laboratory furnace are consistent in both magnitude and trend with other pilot and full scale data.

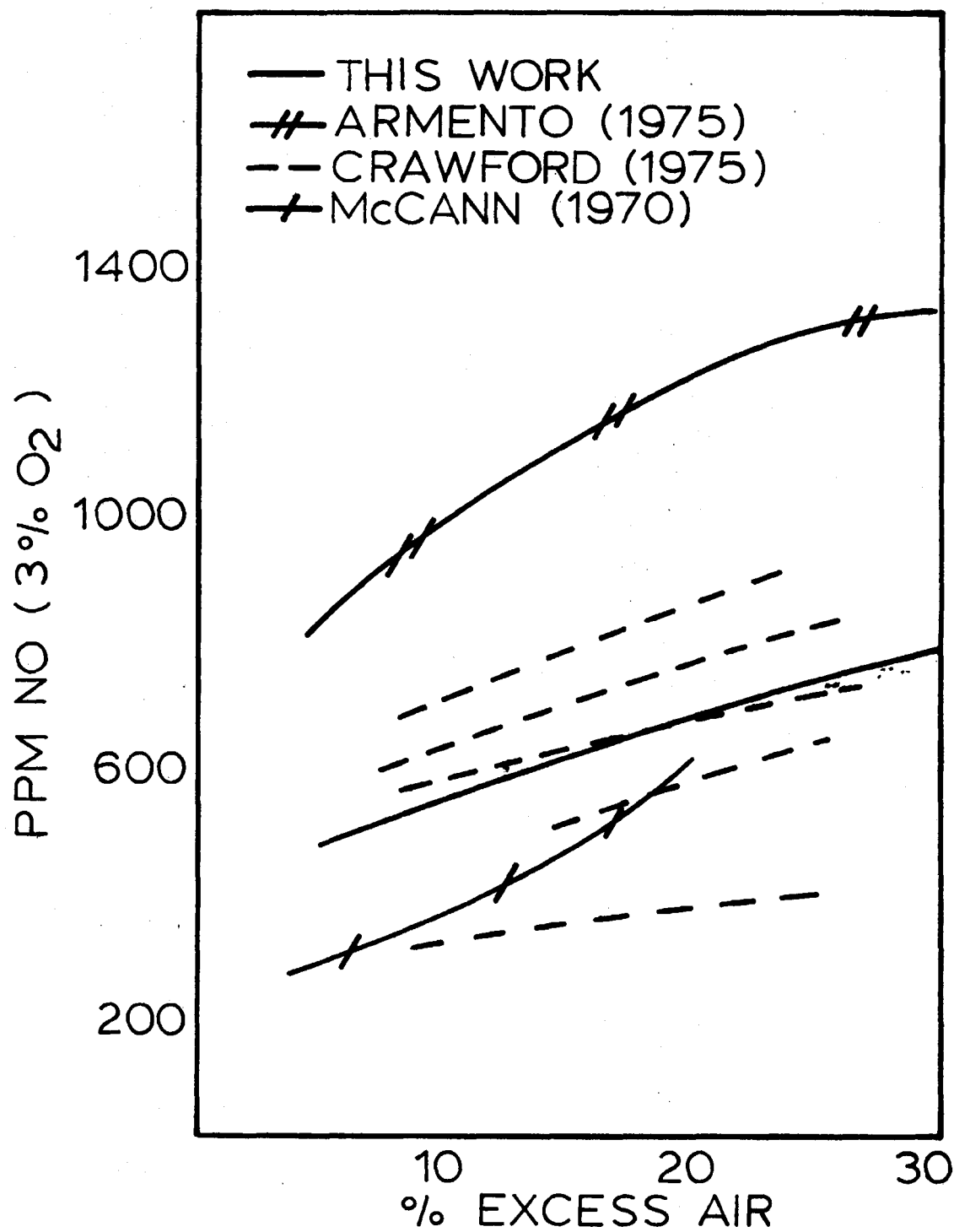


FIGURE 8. EXCESS AIR - COMPARISON

Figure 9 shows that as the percent swirl is increased above 50% the NO emissions start to increase. Visually it was noted that increasing the swirl caused the flame to be shorter and more compact. Heap et al. (1973) have shown that the dependence on swirl is extremely complicated and a function of many variables including fuel injector type, quarl angle, swirl generation method, etc. The increase observed in this current study could either be due to an increase in thermal NO because of higher local temperatures or increased fuel NO due to better early mixing. Further definitive testing is needed to resolve this problem.

Figure 10 shows that reducing the secondary air preheat from 510°F to 155°F had a very unusual effect on the NO emissions. Above approximately 25% excess air the emissions decreased slightly as the temperature was lowered. This is consistent with the data of Armento (1975) and Heap et al. (1975). At the lower excess air levels the 155°F preheat data is considerably higher than the baseline case and it was noted visually that the "flame" was completely detached from the burner in which case ignition took place at some distance down in the cylindrical chamber. The measured increase in NO is, therefore, probably due to a major change in the particle heating rate and/or local environment (due to mixing prior to ignition) rather than the decreased air preheat temperature. It has been shown (Sarofim and Pohl, 1975a) that both particle heating rate and local air fuel ratio can potentially affect fuel nitrogen conversion from coal.

Figure 11 shows that increasing the secondary air velocity (by reducing the size of the burner throat) slightly decreases the NO emissions if a constant swirl percentage is maintained. If the swirl is then increased the emissions again increase as was noted at the lower air velocity. These data are in general

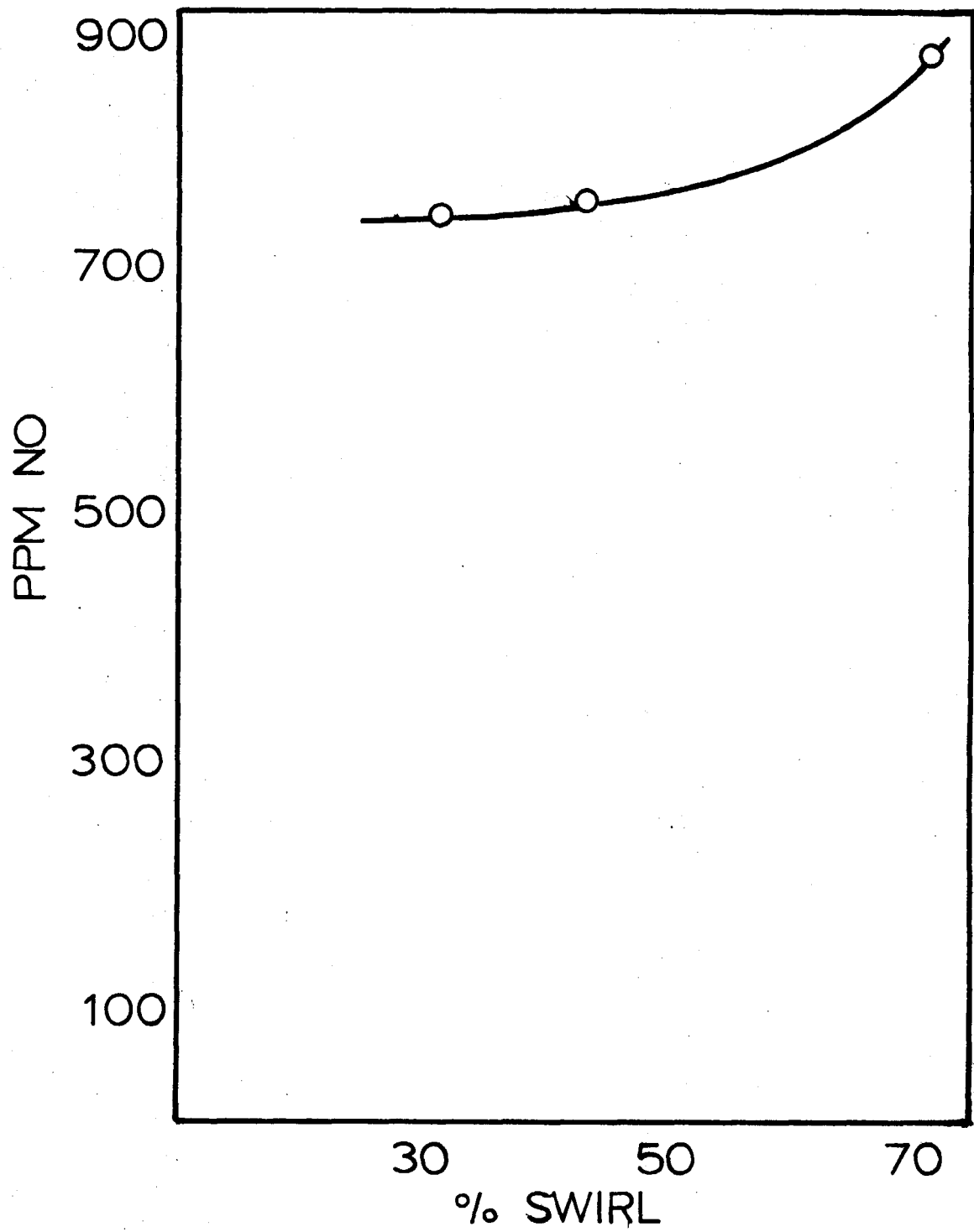


FIGURE 9. INCREASING SWIRL
INCREASES NO

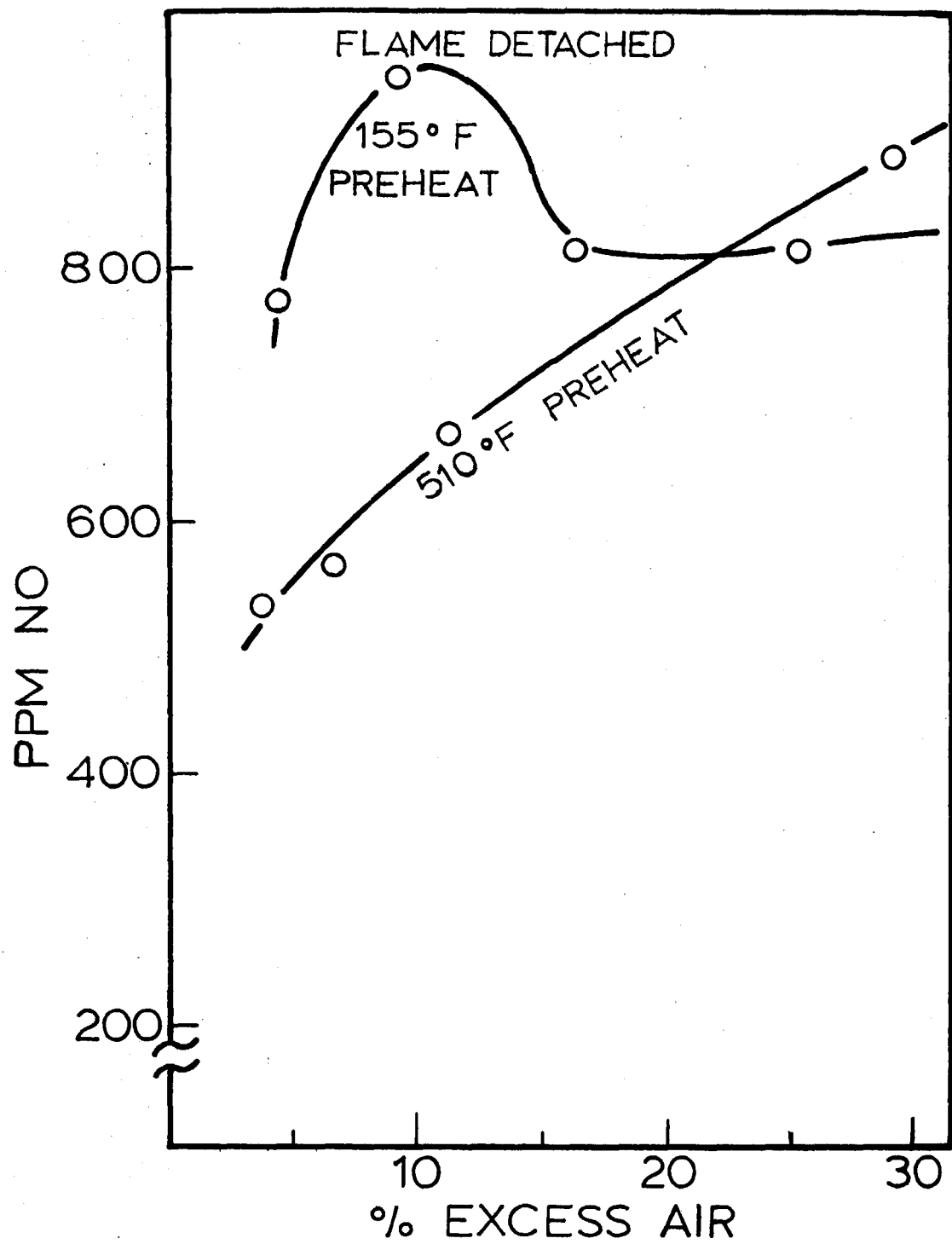


FIGURE 10. EFFECT OF AIR PREHEAT

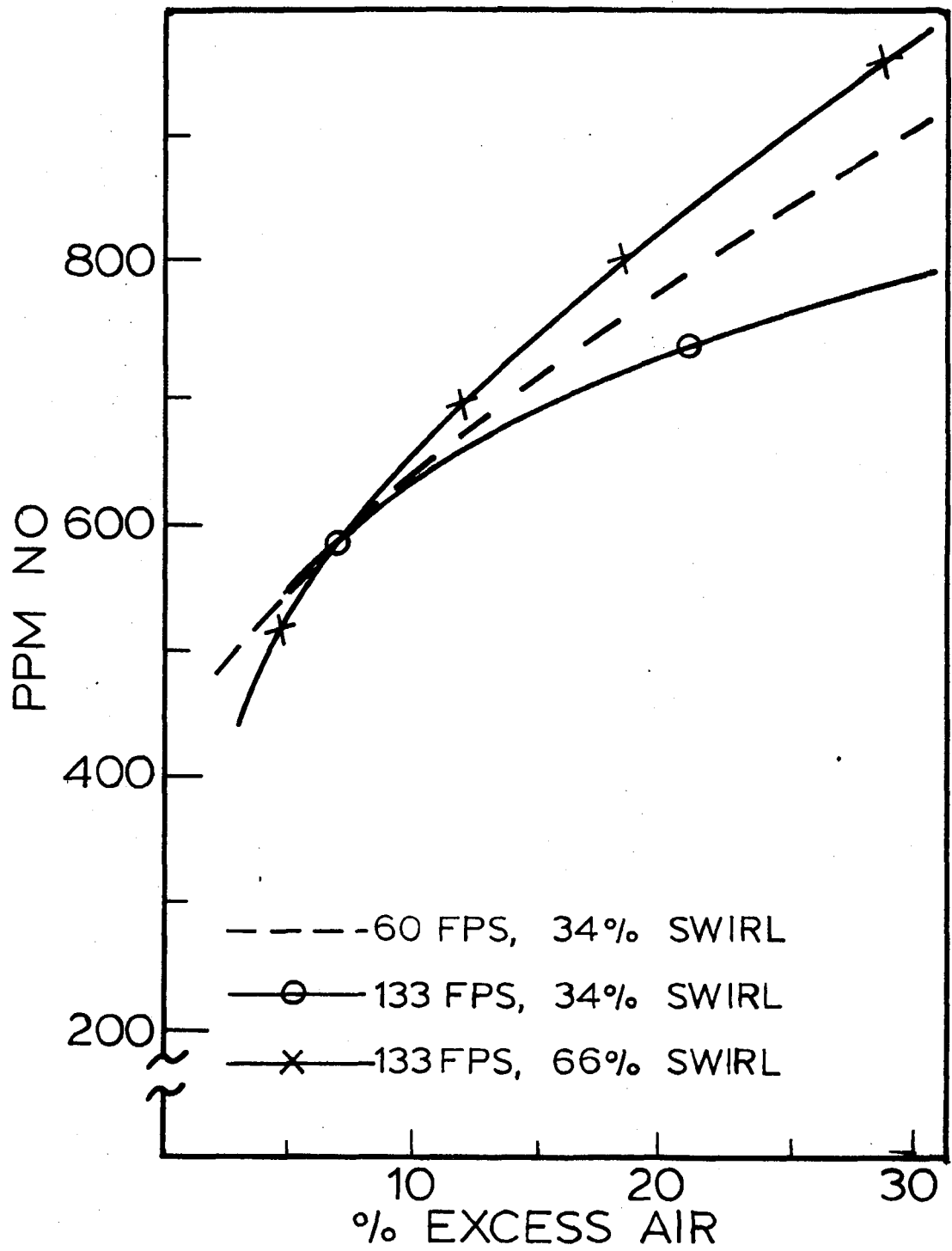


FIGURE 11. EFFECT OF SECONDARY AIR VELOCITY

agreement with those obtained previously by Pershing et al. (1973).

Figure 12 shows that increasing the primary percentage has a small effect up to the point where the flame is no longer stable on the burner. As was noted previously, once the flame lifts off, the NO emissions increase dramatically. It should also be noted that the coal was still burning out even with the flame detached; the CO emissions were less than 200 ppm.

3.2.3 Fuel vs Thermal NO

After the baseline characterization experiments were completed, a series of special tests was undertaken in an attempt to provide definitive answers to a few of the many questions regarding the mechanism of NO formation during pulverized coal combustion.

It was once thought that nitrogen oxide emissions from residual oil and coal combustion were totally due to the fixation of atmospheric nitrogen. Martin (1972) and a variety of other investigators have shown conclusively, however, that the conversion of nitrogen chemically bound in the fuel can be significant under many conditions. Sarofim et al. (1975b), DeSoete (1973), Axworthy (1975), Sawyer (1975), and Merryman and Levy (1975) have studied the oxidation of typical nitrogenous compounds in laboratory flames and found the fuel NO conversion to be very sensitive to oxygen availability but only mildly dependent on temperature. Sternling and Wendt (1972) have considered the fate of chemically bound nitrogen during pulverized coal combustion and concluded that a major portion of the nitrogen may appear in the coal char. Recent experimental work by Sarofim and Pohl (1975a) supports this conclusion and indicates that the division of the nitrogen be-

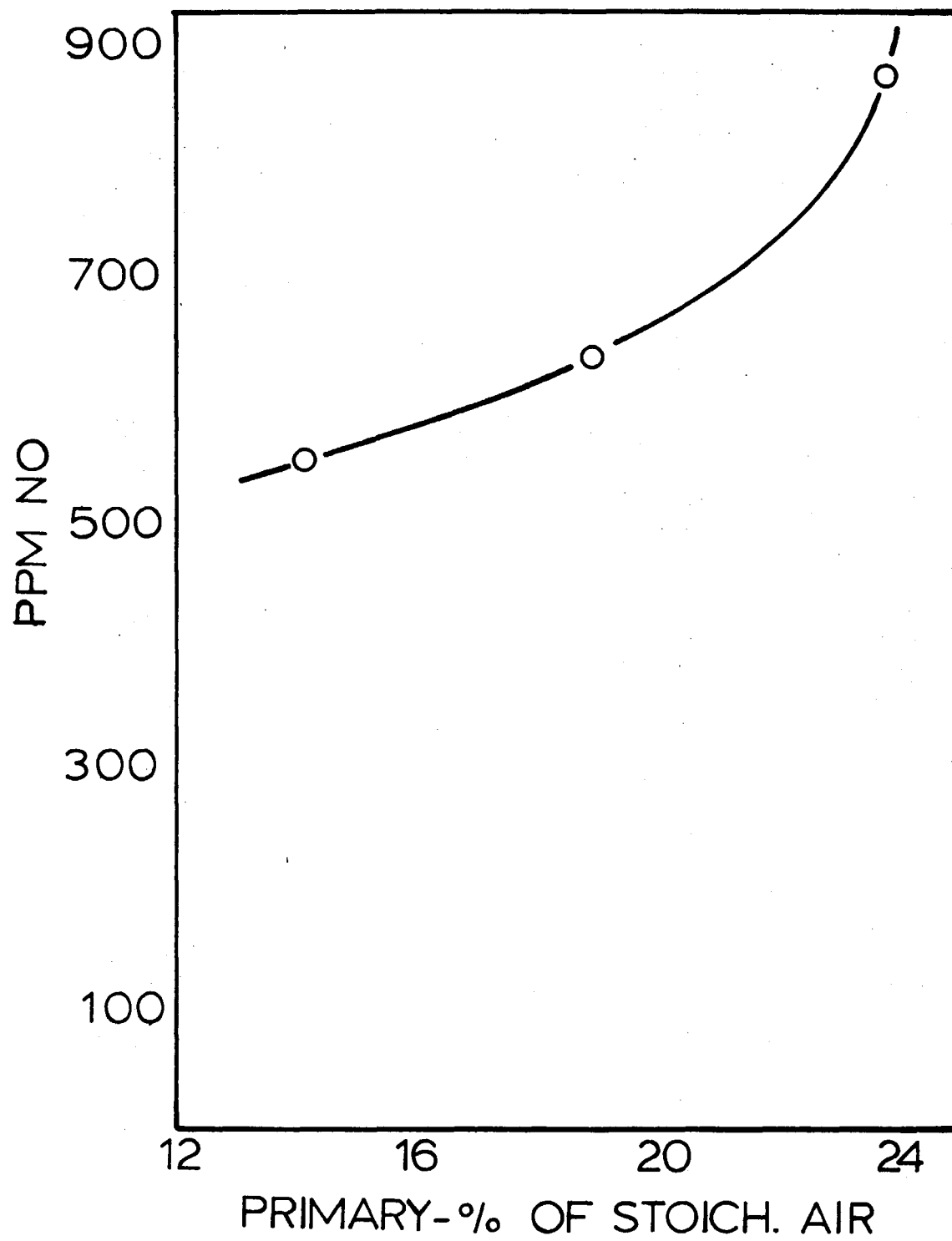


FIGURE 12. INCREASING PRIMARY AIR INCREASES NO

tween the char and volatiles is dependent upon particle heating rates.

Thus while the potential of fuel NO is well established and considerable work is underway to elucidate the relevant mechanism(s), its absolute importance is not yet known. Based on a study of the influence of burner parameters on NO formation, Heap et al. (1973) postulated that fuel NO accounts for the major portion of the NO_x formed during the combustion of pulverized coal. Pershing et al. (1975) later partially verified this hypothesis by burning pulverized coal in both air and argon/oxygen. This work was not absolutely definitive, however, because of the increased temperature associated with the argon/oxygen flames. Therefore, the following critical questions remain unanswered:

-
- 1.0 How does one determine "fuel NO"; i.e. is argon/oxygen replacement a valid method or should the theoretical flame temperatures be matched with the air oxidant case.
 - 2.0 What fraction of the total NO emission at a particular condition is the result of fuel nitrogen oxidation?
 - 3.0 What is the effect of temperature on fuel nitrogen conversion?

Finally, during the combustor characterization testing, lifted flames were accidentally obtained by two completely different methods: reducing the air preheat to 150°F and increasing the primary percentage above 23%. In both cases dramatic increases in NO were noted. This effect appears to be similar to that previously observed by Heap et al. (1973)

using a single hole injector. The reason for this effect is still unclear, hence the fourth question:

4.0 Is the large increase in NO emissions from lifted flames due to substantial increases in fuel and/or thermal NO?

In an attempt to answer these questions a variety of tests were conducted. The initial experiments were designed to help define how to determine fuel NO. Replacing the combustion air with 21% oxygen in argon provides a means of separating the thermal and fuel NO contributions since with Ar/O₂ there can be no thermal fixation. It does, however, suffer from at least three potential weaknesses:

- Since the Ar, O₂ (and later CO₂) are commercial grade they could contain significant impurities (e.g. N₂ or NO) which would invalidate the results.
- If the furnace were not either leak tight or under positive pressure everywhere there could be significant N₂ present from the room air
- Substitution of the Ar/O₂ for air results in a flame that is approximately 400°F hotter due to the difference in heat capacities of the Ar and N₂.

To evaluate the possibility of contamination of the Ar, O₂ and CO₂ and to demonstrate that there were no air leaks in the system, tests were run with 2-propanol and distillate oil. Burning the 2-propanol at 0.5 GPH without air preheat produced 53 ppm of NO. When the air was replaced with Ar/O₂ the emission dropped to below 6 ppm. Burning No. 2 oil with 500°F air preheat under similar conditions produced 72 ppm NO in air and 11 ppm in O₂/CO₂/Ar. In the latter case

the bulk of the 11 ppm is probably due to nearly complete oxidation of the small amount of fuel nitrogen in the distillate oil (Martin 1972). Both tests, however, demonstrate that it is possible to prevent the formation of thermal NO by using a synthetic atmosphere.

To assess the importance of flame temperature change two sets of experiments were conducted. In the first the combustion air was replaced by 21% oxygen in argon (theoretical flame temperature of 4090°F). In the second the oxidizer was 21% oxygen, 18.8% CO₂ and the balance Ar. This latter mixture gives a theoretical flame temperature of 3670°F which is very near that of normal air (with 500°F preheat). Figure 13 shows these results at various excess air levels. The data indicate that for this Colorado coal, temperature is not of first order importance within this range. Therefore, it is valid to replace the air with Ar/O₂ and thereby determine fuel NO.

Figure 14 shows the baseline fuel and thermal NO emissions as a function of excess air. The fuel NO was determined using the 21% oxygen in argon atmosphere. As the data indicate approximately 80% of the total NO is the result of the oxidation of bound nitrogen in the fuel. Both the fuel and thermal NO increase with increasing excess air for the baseline conditions (510°F preheat, 45% swirl, 19% primary air and 60 ft/sec throat velocity.)

To investigate the effect of combustion temperature on both fuel and thermal NO a variety of oxidizer combinations were used in addition to simple preheat changes. Increasing the oxygen percentage markedly increases the theoretical flame temperature (in either N₂ or Ar); however, it could also potentially cause an increase in the NO due to increased

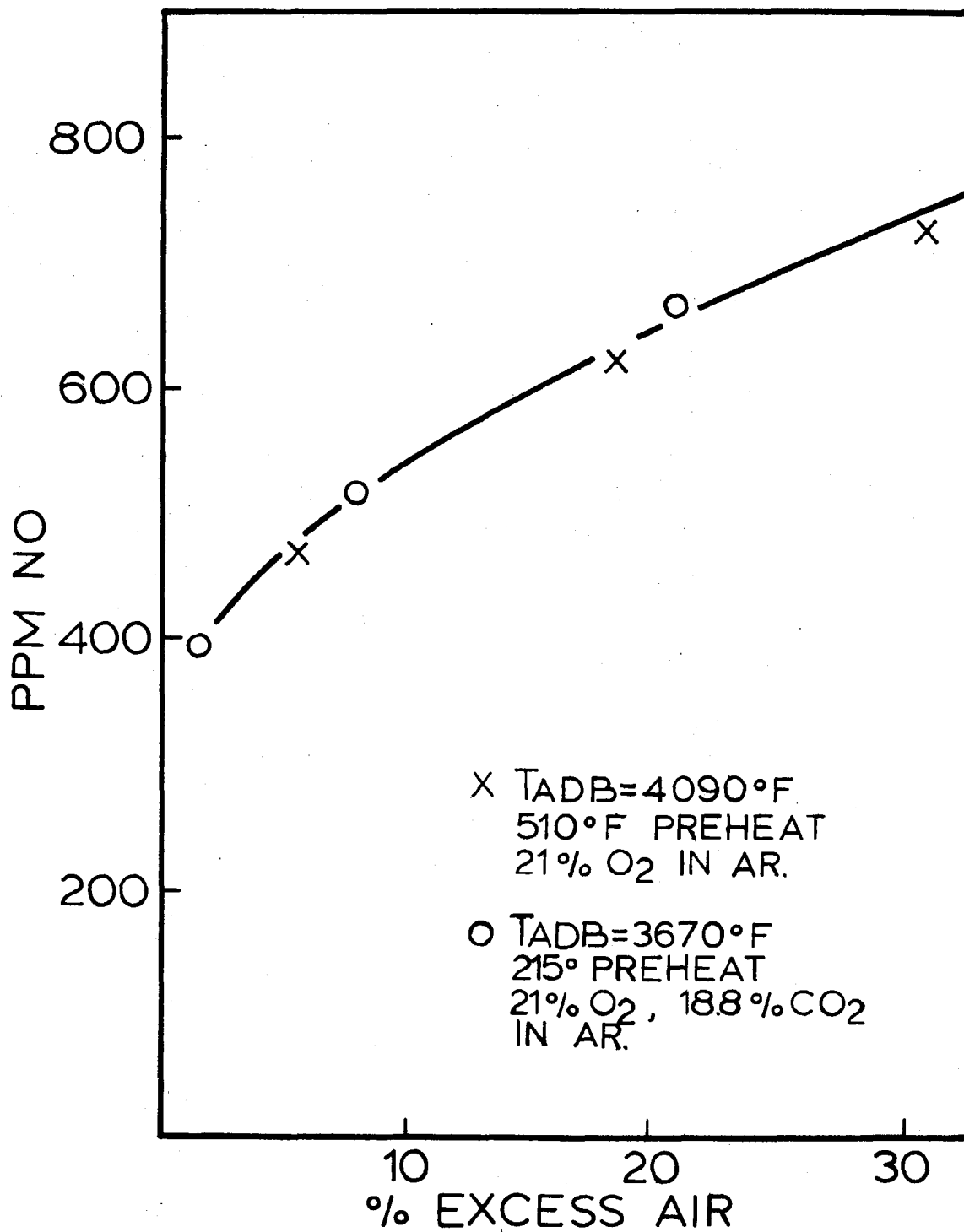


FIGURE 13. FUEL NO HAS A WEAK TEMPERATURE DEPENDENCE

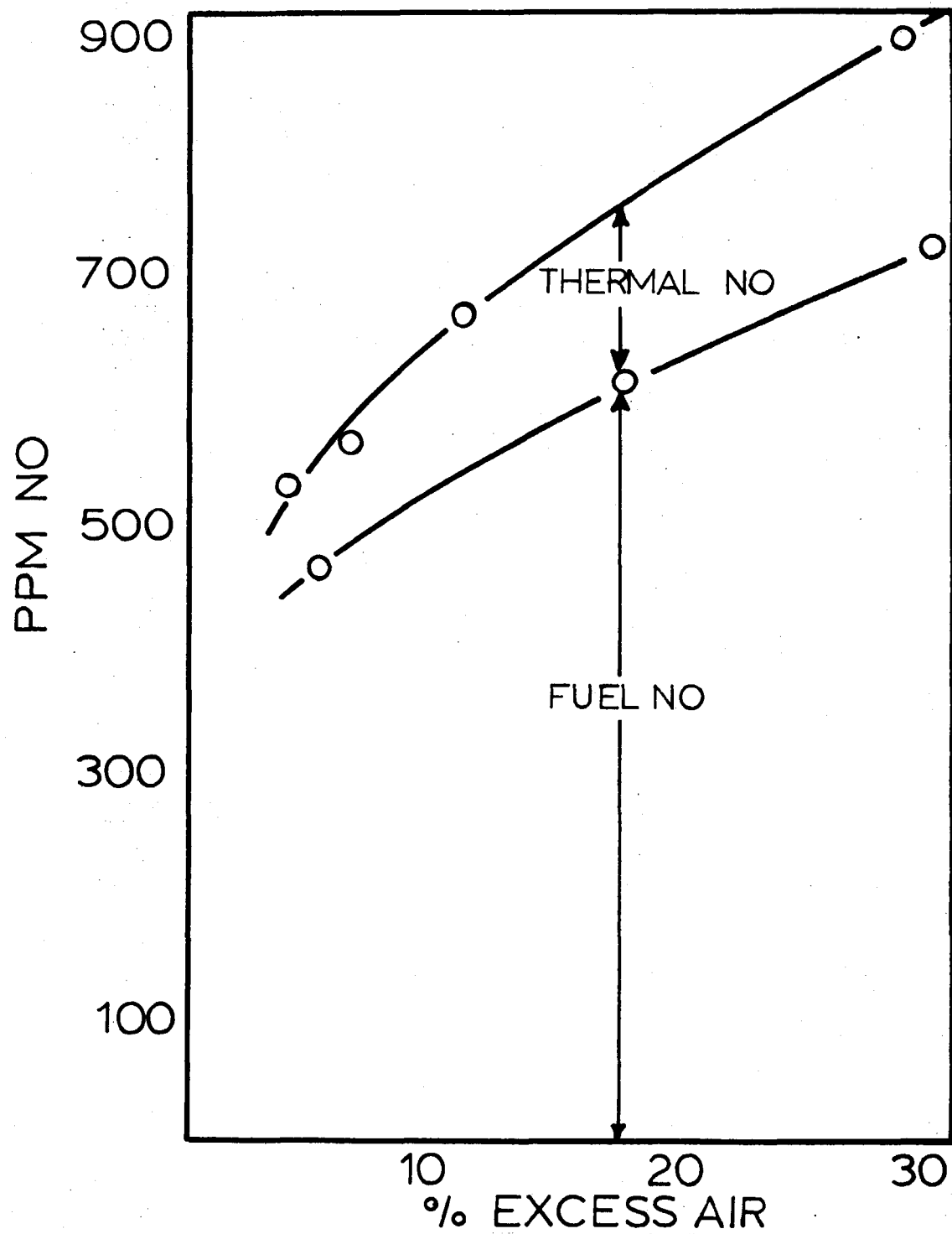


FIGURE 14. BASELINE FUEL AND THERMAL NO EMISSION

oxygen partial pressure. To determine the importance of this partial pressure increase two sets of experiments were run where the theoretical flame temperature was held constant at 3640°F and the oxygen percentage was increased from 21% to 23%. (The flame temperature was maintained by reducing the air preheat from 500°F to 100°F.) Figure 15 shows these data and indicates that, within the accuracy of this work, a 2% increase in inlet oxygen percentage has no effect on the NO_x emissions so long as the flame temperature is maintained constant.

Figure 16 is a plot of NO emissions at 15% excess air for a variety of flame temperatures. Since no actual experimental measurement of the local flame temperatures is available the data are plotted against the adiabatic flame temperature. This does not, however, imply that the authors think the combustion is occurring at this temperature; it is merely a correlating parameter.

As the temperature is increased above the baseline condition (500°F preheat) the thermal NO begins to increase markedly. Reducing the temperature essentially eliminates the thermal NO; however, the combustion also becomes more unstable. Over most of the range the fuel NO is essentially constant; however, there appears to be a point beyond which it begins to increase. In these experiments this was achieved in 24% O₂/76% Ar with 500°F air preheat.

These results indicate that within a fairly wide temperature range, temperature affects both the physical behavior of coal particles and the fuel nitrogen kinetics only slightly. However, at very high temperatures, this is not true, and radical differences in the physical behavior of the coal particles may result in high fuel nitrogen conversion. It would be interesting to determine if the new high NO level is also

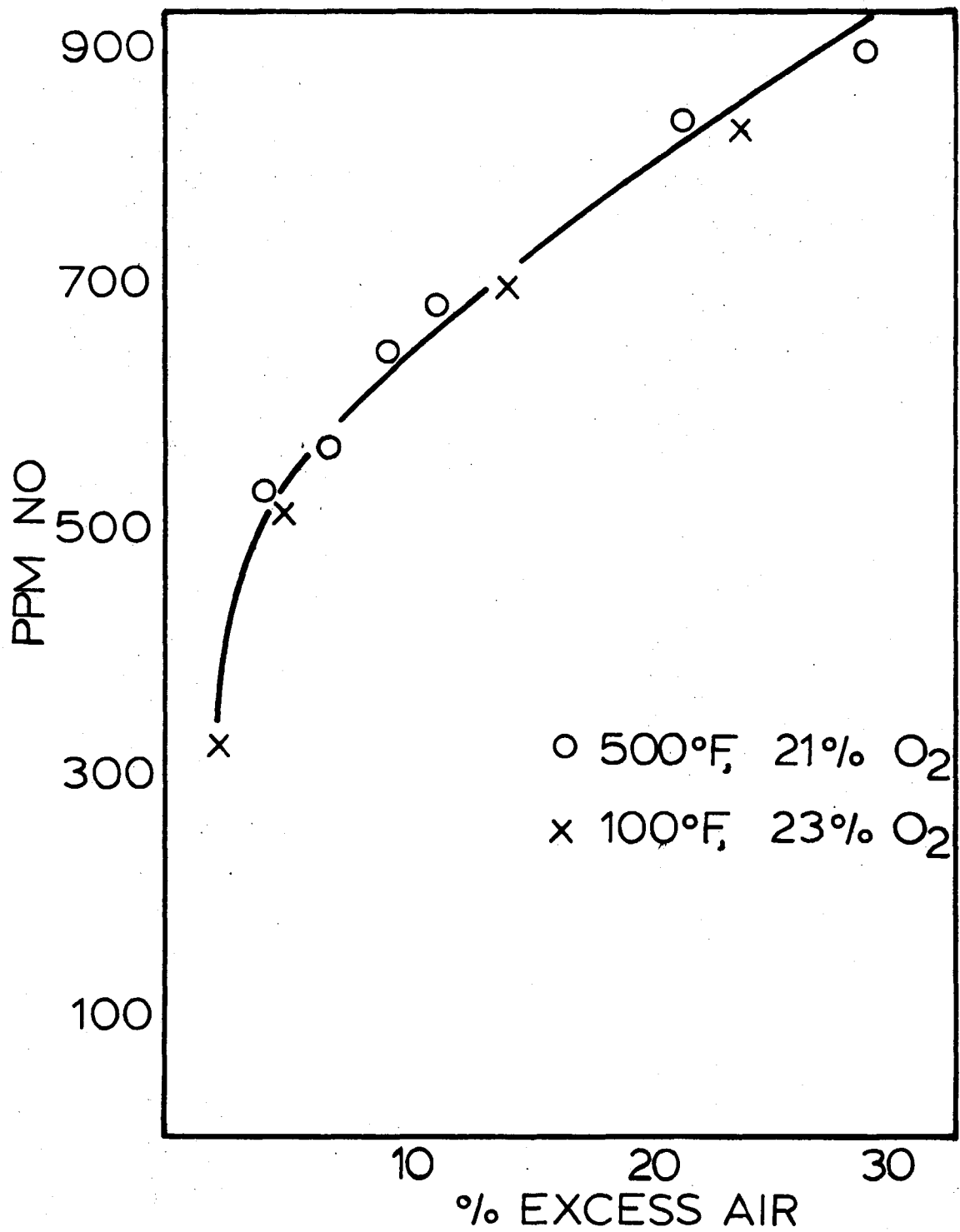


FIGURE 15. NO EMISSIONS ARE A
WEAK FUNCTION OF INLET O₂

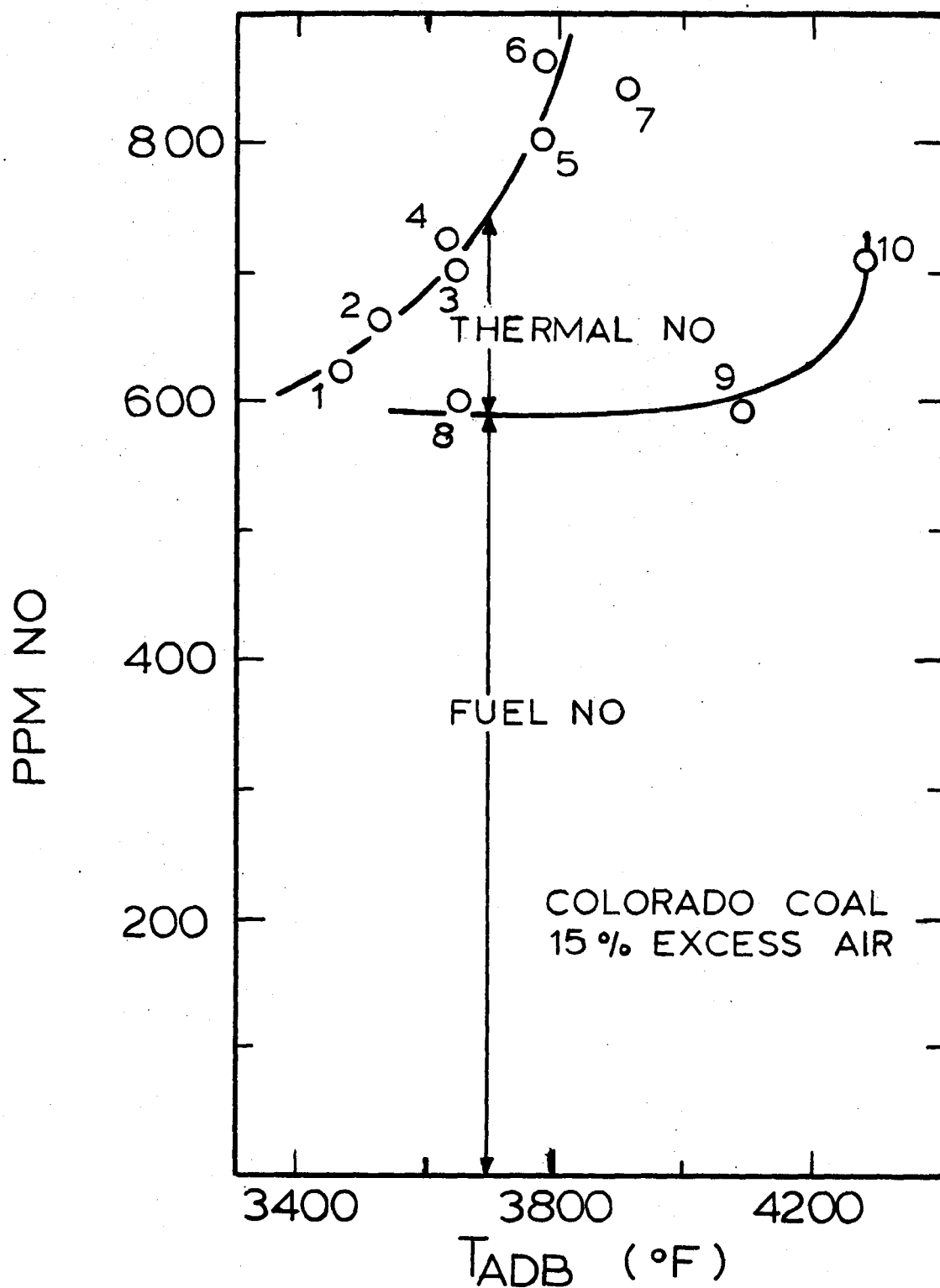


FIGURE 16. TEMPERATURE DEPENDENCE
OF FUEL & THERMAL NO

Explanation of Points - Figure 16

Point No.	Conditions
1	530°F preheat 11.8 CO ₂ , 20.7% O ₂ , bal N ₂
2	515°F preheat 7.7% CO ₂ , 20.9% O ₂ , bal N ₂
3	90°F preheat 23% O ₂ , bal N ₂
4	505°F preheat 21% O ₂ , bal N ₂
5	516°F preheat 22.9% O ₂ , bal N ₂
6	506°F preheat 23.0% O ₂ , bal N ₂
7	501°F preheat 25% O ₂ , bal N ₂
8	215°F preheat 18.7% CO ₂ , 21% O ₂ , bal Ar
9	476°F preheat 21% O ₂ , bal Ar
10	481°F preheat 23.8% O ₂ , bal Ar

maintained over a new fairly wide temperature range, and also if the point at which a temperature dependence of fuel nitrogen conversion becomes significant, is a function of coal type. Future work will investigate both these aspects.

Figure 17 shows the effect of blowing the flame off the burner with air and Ar/O₂. The marked increase in NO with the flame lifting noted in the characterization experiments is clearly due to increased fuel NO. This increase can be attributed to increased oxygen availability at ignition (due to better early mixing) and/or a much slower particle heating rate. Clearly fundamental experimentation (e.g. Sarofim and Pohl 1975a) is needed to resolve this question.

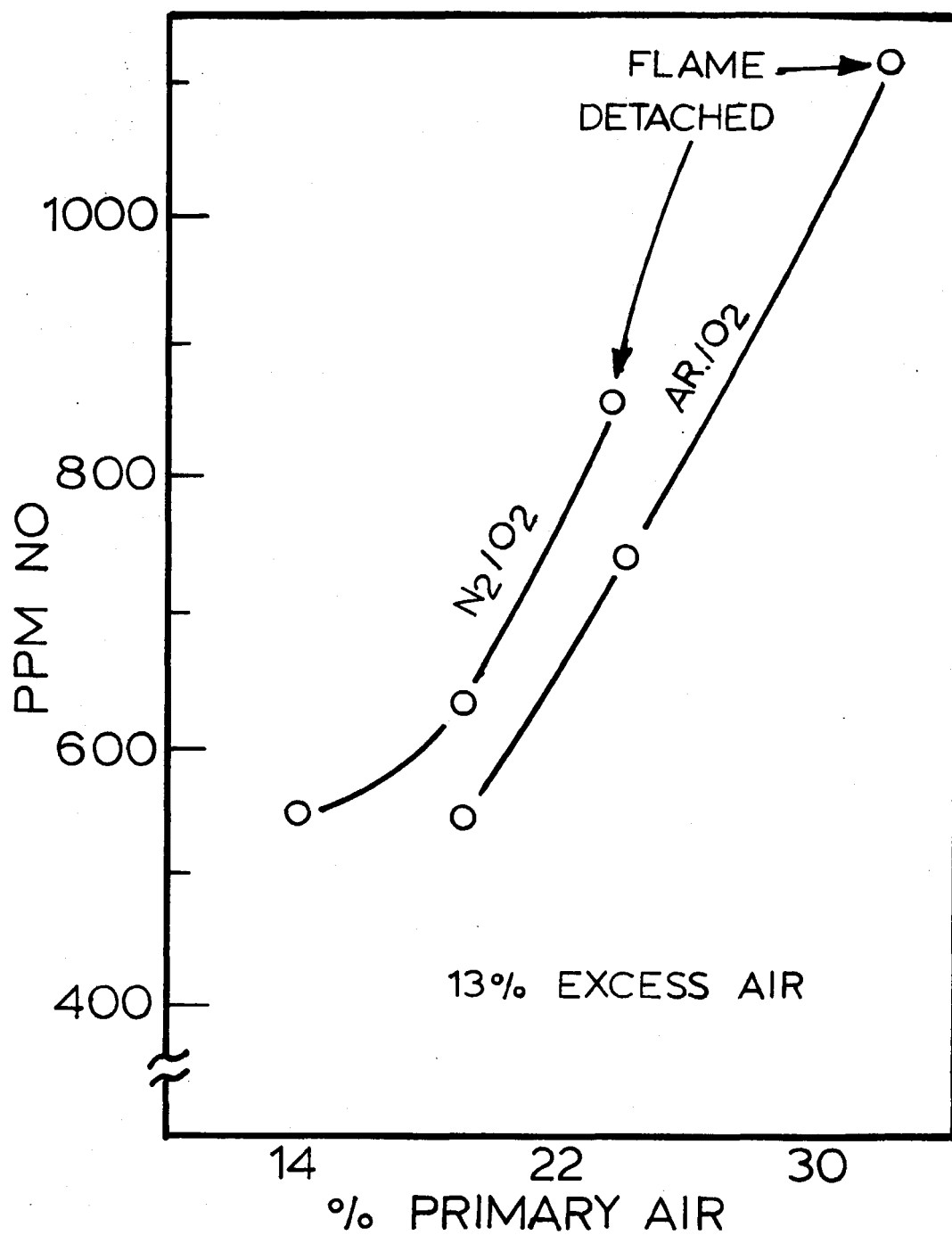


FIGURE 17. INCREASING PRIMARY AIR INCREASES FUEL NO

4. CONCLUSIONS - COLORADO COAL

The experimental pulverized coal combustor, coal feeding system, and flue gas analysis system are complete and fully operational. Baseline NO emission data on the effect of excess air, swirl, air preheat, secondary air velocity and primary percentage are generally consistent in both magnitude and trend with those of other investigators. The results obtained from this facility should, therefore, have some general applicability to other pilot and full scale units.

The relative importance of Fuel NO can be determined by replacing the combustion air with a mixture of O₂, Ar, and CO₂. At typical combustion conditions over 80% of the total NO formed is the result of fuel nitrogen oxidation. Further, within a broad temperature range, oxidation of the fuel nitrogen is very weakly temperature dependent. Thus to obtain significant emission reductions with this coal, control technology must markedly reduce conversion of fuel nitrogen to NO and this cannot be accomplished by reducing the flame temperature (as with flue gas recirculation.)

At very high temperatures, fuel nitrogen oxidation dramatically increases, perhaps because of radical differences in coal particle behavior. This result suggests that large pulverized coal flames with very high (800-1000°F) air preheats may result in very high NO emissions.

REFERENCES

Armento, W.J., Environmental Protection Technology Series,
Report EPA-650/2-74-002b (1975)

Axworthy, A.E., paper presented at the EPA Stationary Source
Combustion Symposium, Atlanta (1975)

Beer, J.M. and M.W. Thring, Anthracite Conference,
Pennsylvania State University (1960)

Bittner, J.D., R.A. Hites, J.B. Howard, P.H. Lin and G.P. Prado,
paper presented at the EPA Stationary Source Combustion
Symposium, Atlanta (1975)

Crawford, A.R., E.H. Manny, W. Bartok, and R.E. Hall, AIChE
Symp. Ser. No. 148, 71 75 (1975a)

Crawford, A.R., E.H. Manny, M.W. Gregory, and W. Bartok,
paper presented at the EPA Stationary Source Combustion Symp.,
Atlanta (1975b)

DeSoete, G., Revue del Institut Francois du Petrole, 28, 95 (1973)

Heap, M.P., T.M. Lowes, and R. Walmsley, Proc. Combustion
Institute European Symp. (1973)

Heap, M.P., T.J. Tyson, and T.M. Lowes, paper presented at the
68th Annual AIChE Meeting, Los Angeles (1975)

Horton, M.D., F.P. Goodson, and L.D. Smoot, paper presented
at the 68th Annual AIChE Meeting, Los Angeles (1975)

Martin, G.B. and E.E. Berkau, AIChE Symp. Ser. No. 126, 68, 45 (1972)

McCann, C.R., J.J. Demeter, A.A. Orning, and D. Bienstock, paper presented at ASME Ann. Meeting, New York (1970)

Merryman, E.L. and A. Levy, paper presented at the EPA Fund. Comb. Research Contractors Meeting, Menlo Park, California (1975)

Pershing, D.W., J.W. Brown, and E.E. Berkau, paper presented at EPA Coal Comb. Seminar, Research Triangle Park, N.C. (1973)

Pershing, D.W., G.B. Martin, and E.E. Berkau, AIChE Symp. Ser. No. 148, 71, 19 (1975)

Sarofim, A.F. and J.H. Pohl, paper presented at the EPA Stationary Source Combustion Symp., Atlanta (1975a)

Sarofim, A.F., G.C. Williams, M. Modell and S.M. Slater, AIChE Symp. Ser. No. 148, 71, 51 (1975b)

Sawyer, R.G., paper presented at the EPA Fund. Comb. Research Contractors Meeting, Menlo Park, California (1975)

Sternling, C.V. and J.O.L. Wendt, Environmental Protection Tech. Ser., Report EPA-650/2-74-017 (1972)