COMBUSTION AT HIGH TEMPERATURES AND MODERATE PRESSURES

PART I - QUENCHING EQUILIBRIUM CONCENTRATION OF NITRIC OXIDE

by

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ABSTRACT

A pre-pilot plant test rig for the thermal fixation of atmospheric nitrogen has been successfully built and operated.

The furnace was 8 inches I.D. and 14 inches O.D., 36 inches high and was built with interlocking segmental zirconia brick. Preheated air (approximately 700 °C and oxygen concentration 21 - 60%) was passed down the annular space between the furnace wall and the insulating brick, which was backed by a stainless steel shell, insulated with fibrefrax from the pressure shell which can hold pressure up to 100 psi. The air burned fuel injected at the bottom and the hot gases (at a temperature of up to about 3000 °K) passed out through a water-cooled tube at the top and then to the air preheater.

Yields of nitric oxide close to its calculated equilibrium concentrations have been obtained and yields as high as 3.7 percent nitric oxide by volume have been realized experimentally. Moreover, curves have been obtained showing nitric oxide concentrations as a function of furnace gas temperatures and oxygen concentration. Gas temperatures exceeding 3000 °K have been reached but the quenching rates available to fix the nitric oxide were found to be inadequate for the gases at these high temperatures.

Other methods of quenching the nitric oxide have been attempted; namely, air quenching, kinetic nozzle quenching and water spray quenching. Insufficient data prohibit forming any conclusions about the last two methods. Quenching by mixing cold air with the hot gases does not appear to be effective. However, indications were that this may be due to the improper mixing of the cold air with the hot gases and later tests with improved mixings gave encouraging results.

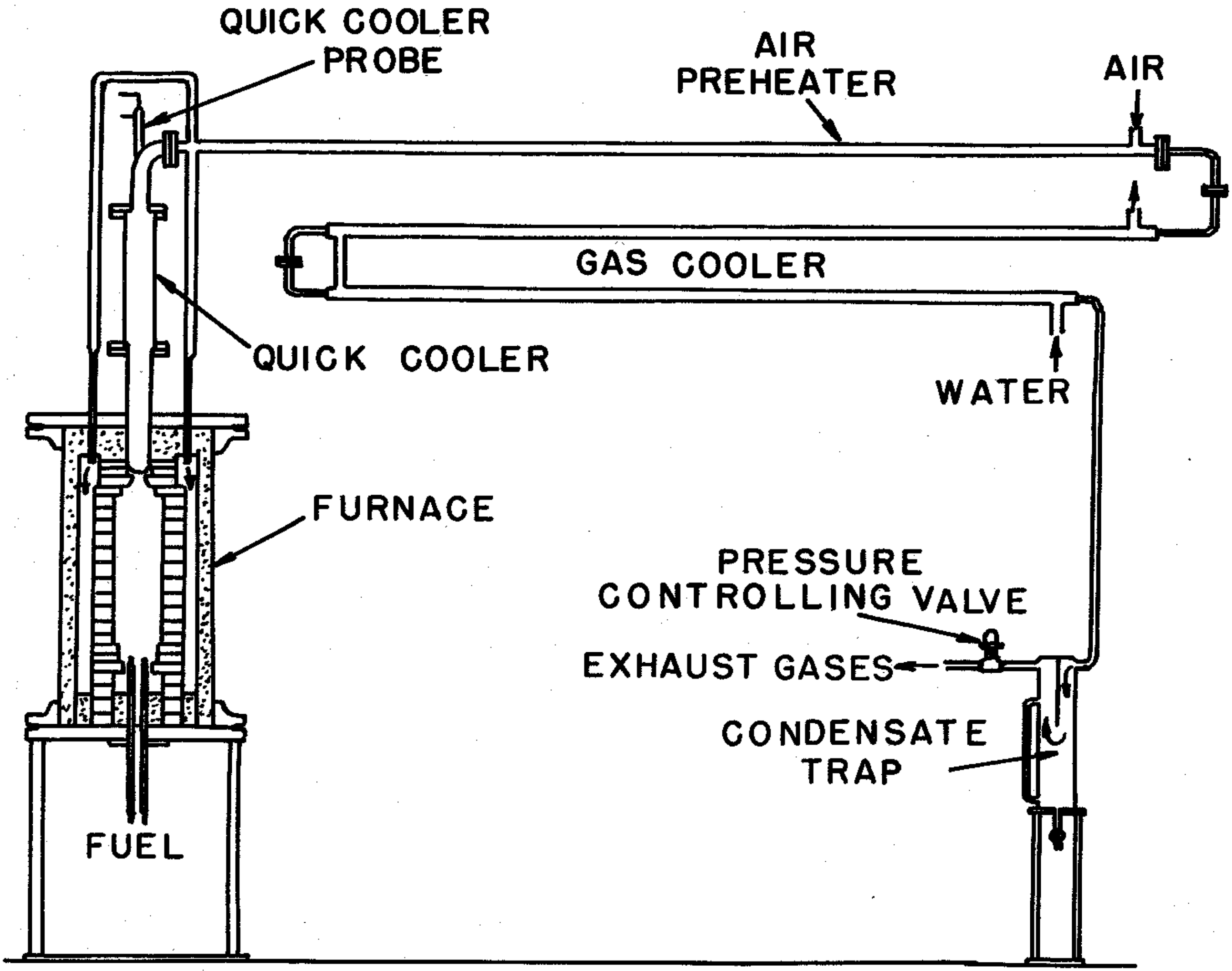
Further improvements have been made on the rig to reduce bypass leakage and to prevent combustion in the wrong place. These have resulted in more reliable operation and more confidence can be placed in the results which confirm previous observations that 3.7 per cent nitric oxide by volume is the yield at 3000 °K. The separate water cooled sampling probe inserted at the top of the furnace gave quenching rates of the order of 10^6 °C/sec. This also permitted the study of the effect of variation in the quenching rate while maintaining other conditions constant. Suitable instrumentation was provided to estimate the furnace gas temperature and to compare with other methods. However the oxygen concentration appeared to have less effect than previous results indicated but this may have been due to uncertainties in estimating gas temperatures near 3000 °K.

INTRODUCTION

Early experiments on a small scale (1, 2) had shown that useful concentrations of nitric oxide could be obtained thermally in a continuous flow process where propane was burned with preheated air. Moreover, a study of methods to recover nitric oxide from a gas containing dilute concentration of nitric oxide showed that two methods; the silica gel adsorption process (3, 4, 5) and the freeze-out process commercially known as the Fauser process (6), can be utilized to yield recovery efficiencies over 90 percent. The scientific and patent literature has been reviewed and some of the most pertinent work is listed (7 - 15).

It was realized that the process would operate most efficiently with the maximum air preheat temperatures (of the order of 1500 °C) which could be obtained with a counterflow or regenerative ceramic heat exchanger. However because of the additional cost and uncertainty in operation it was decided to proceed with a pre-pilot plant test rig based on a stainless steel heat exchanger which would provide some useful information on the influence of oxygen concentration, temperature and necessary quenching rates.

Work on this test rig was begun in February, 1954. The design of the new rig was finished by May and the rig construction was completed during the summer of 1954. Preliminary tests were held in September with the actual test runs commencing during the following month. Tests continued until late 1955 when one of the authors (G.Y.) left the project. Further improvements on tests to provide confirmation of previous results were conducted with the assistance of S.K. Fang for about a year ending in May 1957.



NITRIC OXIDE RIG

FIG. I

EXPERIMENTAL TEST RIG

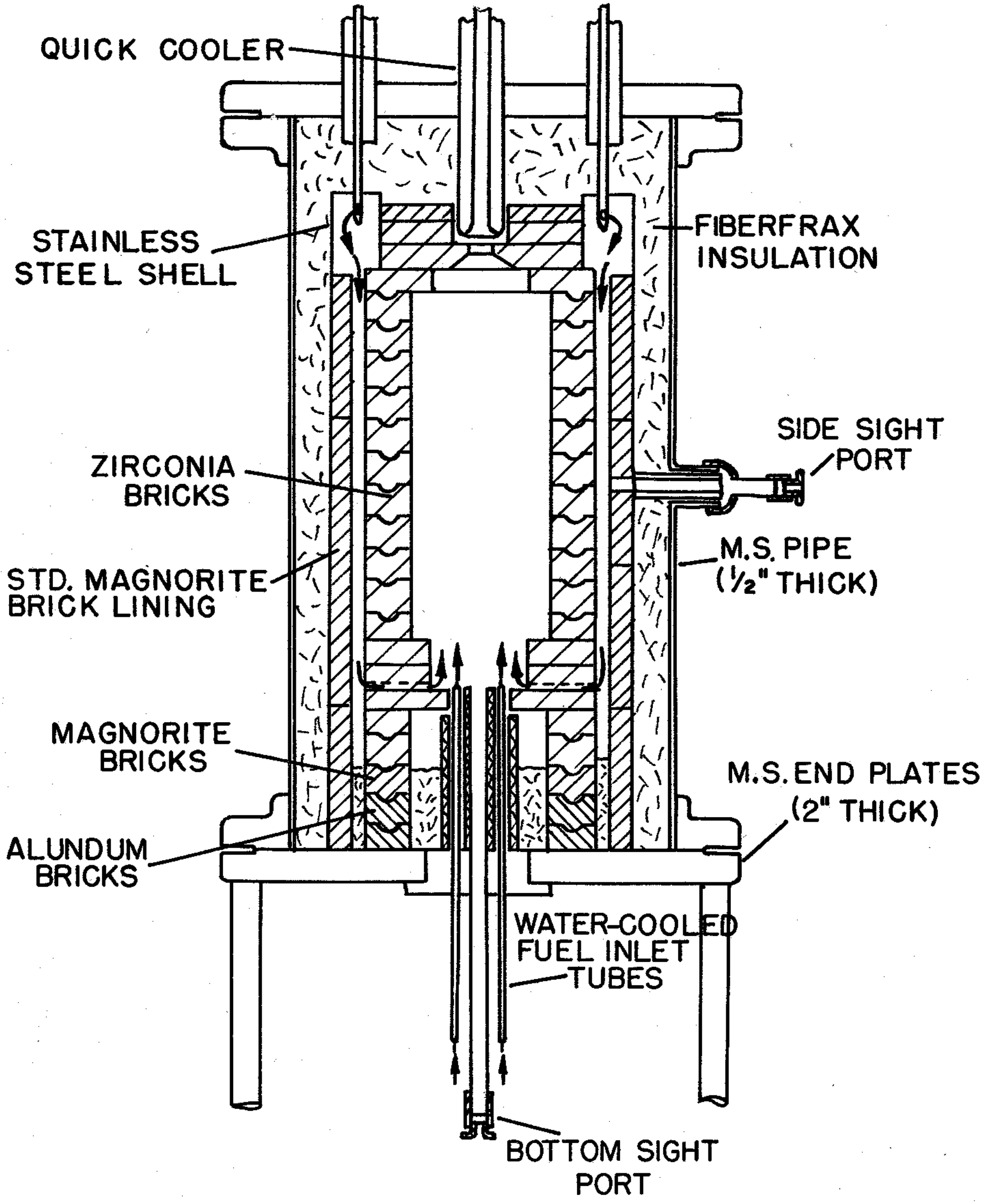
A brief sketch of the experimental test rig is shown in figure 1.

The air is preheated to 1000 °K in the air preheater and burns propane (the most convenient gaseous fuel available at the laboratory) in the zirconia brick furnace to achieve flame temperatures of the order of 3000 °K. Under these conditions, appreciable nitric oxide is formed by the direct thermal reaction of nitrogen with oxygen. The hot combustion gases leave the furnace through a water jacketed tube assembly referred to here as the "quick cooler" where the gases are chilled rapidly to fix the nitric oxide at close to its equilibrium concentrations. The gases leave the quick cooler at approximately 1300 °K and are used to preheat the incoming air in the air preheater. From the preheater, the gases enter the gas cooler where they are cooled to about 300 °K and the water condensate from the combustion of the hydrocarbon fuel is removed in the condensate trap.

A more detailed description of the rig is given as follows:

(1) Zirconia Brick Furnace

A sketch of the furnace is shown in figure 2. The furnace is built with interlocking zirconia bricks with suitable zirconia plates at the top and bottom of the furnace and the base for the furnace is formed with interlocking alundum and magnorite bricks. The magnorite bricks separate the zirconia bricks from the alundum bricks to prevent interaction between these two types of refractories at the high temperatures. The refractory bricks for the furnace were purchased from the Norton Company in Worcester, Mass.



NITRIC OXIDE RIG FURNACE

FIG.2

The furnace is designed to provide sufficient reaction time to form 90 percent of the equilibrium concentration of nitric oxide at the minimum furnace temperature of 2400 °K for a combustion gas flow rate of 0.1 lb/sec. and a furnace pressure of 40 psia. The inside and outside diameters of the furnace are 8 inches and 14 inches respectively with an overall furnace height of 36 inches. The actual combustion chamber, however, is 22 inches in length. This zirconia furnace is enclosed by a refractory shell constructed from standard magnorite bricks (1-1/2 x 4 x 9 inches) with an intervening space of about 1/2 inch where the preheated air passes through to the combustion chamber. Small magnorite refractory pieces are used as spacers between the zirconia furnace and the magnorite shell to ensure that the zirconia bricks are jammed together. The magnorite brick shell is supported in turn by a high temperature resistant 310 stainless steel shell. A smaller stainless steel shell supports the three top plates when they inevitably crack into smaller pieces as a result of thermal shock. The space between the inner stainless steel shell and the outer shell of 24" standard pipe is packed with fiberfrax insulation.

The preheated air enters at the top of the furnace shell and passes down through the annulus between the zirconia furnace and the magnorite brick shell and enters the combustion chamber through the "spiral plate". The spiral plate has four grooves through which the incoming air is directed into a spiral motion, counter-current to the spiral flow of the propane gas from the burners. This ensures turbulent mixing which is a prime requisite for good combustion.

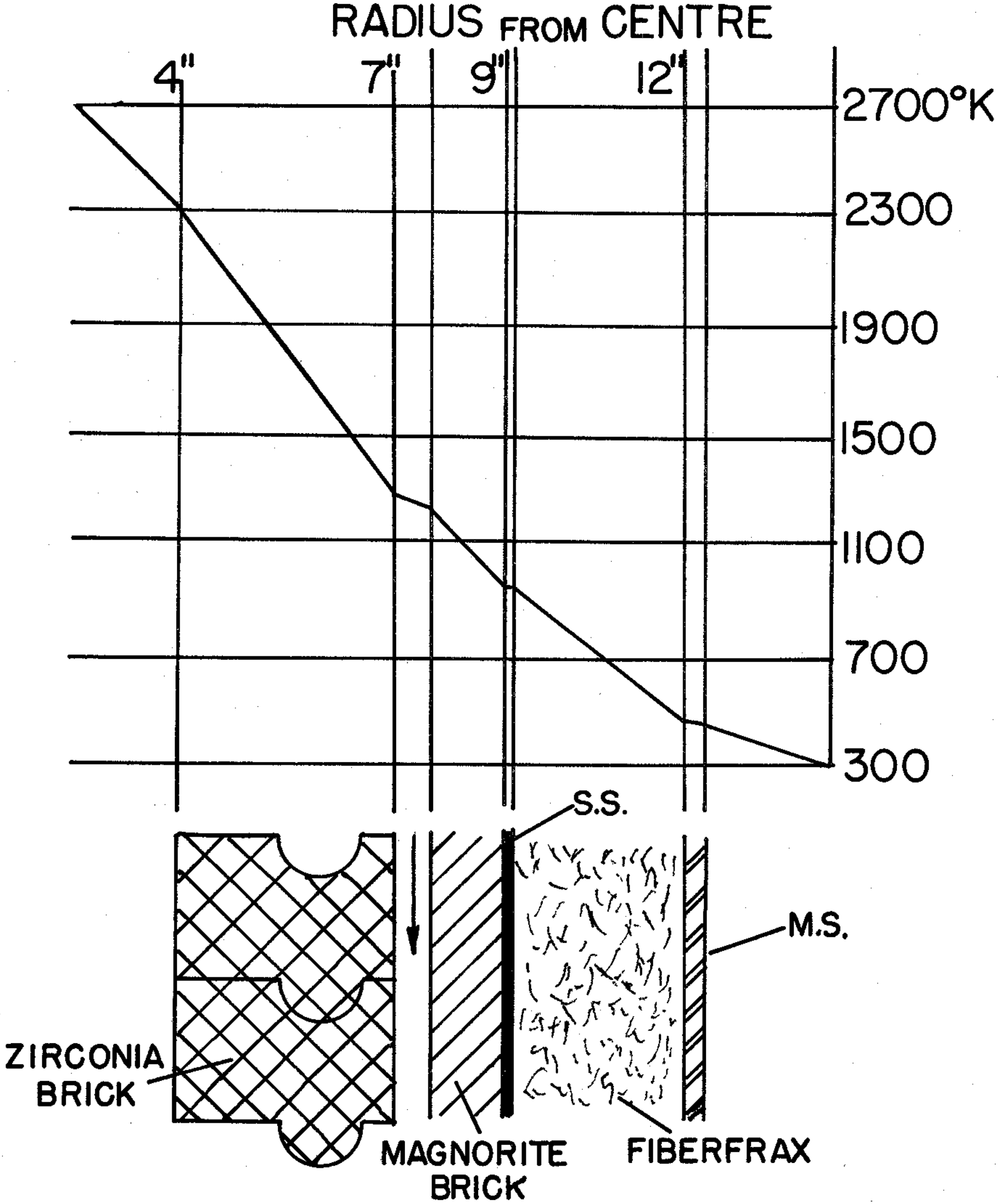
The reason for passing the preheated air through the annulus between the furnace proper and the magnorite shell is to keep the temperature of the zirconia bricks down to a reasonable level by means of the heat transfer to the cooler preheated air. A typical temperature profile across the furnace is shown in figure 3.

For runs 13 and 14 sighting ports were provided diametrically opposite in line with the entrance to the nozzle at the lower end of the quick cooler to permit an estimation of the gas temperature with a radiation pyrometer or by line reversal spectroscopic technique. These were not very satisfactory because of trouble with water and soot accumulation on the windows and air leakage through the openings in the inner brick lining. These sighting ports were removed for run 15. It is hoped that this facility will be reinstalled with an improved design to provide valuable information on the correlation of temperature measurement by various methods.

(2) Quick Cooler

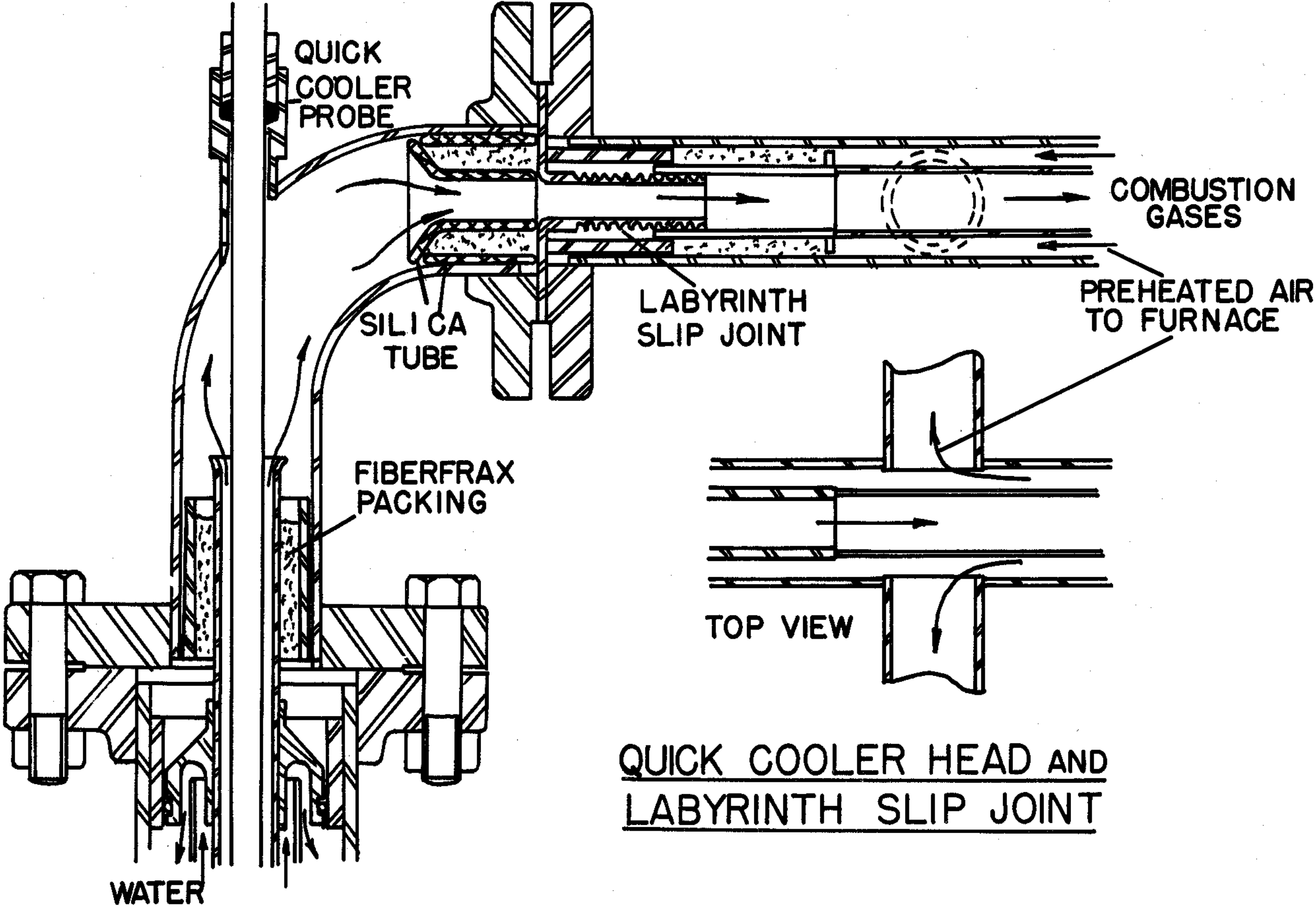
A diagram of the quick cooler is shown in figures 1 and 4. The inner tube of the quick cooler through which the hot combustion gases flow is a one inch O.D. type 316 stainless steel tube, 0.065 inch thick. A sliding O-ring seal at the end of the water jacket takes care of the thermal expansion of this tube.

The quick cooler is designed to cool very rapidly a gas flow of 0.1 lb/sec from about 2500 °K to 1350 °K. Furnace temperatures greater than 2500 °K were to be handled by adjusting water flow rates to the quick cooler to promote boiling with the resulting high boiling heat transfer coefficient. However, as it happened, the heat transfer coefficients were lower than calculated due to a film of carbon soot adhering to the inner tube which meant an unusually



TYPICAL TEMPERATURE PROFILE ACROSS THE FURNACE

FIG.3



QUICK COOLER HEAD AND LABYRINTH SLIP JOINT

FIG. 4

large fouling factor. Consequently, a quick cooler probe was found to be necessary to provide the additional cooling. The incorporation of the probe with the quick cooler provides an additional advantage of permitting greater flexibility in the control of the outlet gas temperature merely by changing the depth of the probe in the quick cooler tube.

INSTRUMENTATION

The instrumentation of this test rig consists essentially of thermocouples for the higher gas temperatures; resistance thermometers for the low gas temperatures and for the water temperatures; bourdon gauges for the pressures; and sharp-edged orifices and rotameters for the flow rates.

Optical and radiation pyrometers are used for those temperatures beyond the range of thermocouples. Pressure regulators are installed in the propane, air, and oxygen lines to ensure steady flow rates and an automatic pressure controlling valve is used to control the pressure in the furnace. Finally, numerous safety devices are used to provide some measure of safety in case of emergency. Details are provided in reference (16).

MODIFICATIONS TO EXPERIMENTAL TEST RIG

For Runs No. 11 and 12 certain changes were made in the furnace and quenching system in order to test the effectiveness of air quenching, water quenching and kinetic quenching.

Mixing Zone and Quenching Probes

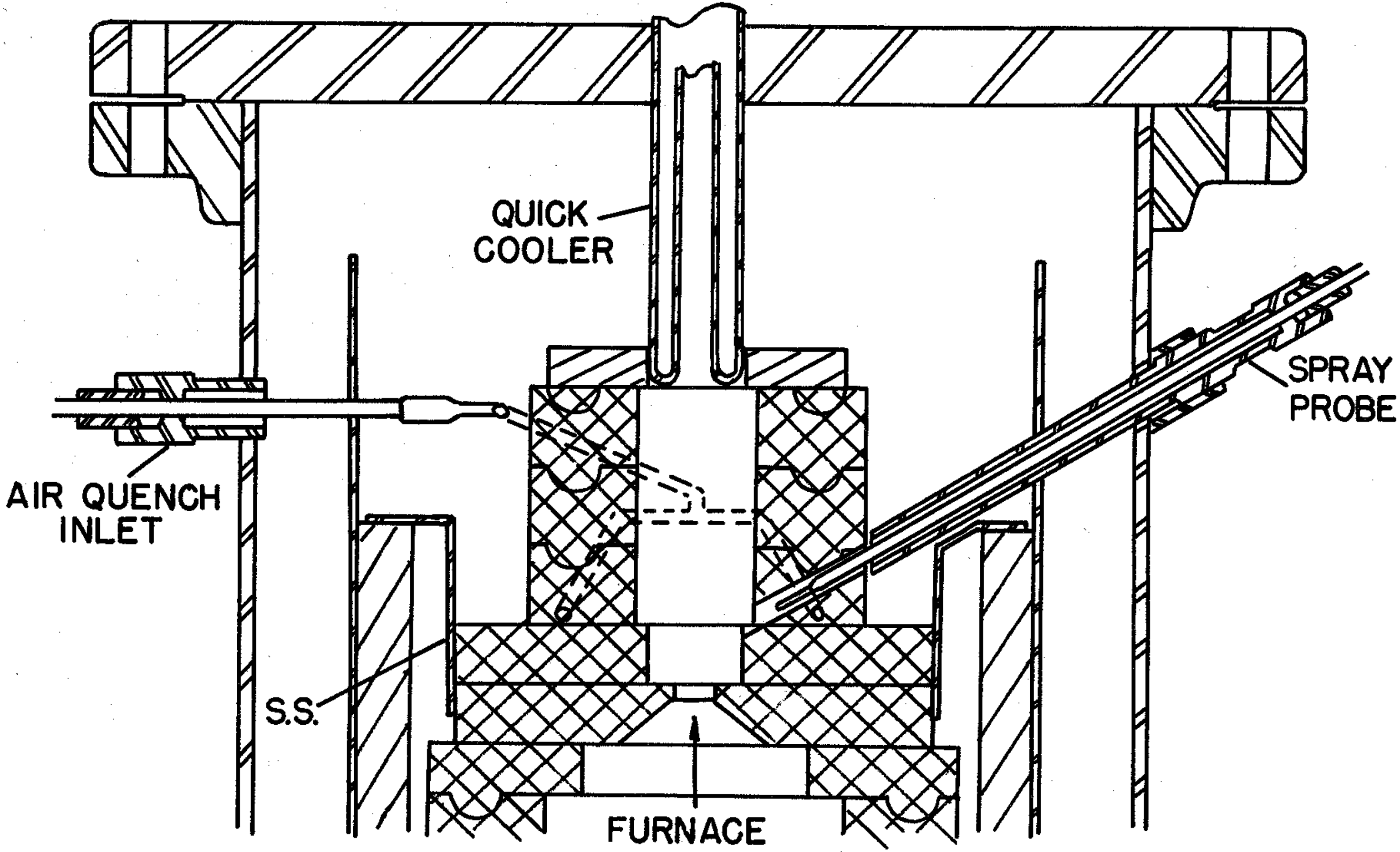
Sketches of the quenching air manifold, the water spray probe, and the mixing zone are shown in figures 5 and 6.

The purpose of the mixing chamber and the various probes is to determine the effectiveness of quenching the nitric oxide with a jet of cold air or with a spray of water directed into the mixing zone.

Once the effectiveness of air quenching is established, it is proposed to recycle, as the quenching gas, part of the cold exhaust gases containing nitrogen dioxide to prevent dilution of nitrogen dioxide concentration that occurs when quenching with air. The mixing zone is constructed from standard interlocking zirconia bricks held together with zirconia cement. It is roughly 2-3/4 inches square and has a height of 7 inches. Also, the port through which the water spray probe is inserted can be used alternatively as a sight port to measure flame temperature, and radiation and absorption characteristics simply by removing the probe and screwing on the sight glass holder.

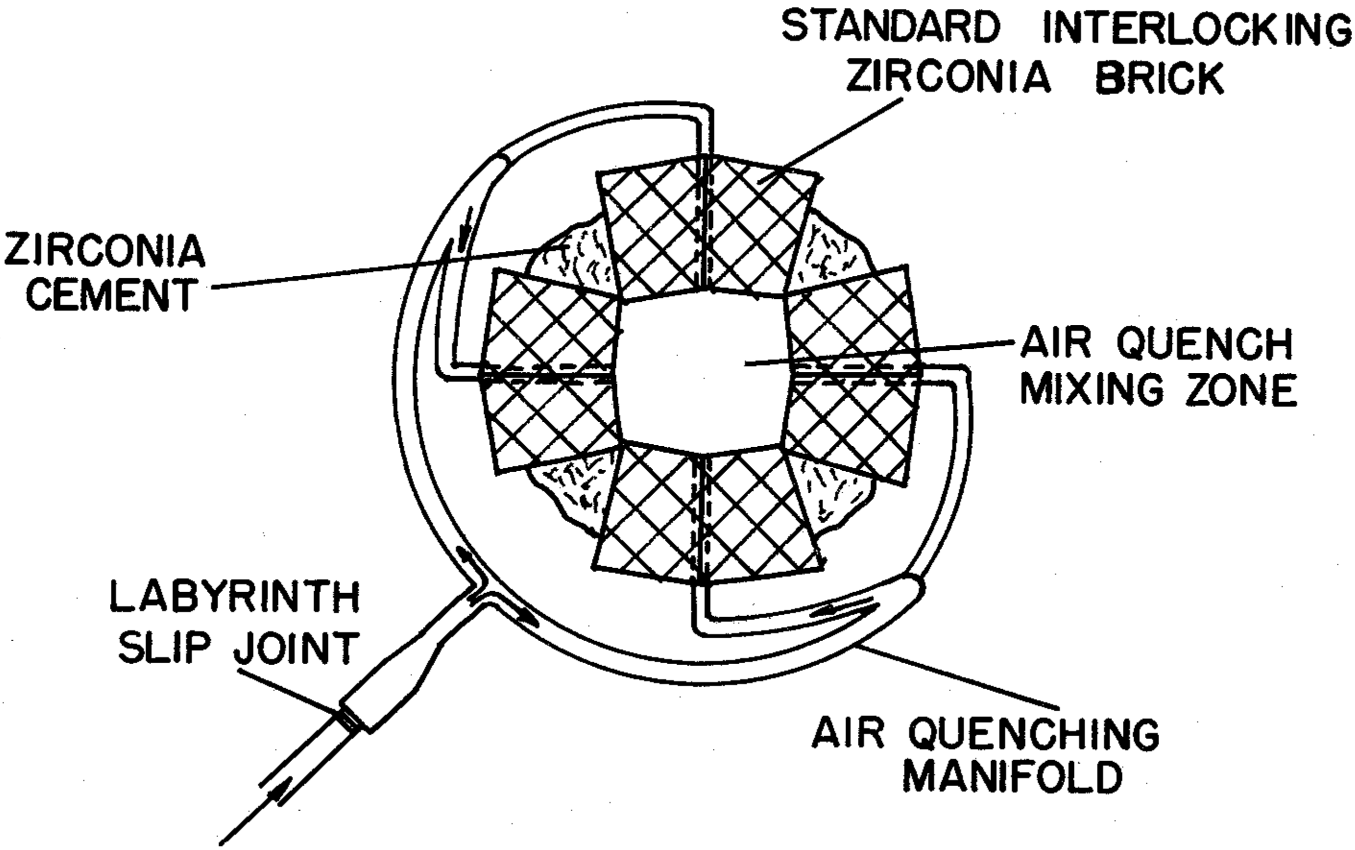
Quenching Nozzle

One type of quenching nozzle is shown in figure 7a. It consists of a coil in the shape of a nozzle and is made from a length of 1/4" O.D. type 310 stainless steel tube. A machined type is shown



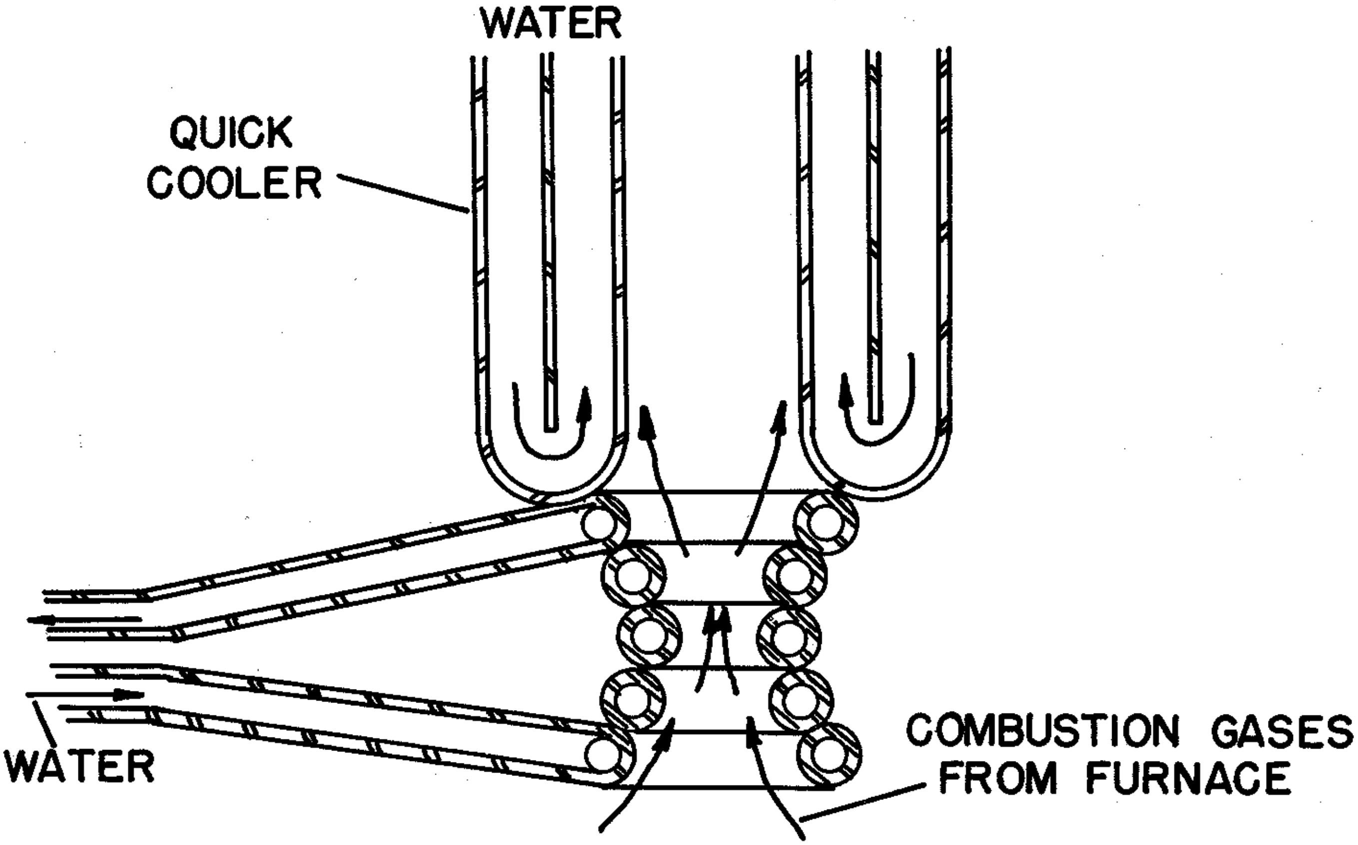
MIXING CHAMBER WITH WATER SPRAY PROBE AND AIR QUENCH MANIFOLD (SIDE VIEW)

FIG. 5

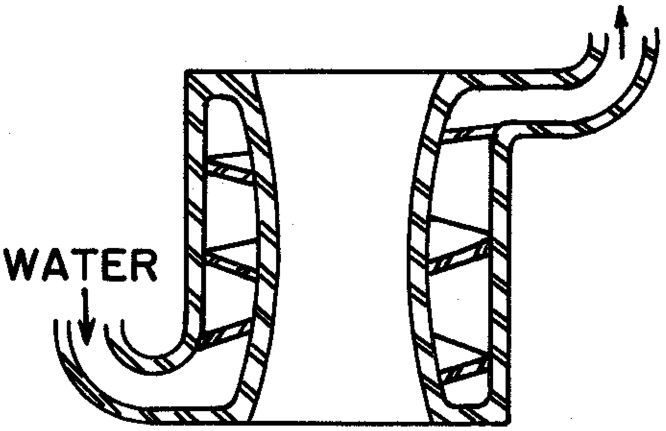


MIXING CHAMBER AND AIR QUENCHING MANIFOLD (TOP VIEW)

FIG. 6



(A) COILED S.S. TUBE NOZZLE



(B) NOZZLE MACHINED FROM S.S.

QUENCHING NOZZLES

FIG. 7

in figure 7b. The nozzle is expected to cool the combustion gases by the acceleration of the gases through the nozzle. The kinetic energy thus acquired must come from the internal energy of the gases. The directed kinetic energy comes at the expense of the mean random molecular energy and since random molecular motion is responsible for collision, it is reasonable to assume that reaction rate is a function of the static temperature of the gas rather than the total temperature. (See Penner, 11).

The relation between the total temperature and static temperature is given as follows:

$$t = T - \frac{V^2}{2\ Cp}$$

where t = static temperature of gas

T = total temperature of gas

V = mean velocity

Cp = specific heat in absolute mechanical units.

Thus for a gas velocity of 2500 ft. per sec. in the nozzle with a length of about 0.1 feet, the temperature drop $(T-t)$ is 280 °C and the cooling rate $\frac{280 \times 2500}{0.1 \times 2}$ or 3.5×10^6 °C/sec.

PERFORMANCE OF RIG

The experimental rig on the whole has functioned quite satisfactorily although there have been some mishaps; for example, the melting of certain areas of the inner stainless steel lining, the failure of burners, blockage of the water line to the quick cooler probe, etc.

(1) Zirconia Brick Furnace

The zirconia brick furnace has been successfully operated with estimated flame temperatures exceeding 3000 °K. The interlocking zirconia bricks have stood up quite well and have retained their original shape after a total running time of almost 100 hours at temperatures of 2200 °K to over 3000 °K. However, tiny cracks have begun to appear near the inner surface of the bricks; due probably, to the thermal shocks encountered during the relatively rapid heating and cooling of the furnace. The average rate of heating the bricks has been of the order of 300 degrees centigrade per hour up to Run No. 10. For the following runs the heating rate was reduced to about 100 degrees per hour with the result that no further damage to the interlocking bricks is evident.

Aside from these small cracks, the only other sign that the bricks were exposed to extremely high temperatures is the discolouration of the brick from a normal yellowish brown colour to a greyish brown colour to a depth of about one inch from the inner surface. The discolouration is at a maximum at the middle of the furnace where the temperature is the highest.

The zirconia plates at the bottom and the top of the furnace all cracked into several pieces eventually, as predicted by the manufacturers since the large sizes and flat shapes result in poor thermal shock resistance. However, the cracks became stabilized after a few high temperature runs and no further damage was noticed except to the top plate closest to the combustion chamber. The area around the central hole in this plate shows increasing signs of erosion because at this point the gases have the maximum velocity and consequently the highest refractory temperature is reached.

The magnorite bricks used in the refractory shell surrounding the zirconia furnace show no signs of deterioration. On the other hand, the stainless steel shell supporting the magnorite bricks melted in spots during Run no. 6. The temperature of the shell near the local hot spots rose very suddenly, indicating that propane gas leaked in some way into the space between the magnorite bricks and the stainless steel lining and the combustion of the gas in that region raised the temperature to a level where exposure to the oxygen enriched air caused local burning of the stainless steel shell. After this, the space between the magnorite bricks and the stainless steel shell was filled with magnorite cement to eliminate exposure of the shell to the oxygen enriched air. No further trouble with the stainless steel shell was experienced thereafter even though propane gas still burned in the annulus periodically.

An interesting observation on inspecting the furnace after a run is the carbon soot that accumulates in such places as, between the bricks below the bottom plates, on the zirconia tubes at the bottom, between the stainless steel shell and the fiberfrax insulation, and between the top steel flange and the fiberfrax in the area of the quick cooler. It is apparent that under certain conditions propane enters the annulus between the furnace and the magnorite shell. The actual burning of either propane or carbon in the annulus has been observed through the side sight port. The occurrence of minute explosions in the annulus has also been noted.

(2) Combustion

Several methods of air-propane mixing have been tried. The first system had the air inlet plate with four 1/4 inch slots grooved in a position which provided a spiral flow of preheated air roughly in parallel with the propane gas flow with the air entering about 1-1/2 inches below the fuel outlet jets. With this system, the combustion was poor and resulted in an appreciable carbon deposit at the furnace bottom. The poor combustion thus indicated was attributed to the relatively high pressure drop across the 1/4 inch slots which caused considerable amount of the preheated air to leak through the interlocking bricks of the furnace and thereby created a shortage of oxygen at the furnace bottom. This hypothesis was strengthened in the following run when two standard interlocking bricks were removed from the furnace bottom to permit the preheated air to enter the combustion chamber with negligible pressure loss with the result that the leakage was reduced considerably. The improvement in combustion was indicated by the fact that carbon formation was reduced considerably in spite of the drastic reduction in the entering air velocity which meant far less turbulent mixing than in the previous run.

For further improvement it was desirable to have both the low pressure loss and the fast air velocity and with this in mind, the spiral plate was cut as shown in figure 8. The enlargement of the air inlet slots decreased the pressure drop whereas the air velocity was maintained by leaving the original slots near the entrance to the furnace intact. Further improvement in combustion was made by decreasing the outlet holes for propane from the original 1/8 inch to 1/16 inch and then finally to three 1/32 inch holes. After these adjustments were made, there has no longer been any carbon left at the end of the runs.

However since there was still the problem of combustion of the propane in the annulus and of its thermal decomposition in the insulation further improvements were made (see figure 9). The air is injected radially close to fuel inlets and hence there is a rapid mixing with little or no chance of the fuel jetting or leaking anywhere except up into the furnace. Further improvements are incorporated in the sealing arrangement at the top of the furnace. These include a more positive seal with fibrefrax rope, allowing for expansion; better seals for the air inlet tubes and spring loading of the top of the furnace to improve the sealing of the upper plates. Better sealing was installed to prevent any back diffusion of the propane to the bottom of the furnace.

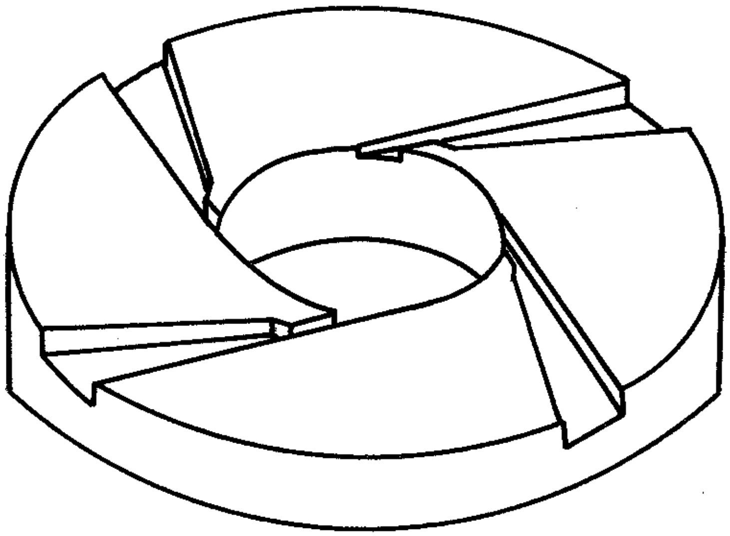
(3) Mixing Chamber

Considering the severe thermal shocks that the bricks in the mixing zone undergo the zirconia bricks have stood up fairly well when air alone was injected into the mixing zone. However, inspection of the bricks after Run no. 12 during which water was sprayed into the mixing zone, revealed the bricks to be in poor condition. Almost all of the bricks were cracked and many had pieces broken completely off.

The mixing of the cold air with the hot combustion gases has been unsatisfactory due probably to the swirling effect that occurs during the mixing with the result that the denser cold air is centrifuged out while the hot gases pass up through the center. Consequently, the cold air molecules are not meeting the hot gas molecules for a rapid transfer of heat. This centrifuging effect was confirmed in Run no. 12 when gas samples taken near the inside wall of the mixing chamber showed zero concentrations of carbon dioxide which could only mean that the combustion gases are not mixing thoroughly with the entering air. As a result, yields of nitric oxide in the gases for an air quench process are appreciably lower than those for the quick cooler quench process.

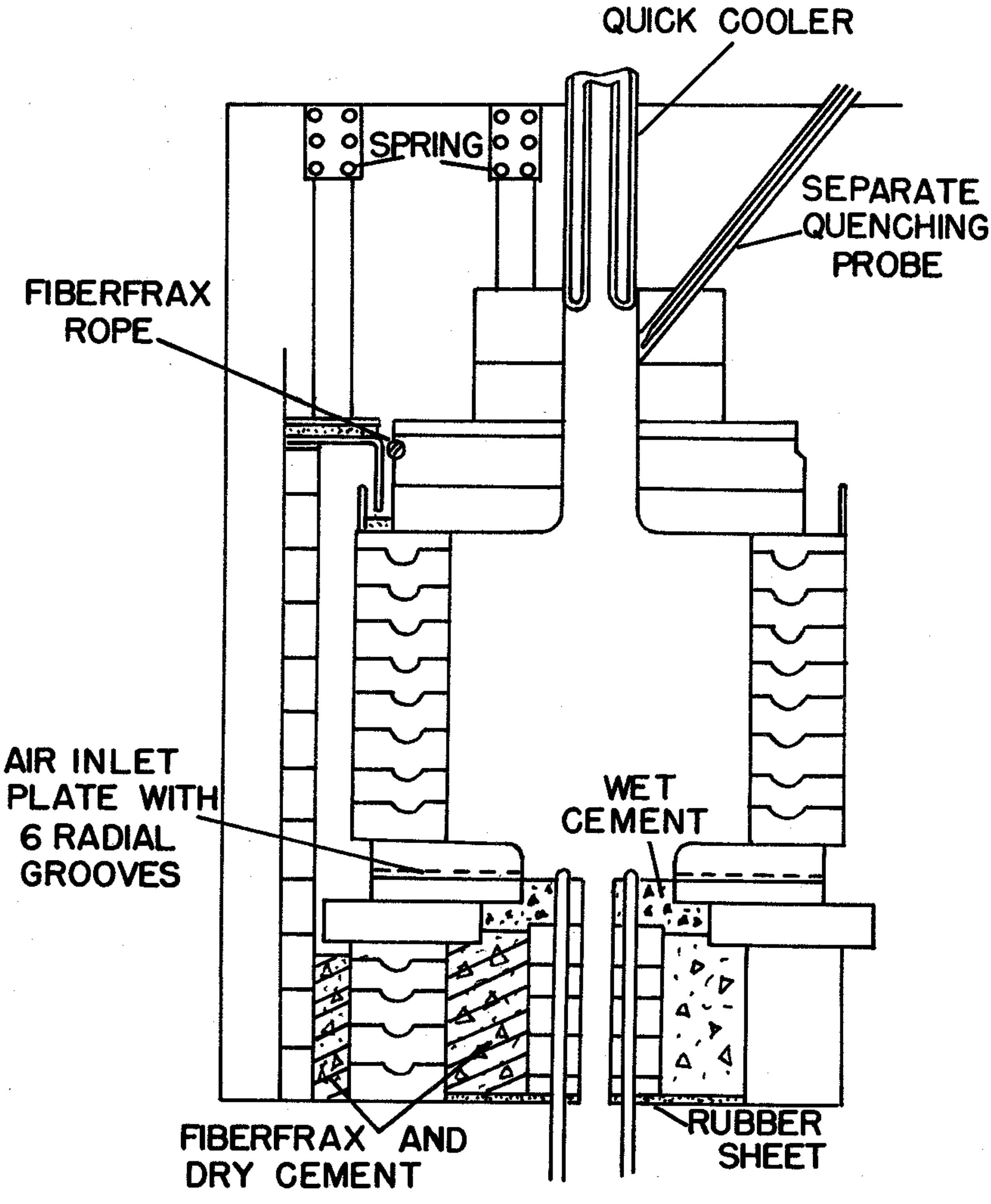
(4) Quenching Nozzle

The quenching nozzle has readily withstood the high gas temperatures although a considerable knocking sound was emitted during the run due to the violent formation of steam in the nozzle. Actually the kinetic quenching principle has not yet been given a fair test because of the leakage that occurs between the nozzle and the quick cooler entrance and because of the leakage that occurs between the coils of the nozzle. In the test on the type shown in figure 7b there were difficulties with unstable combustion and bypass



ZIRCONIA PLATE WITH SPIRAL AIR INLET SLOTS

FIG. 8



MODIFIED FURNACE CONSTRUCTION FOR RUN N°. 15

FIG. 9

leakage in the furnace and no reliable results have been obtained.

(5) Quick Cooler

The quick cooler has stood up very well. The O-ring expansion joint is functioning without any trouble and the quick cooler tip has shown no sign of deterioration from exposure to the high gas temperatures. The inside diameter of the quick cooler tube was measured to be 0.870 inch and after approximately 100 hours of operation at high temperatures, the inside diameter has remained virtually the same at 0.869 inch.

The quick cooler, unfortunately, did not have the heat transfer capacity predicted by the design calculations so that the maximum permissible gas temperature was 2350 °K instead of 2500 °K. The optimum design gas temperature drop from 2800 °K to 1400 °K was calculated to be obtainable only by means of a boiling water coefficient to provide a greater overall heat transfer coefficient. However, because of the extremely high gas temperatures, it was felt that due to an excessive temperature difference the boiling coefficient was diminished by superheated vapour boiling with the result that the inner quick cooler tube would be overheated. Consequently, the quick cooler by itself is capable of safely cooling the gas from a maximum temperature of only 2350 °K at a quenching rate up to 150,000 °C/sec.

The experimental overall heat transfer coefficients were found to be lower than the theoretical coefficients as predicted by the equations in McAdams "Heat Transmission" (17, page 219). This discrepancy is probably due to the thin layer of carbon soot that deposited on the quick cooler tube. The amount of fine carbon particles collected after the run from the quick cooler tube was calculated to give a layer thickness of 0.008 inches. Calculations of the theoretical heat transfer coefficients with this layer of soot brought these values down to within 5 percent of the experimental heat transfer coefficients. The soot deposition is the result of the poor combustion in the relatively cold furnace at the time of the quick cooler insertion. Once the soot collects on the tube surface the water cooling effect keeps the temperature of the carbon particles below the ignition point:- thus preventing the soot from burning off.

(6) Quick Cooler Probe

The quick cooler probe was designed and constructed when it was discovered that the quick cooler alone could not handle normal gas flows at temperatures exceeding 2350 °K. With this probe gas temperatures exceeding 3000 °K could be permitted in the furnace without any trouble. This probe also lends flexibility in controlling the exhaust gas temperature simply by varying the depth of the probe in the quick cooler. Furthermore, by lowering the probe down to the lower tip of the quick cooler, the quenching rates can be more than doubled from the combined effects of faster gas velocity, higher heat transfer rate, and greater heat transfer surface.

Because of space considerations, the quick cooler probe is limited in its construction to a 1/2 inch O.D. tube with the resultant small cross-sectional area for water flow. This constriction eventually led to a plug in the water flow due to accumulation of weed and dirt that slipped through the river pump filter and the additional filter in the water line. The water flow stoppage caused the probe to melt and the resultant loss of cooling capacity allowed the temperature of the exhaust gases from the quick cooler to increase rapidly and damage the connecting tube and part of the air preheater. An additional fine screen filter just before the new quick cooler probe has prevented recurrence of this problem.

(7) Slip-joints

The thermal expansions of the quick cooler tube and the air preheater tube were taken care of initially by a connecting tube with two plain slip-joints. However, the leakage through these slip-joints was of the order of 30 percent. Consequently, when the connecting tube was destroyed along with the quick cooler probe, a new labyrinth type of slip-joint as shown in figure 4 was used. This arrangement with the fibrefrax packing around the slip-joint proved quite successful in decreasing the leakage to approximately 1 or 2 percent.

(8) Air Preheater

The air preheater has functioned quite successfully. The preheater was designed to provide an air preheat temperature of 1000 °K and experimentally, 1030 °K has been achieved without difficulty. The inside tube is made of type 310 stainless steel which has the highest heat resistance properties among the stainless steels. For the preheater, the theoretical heat transfer coefficients are close to the experimental ones since no carbon particles could accumulate in the inner tube due to the tube's high temperature which allows the carbon to burn off.

(9) Gas Cooler

The gas cooler serves its purpose well in cooling the gases from a temperature of approximately 500 °C to 20 - 30 °C.

(10) Separate Quenching Probe

Since there were operational problems in run 13 using the water-cooled quenching nozzle welded to the quick cooler it was removed for runs 14 and 15. A separate quenching probe (see figure 9) was provided to permit a study of the effect of a varied quenching rate which would not influence the overall operation and to provide an independent estimate of gas temperature.

RESULTS

Quick Cooler Quenching

The results of Runs no. 6 to 12 are presented here. Those of the previous runs can be used only as indications since the true temperatures in the furnace could not be calculated due to the lack of by-pass data in the slip-joints.

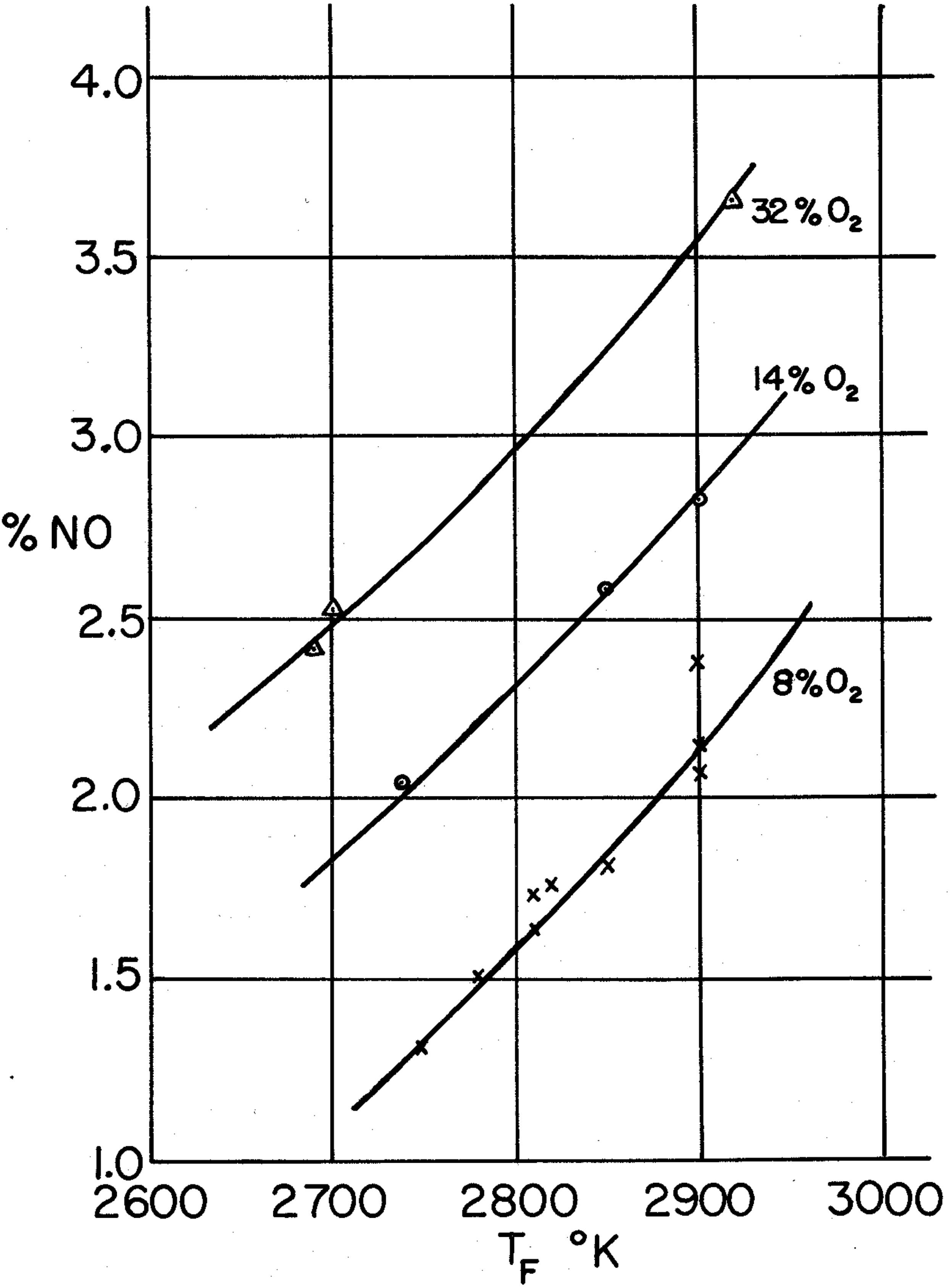
The results with quick cooler quenching are plotted in figures 10 and 11 and tabulated in Table I. Figure 10 shows the "NO" concentration in the furnace as a function of furnace gas temperature and figure 11 shows the "NO" concentration as a function of oxygen concentration in the furnace. This oxygen concentration includes the oxygen made available when the carbon dioxide and water vapour dissociate at the high temperatures prevailing in the furnace. The oxygen concentration of each curve is the average of the individual oxygen concentrations of the points on that particular curve. Only those results that gave three or more points through which a curve can be drawn are plotted for the sake of simplicity. The points of figure 11 are obtained from a more detailed set of curves of figure 10 and there is a comparison of the experimental "NO" concentrations with the theoretical concentrations (16).

In Table I, "T_F" is the temperature of the gases leaving the furnace and is calculated by a series of heat balances using published mean values for Cp (16). The effect of dissociation of carbon dioxide and water vapour is considered in the calculation of "T_F". The absolute value of "T_F" is probably not accurate to more than plus or minus 50 °K, but since the factors contributing to this

TABLE I

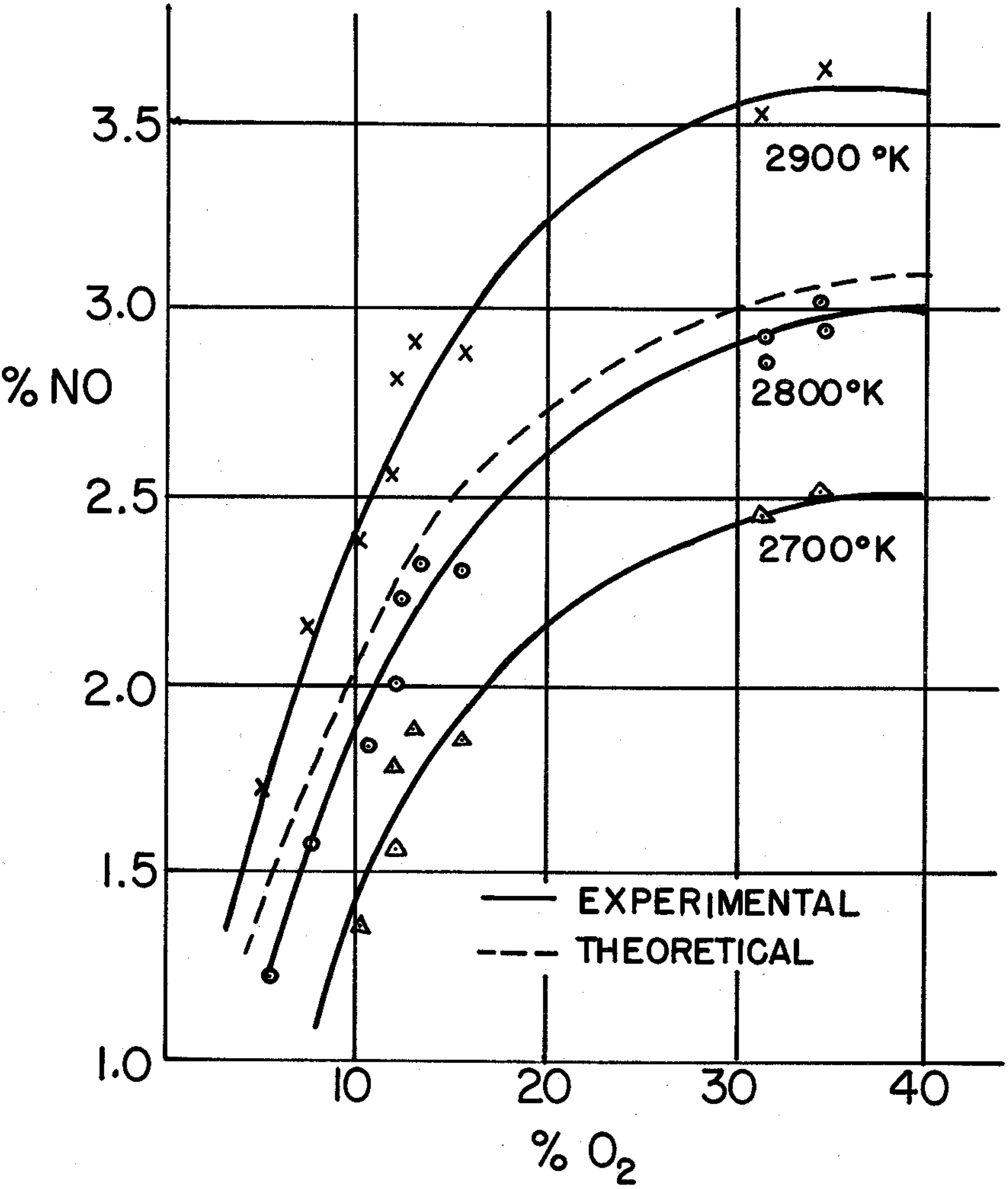
Run No.	T_F °K	P psia.	Quenching Rate °C/sec	Reaction Time sec.	% O_2	% O_2 plus +% O_2 from Dissociation	% NO
6	2730	44.9	244,000	0.396	1.3	4.5	0.92
	2830	48.1	288,000	0.351	2.3	6.6	1.25
	2810	47.9	278,000	0.368	4.4	8.0	2.25
	2900	47.9	302,000	0.335	8.4	12.1	2.82
7	2680	35.4	336,000	0.289	10.0	12.0	1.46
	2750	36.5	345,000	0.288	6.9	10.2	1.49
	2740	35.4	354,000	0.278	10.7	13.1	2.05
	2780	36.8	350,000	0.280	3.6	7.6	1.50
	2850	43.7	398,000	0.256	12.8	15.8	2.58
8	2750	36.7	340,000	0.295	4.2	7.8	1.31
	2820	55.4	223,000	0.445	4.1	800	1.76
9	2800	73.9	168,000	0.540	2.0	5.4	1.21, 1.36
	2810	74.4	170,000	0.580	4.2	7.5	1.63, 1.73
	2820	84.0	148,000	0.637	2.9	6.6	1.51
	2850	83.5	182,000	0.563	4.7	8.5	1.81
	2900	76.0	160,000	0.620	3.9	7.7	2.05, 2.38, 2.15
11	2700	56.0	304,000	0.233	33.4	34.2	2.52, 2.24
	2890	56.5	349,000	0.206	28.7	31.2	3.33
	2920	56.5	376,000	0.191	32.4	34.6	3.66, 3.54
12	2690	55.7	342,000	0.199	30.4	31.2	2.60, 2.23
*	3010	56.8	-	0.214	24.4	24.4	2.69
*	3050	55.9	-	0.203	23.3	27.6	3.31
*	3060	55.7	-	0.216	23.1	27.1	3.43

* For these temperatures, the quenching quick cooler probe was 6 inches from bottom of quick cooler, whereas the probe was down to the bottom for the others.



"NO" CONCENTRATION AS FUNCTION OF FURNACE GAS TEMPERATURE

FIG.10



"NO" CONCENTRATION AS FUNCTION OF OXYGEN CONCENTRATION

FIG. 11

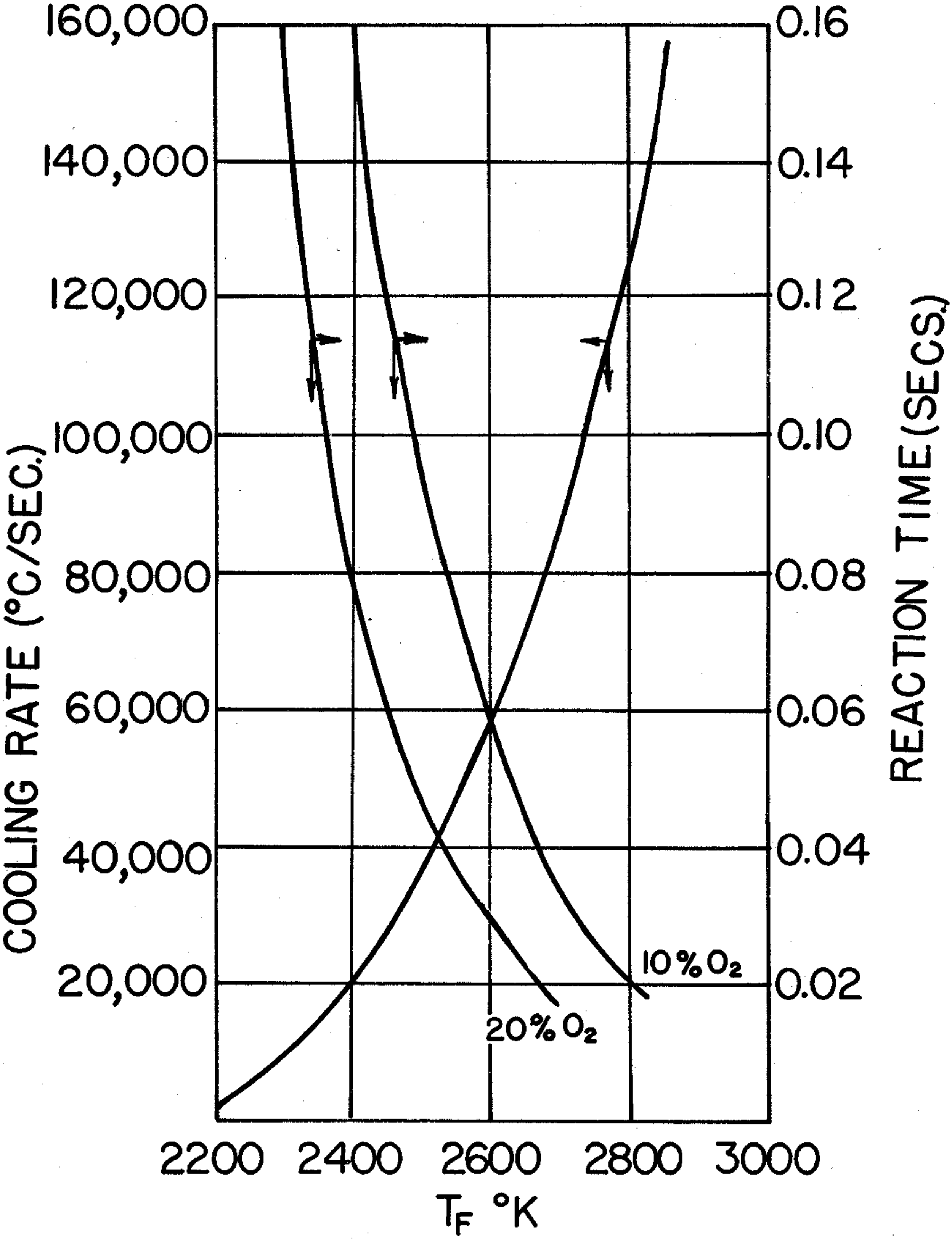
inaccuracy are approximately the same for each temperature determination, the calculated temperatures relative to each other for the purpose of drawing trends should be quite reliable.

The quenching rates for the last three temperatures in Table I are not given since they could not be calculated due to the fact that the quick cooler probe was not inserted down to the tip of the quick cooler. For those high gas temperatures, further lowering of the probe into the hot gas stream would have caused violent boiling to take place in the probe with a serious threat of probe failure. The first column of "% O_2" in Table I shows the oxygen concentration calculated from the complete combustion of propane going into the furnace. These values have been periodically checked with values obtained from the back calculation from the orsat analysis of the exhaust gases. The "% O_2" in the second column includes the additional oxygen from the dissociation of part of the carbon dioxide and water vapour into carbon monoxide, hydrogen, and oxygen. The "% NO" in the last column of Table I is the nitric oxide concentration actually in the furnace as calculated from the "NO" analysis of the exhaust gases after most of the water is condensed. The methods of sampling and analysis are presented in Appendix I.

Figure 12 presents the cooling rates and reaction times theoretically required for fixing and forming nitric oxide as a function of furnace gas temperature. The curves are obtained from the extrapolation of data presented in a paper by Gilbert and Daniels (8).

Air Quenching

The results with air quenching are plotted in figures 13 and 14. Figure 13 shows the "NO" concentration as a function



REQUIRED COOLING RATE AND REACTION TIME (TO FORM 90% EQUI. CONC.) AS A FUNCTION OF FURNACE GAS TEMPERATURE

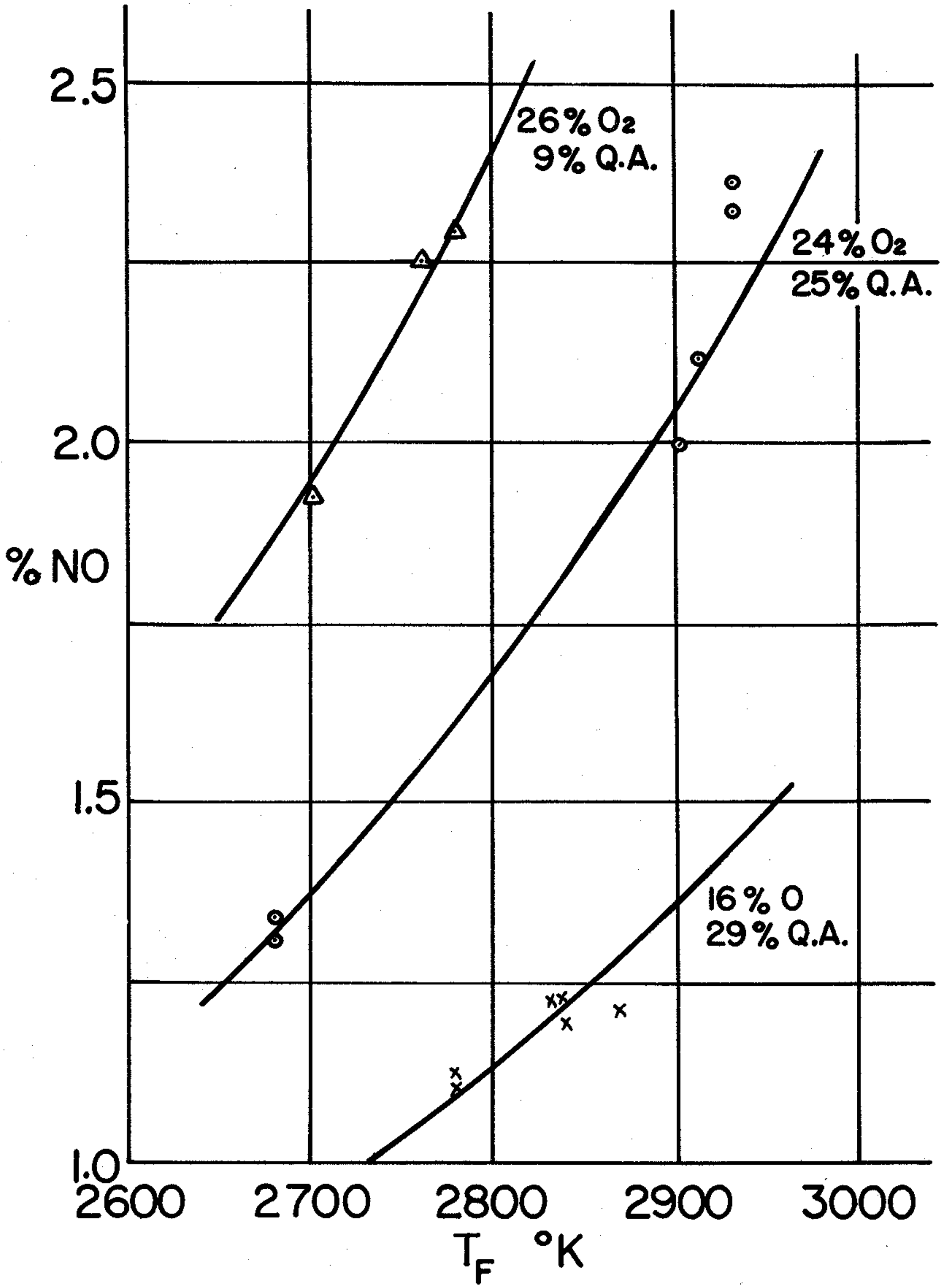
FIG. 12

of furnace gas temperature when quenching with air and figure 14 shows the "NO" concentration as a function of percent quenching air. Here again, the oxygen concentration and the percent quenching air are the average of the individual points on the curves. Figure 15 presents a comparison of quick cooler quenching and air quenching.

Separate Quenching Probe

The values obtained for furnace gas temperatures are not too reliable because of experimental and operating difficulties (e.g. unforeseen problems with water condensation in the lines resulting in inaccurate measurement of the gas flow and the relatively large heating of the probe by the gases flowing on the outside and by radiant heating). However the results as given in Table II indicate that in the region of 3000 °K the oxygen concentration appears to have less effect on the NO yield than at lower temperatures.

The quenching rate was about 2×10^6 °C/sec to 1500 °K and 0.62×10^6 °C/sec to 500 °K at the outlet of the 0.125 inch I.D. tube.



"NO" CONCENTRATION AS FUNCTION OF FURNACE TEMP. FOR AIR QUENCHING

FIG. 13

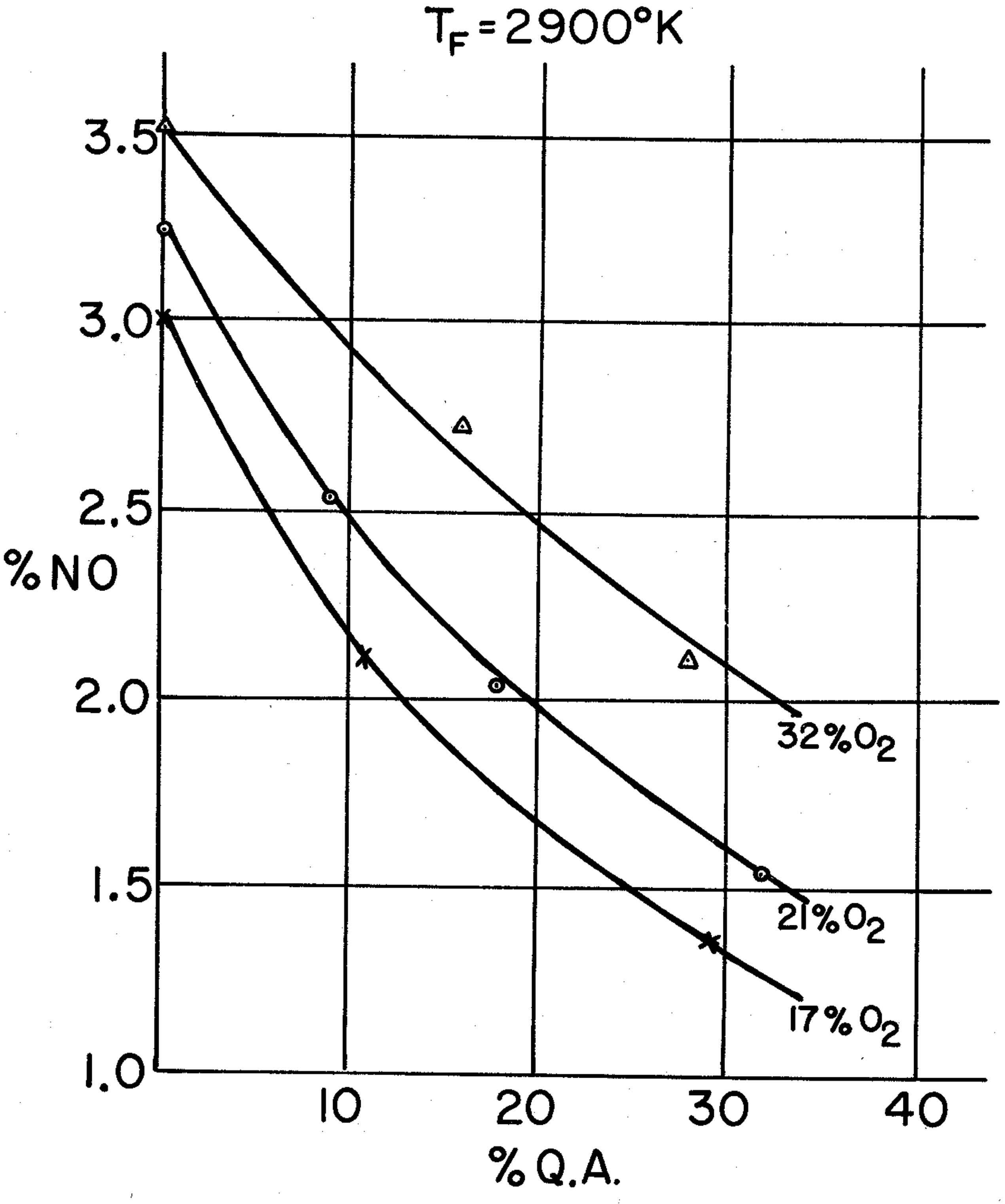
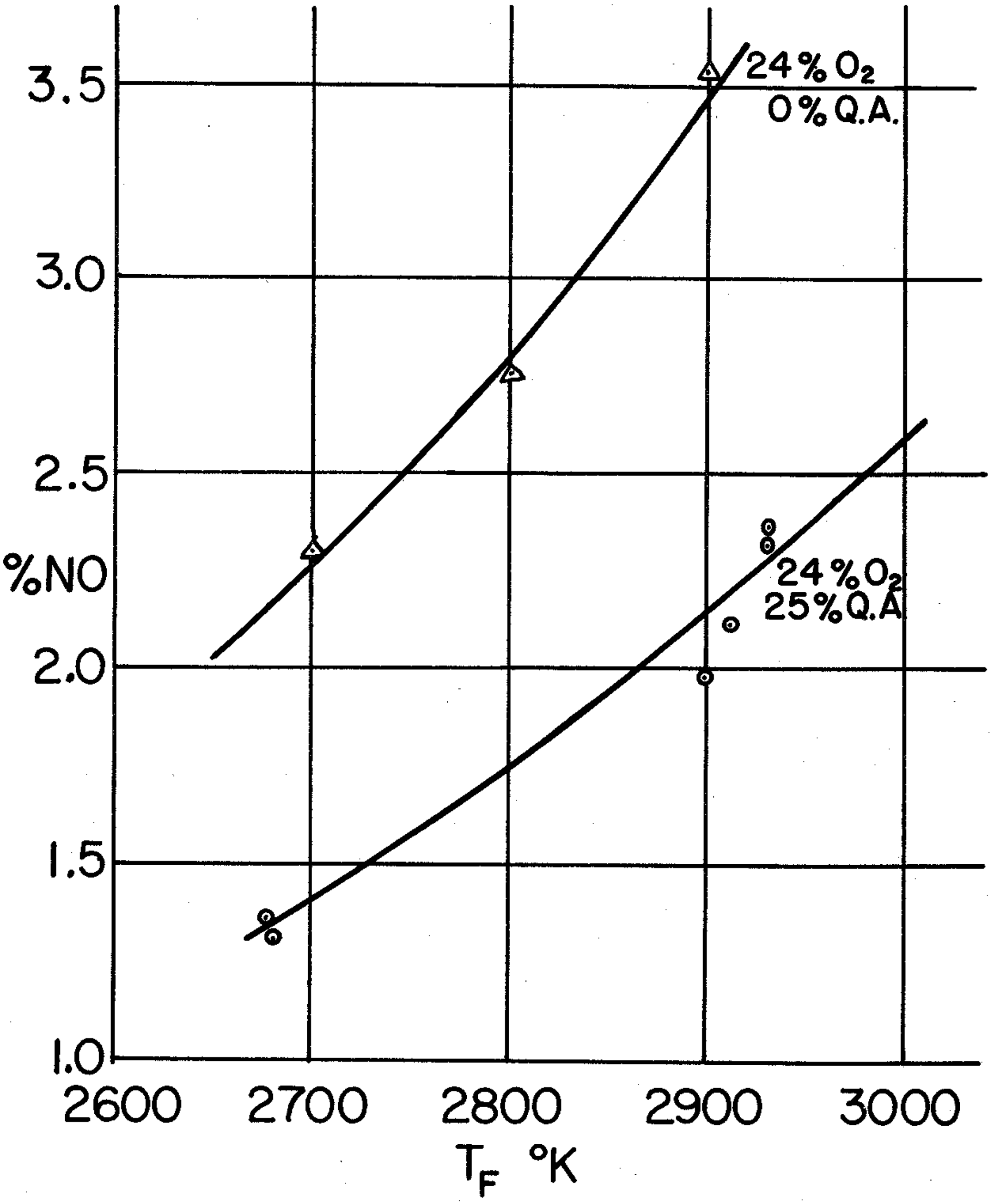


FIG. 14. "NO" CONCENTRATION AS FUNCTION OF PERCENT QUENCHING AIR



COMPARISON OF QUICK COOLER QUENCHING WITH AIR QUENCHING

FIG. 15

TABLE II

SUMMARY OF RESULTS FROM RUN NO. 15

(Using separate quenching probe)

Reaction Time = 0.25 seconds

Furnace Pressure = 75 psia.

Test No.	T_F (corrected for dissociation) °K	% O_2 In Furnace	% O_2 + % O_2 from dissociation.	% NO
9	2810	14.5	17.4	3.5
10	2870	14.6	18.2	3.0
11	2860	23.7	26.7	3.3
12	2935	30.3	33.7	3.5
13	2960	35.9	39.3	3.4
14	2980	44.1	47.6	3.7

DISCUSSION OF RESULTS

Figure 10 indicates that the nitric oxide yield increases rapidly with temperature and that concentrations of nitric oxide greater than 4 percent should be obtained quite readily. Actually for the purpose of nitric oxide recovery the "NO" concentration in the exhaust gases will be about 20% greater than that in the furnace since the water vapour formed from combustion is condensed out with but a minor loss of nitrogen dioxide. As a result, the "NO" concentration for purposes of recovery can be as high as 5 percent.

The quenching process at the highest temperature is unsatisfactory since the maximum quenching rate of 150,000 °C/sec obtainable without a quick cooler probe is far too low to effectively quench any nitric oxide at temperatures over 3000 °K. This fact is clearly indicated in the curve of figure 12 which shows the relationship between required quenching rates and gas temperatures. Another reason for the poor yields could be that the dissociation of nitric oxide itself is beginning to have effect at the high gas temperatures.

Figure 11 shows that nitric oxide concentration increases with oxygen concentration at a decreasing rate and indicates that for the conditions prevailing in the experimental runs, the maximum yield of nitric oxide will be obtained at about 38% oxygen concentration. Theoretically, the maximum yield should be obtained when the gases contain equal molar concentration of oxygen and nitrogen. The maximum equal molar concentration of oxygen and nitrogen is a function of the air preheat temperature which determines the amount of fuel required to heat the gases up to reaction temperature.

A higher preheat temperature means lower fuel consumption which, in turn, means less carbon dioxide and water vapour.

Thus for a given reaction temperature, the point of maximum yield increases with higher preheat temperatures. For the experimental preheat temperatures of about 1000 °K, the maximum equal molar concentrations of oxygen and nitrogen are found to be about 35% from the orsat analysis of the exhaust gases. This is in agreement with the theoretical curve in figure 11. This curve which gives the equilibrium concentrations of nitric oxide for a preheat temperature of 850 °K using propane as the fuel, reaches a maximum at approximately 35% oxygen concentration. The discrepancy between the theoretical 35% and the experimental 38% for the point of maximum yield is well within the range of possible errors. Figure 11 also shows that concentrations of nitric oxide close to their theoretical equilibrium concentrations can be achieved with but a small loss during quenching.

Table I indicates that the variations in quenching rates, reaction times, and pressures appear to have no effect on the yield of nitric oxide. Figure 12 shows that the cooling rates obtained experimentally are more than adequate to quench the nitric oxide at temperatures below 2950 °K. However, for those temperatures above 3000 °K where the experimental cooling rates can not be calculated but are probably lower than 150,000 °C/sec, the cooling rates are much too low. Figure 12 also shows that the experimental reaction times are far in excess of the theoretically required reaction times. That pressure has no effect on the yield of nitric oxide is in accordance with theory since there is no volume change in the reaction.

$$N_2 + O_2 \rightleftarrows 2\,NO$$

However, pressure increase is advantageous in that increased pressure decreases the amount of carbon dioxide and water vapour dissociation in proportion to the square root of the pressure. Consequently, the furnace gas temperatures can be increased for the same air/fuel ratio simply by increasing the pressure in the furnace.

Figure 13 reveals that for the air quench process, the nitric oxide yields also increase rapidly with temperature but they are considerably lower than those for the quick cooler quench process. The ineffectiveness of air quenching is more clearly shown in figures 14 and 15. Figure 14 shows that the "NO" yield decreases rapidly with increase in the amount of quenching air and figure 15 reveals that the "NO" yields by air quenching are roughly 40% lower than the yields by quick cooler quenching. The reason for the rather poor results is that the quenching air is not mixing thoroughly with the hot combustion gases but is kept separated by a centrifugal effect in the mixing zone causing the far denser cold air to centrifuge out and spiral around the core of hot gases. It is quite conceivable that if this centrifugal effect can be eliminated, quenching by air can be as effective as quick cooler quenching.

Although some results were obtained with the quenching nozzle and water spray quenching, these results are too meagre to be included in this report. Additional work with more rigid control will have to be performed to obtain more reliable data.

The results with the separate quenching probe are preliminary and serve to point up the great difficulties of accurate temperature control and measurement in the region of 3000 °K and over.

The decreased effect of oxygen on the yield of nitric oxide has been predicted by Wise and Baker (15) but the quenching rate may still not be high enough.

CONCLUSIONS

1. The air preheater has been designed and operated to provide air preheat temperatures up to 1000 °K.
2. The zirconia brick furnace designed for a maximum flame temperature of 2800 °K has been successfully operated at temperatures exceeding 3000 °K.
3. The quick cooler along with the quick cooler probe has functioned quite well but is still unsatisfactory in handling the gas temperatures beyond 3000 °K.
4. Experimental nitric oxide concentrations close to the theoretical equilibrium concentrations have been achieved. Nitric oxide concentrations up to 3.7 percent have been obtained with every indication that with higher gas temperatures, nitric oxide yields above 4% should readily be realized.
5. The furnace which was designed for a maximum pressure of 120 psia. has been operated at 90 psia, which is limited by the available air, water, and propane pressures in the laboratory. There is no indication so far that the rig could not be operated at its design pressure.

In general, the results have been sufficiently encouraging to continue the experimentation to extend the present data. Extension of the curves to temperatures beyond 3000 °K and to oxygen concentrations beyond 50 percent would be of considerable interest since in both curves, the points of maximum yield can thus be determined. Naturally, for the gas temperatures above 3000 °K, a new quick cooler probe will have to be designed to provide a much higher cooling rate than is now available.

Also, some method of violently mixing the quenching air with the hot gases must be devised to properly assess the value of air quenching. Moreover, additional results are needed to weigh the merits of nozzle quenching and water spray quenching.

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APPENDIX I

THE DETERMINATION OF NITRIC OXIDE IN THE COMBUSTION GASES

The sample is collected by flushing a 2 litre wide-mouth rubber stoppered glass bottle with the cooled gas tapped off just after the condensate trap at a flow rate of approximately 80 litres per minute. A collection period of one minute appears to be adequate since tests with collection periods of 1, 3, and 5 minutes at 2% nitric oxide concentration all gave the same result. Care must be exercised in flushing to avoid applying any back pressure to the bottle particularly at high NO and O_2 concentrations since N_2O_4 may be concentrated in the bottle as a vapour or liquid and hence a high result would be obtained from the unrepresentative sample.

At the end of the sampling period the stainless steel valve is closed and the rubber stopper pushed into the mouth of the bottle at the same time. The rubber tube joining the stainless steel tube to the glass tube which flushes the bottle is closed with a pinch clamp. The sample bottle may then be removed from the sampling line and 100 ml of 6% hydrogen peroxide is added and the bottle shaken periodically for 10 minutes.

The fixed nitrogen in the form of either NO, NO_2, or N_2O_4 is all oxidized and absorbed as nitric acid in solution. An aliquot (e.g. representing 500 ml of gas sample) is titrated with standard sodium hydroxide solution to pH 4 - 5 using a Universal Indicator or a pH meter.

The following relationship is used to calculate the concentration of fixed nitrogen as nitric oxide on a percent by volume basis.

1 milliequivalent of base = 1 milliequivalent of HNO_3

= 22.4 ml. of NO at N.T.P.

= 20.5 ml. when corrected for gas sample temperature of 25 °C.

Therefore, if an aliquot representing 500 ml. of gas sample is titrated, then:

$$\% \text{ NO (by vol.)} = \frac{\text{me. base} \times 20.4}{500} \times 100$$

For convenience when analyzing many samples a graphical relationship between volume of standard base (e.g. 0.05 N) and % NO may be utilized.