

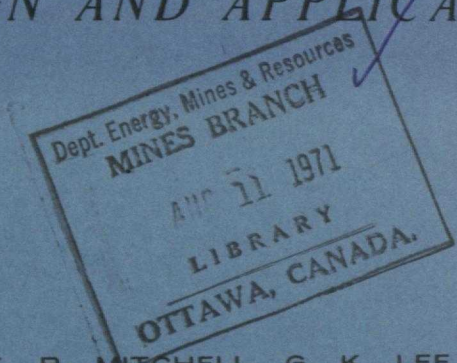
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DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA

*Mines Branch Program
on Environmental Improvement*

*THE CCRL TUNNEL FURNACE
DESIGN AND APPLICATION*



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CANADIAN COMBUSTION RESEARCH LABORATORY

FUELS RESEARCH CENTRE

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The CCRL tunnel furnace - design and application

International Flame Research Foundation

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SUMMARY

To complement the research of the foundation, and to apply it to the field of flame-source pollution, the Canadian Combustion Research Laboratory has designed a 1-meter dia. x 4.25-meter long, liquid-cooled tunnel furnace. This facility will serve both to study combustion aerodynamics and the formation of pollutants in flames.

The furnace is now almost ready for use, and the paper gives details of its construction. It is a series of calorimeters, making possible to measure the heat absorbed by each 6 in. (15 cm) increment of furnace length. A full-length slot with a series of water-cooled ports allows access to the furnace when it is under pressure.

The first project planned for the new furnace is an investigation of the factors affecting the formation of nitrogen oxides in oil flames. The theory of NO formation is reviewed, as are the numerous pitfalls for misleading results due to interacting factors. The paper points out the major parameters for the proposed program and outlines the experimental program.

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May 13th/14th, 1971

IJMUIDEN

LE FOYER-TUNNEL DU LCRC - CONCEPTION ET APPLICATIONS

RESUME

En vue de compléter les recherches de la Fondation et de leur trouver une application dans le domaine de la pollution causée par les flammes, le laboratoire canadien de recherches sur la combustion a conçu un foyer-tunnel, refroidi par liquide, de 1 mètre de diamètre sur 4,25 mètres de longueur. Cette installation servira, à la fois, à étudier l'aérodynamique de la combustion et la formation des agents polluants dans les flammes. Le foyer est actuellement presque prêt à fonctionner, et l'article donne des détails sur sa construction et ses divers éléments. Il est prévu pour brûler du charbon pulvérisé, du fuel-oil ou du gaz à raison de deux millions de Btu/h (600 000 kcal/h). Par construction, le foyer est constitué d'une série de calorimètres permettant de mesurer la quantité de chaleur absorbée par chaque portion de 6 po. (15 cm) de longueur additionnelle. Une fente ouverte sur toute la longueur du foyer et dotée d'une série de portes refroidies par circulation d'eau permet d'introduire des sondes même lorsque le foyer est sous pression.

Le premier projet de recherche prévu pour ce nouveau foyer consiste en une étude des facteurs affectant la formation d'oxydes d'azote dans les flammes de combustion des produits pétroliers. L'auteur passe en revue la théorie de la formation du NO, ainsi que la documentation récente sur les niveaux mesurés de concentration en NO provenant des appareils de combustion. Il fait ressortir le grand nombre d'aveurs possibles imputables à l'action dégroupée de divers facteurs. Le papier pointe out les principaux à considérer pour le programme proposé.

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The CCRL tunnel furnace - design and application

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To complement the research of the Foundation, and to apply it to the field of flame-source pollution, the Canadian Combustion Research Laboratory has designed a 1-meter dia. x 4.25-meter long, liquid-cooled tunnel furnace. This facility will serve both to study combustion aerodynamics and the formation of pollutants in flames. The furnace is now almost ready for use, and the paper gives details of its construction and instrumentation. It is designed to burn pulverized coal, oil or gas at an input rate of two million Btu/hr (500,000 kg. cal/hr). The furnace is constructed as a series of calorimeters, making it possible to measure the heat absorbed by each 6 in. (15 cm) increment of furnace length. A full-length slot with a series of water-cooled doors permits probing even when the furnace is under pressure. The first project planned for the new furnace is an investigation of the factors affecting the formation of nitrogen oxides in oil flames. The theory of NO formation is reviewed, as is the current literature on measured levels of NO from combustion equipment. The tremendous potential for misleading results due to interacting factors is pointed out, and the major parameters for the proposed program are outlined.

LE FOYER-TUNNEL DU LCRC - CONCEPTION ET APPLICATIONS

RÉSUMÉ

En vue de compléter les recherches de la Fondation et de leur trouver une application dans le domaine de la pollution causée par les flammes, le laboratoire canadien de recherches sur la combustion a conçu un foyer-tunnel, refroidi par liquide, de 1 mètre de diamètre sur 4,25 mètres de longueur. Cette installation servira, à la fois, à étudier l'aérodynamique de la combustion et la formation des agents polluants dans les flammes. Le foyer est actuellement presque prêt à fonctionner, et l'article donne des détails sur sa construction et ses divers éléments. Il est prévu pour brûler du charbon pulvérisé, du fuel-oil ou du gaz à raison de deux millions de Btu/h (500,000 kcal/h). Par construction, le foyer est constitué d'une série de calorimètres permettant de mesurer la quantité de chaleur absorbée par chaque portion de 6 po. (15 cm) de longueur additionnelle. Une fente, ouverte sur toute la longueur du foyer et dotée d'une série de portes refroidies par circulation d'eau, permet d'introduire des sondes même lorsque le foyer est sous pression.

Le premier projet de recherche prévu pour ce nouveau foyer consiste en une étude des facteurs affectant la formation d'oxydes d'azote dans les flammes de combustion des produits pétroliers. L'auteur passe en revue la théorie de la formation du NO, ainsi que la documentation récente sur les niveaux mesurés de concentration en NO provenant des appareils de combustion. Il fait ressortir le grand nombre d'erreurs possibles imputables à l'action réciproque de divers facteurs, et indique les paramètres principaux à considérer pour le programme proposé.

DER CCRL KANALOFEN - AUFBAU UND ANWENDUNG

ZUSAMMENFASSUNG

The Canadian Combustion Research Laboratory hat einen 4,25 m langen, thermolgekühlten Tunnelofen mit einem Durchmesser von 1 m aufgebaut. Die ersten Forschungsarbeiten an diesem Ofen werden sich mit flammenerzeugten Luftverunreinigungsprodukten beschäftigen und damit die Arbeit der Flammenforschungsgemeinschaft ergänzen. Die experimentellen Möglichkeiten erlauben neben den Messungen zum obengenannten Zweck auch das Studium der Verbrennungsaerodynamik. Dieser Ofen ist jetzt betriebsbereit, und Einzelheiten seines Aufbaus und seiner Instrumentierung können aus dem Bericht entnommen werden. Es können pulverisierte Kohle, Öl oder Gas mit einem Durchsatz von 500.000 kcal/h verfeuert werden. Der Ofen ist aufgebaut als eine Serie von Kalorimetern, die es ermöglichen, die absorbierte Wärmelänge für jede 15 cm der Ofenlänge für sich zu messen. Ein Schlitz, entlang der ganzen Ofenlänge, abgeschlossen durch eine den Kalorimetern entsprechende Serie von wassergekühlten Türen, ermöglicht Probenahmen, selbst wenn der Ofen unter Druck steht.

Die ersten Untersuchungen, die mit diesem neuen Ofen geplant sind, beschäftigen sich mit der Bildung von Stickoxyden in Öelflammen. Die Theorie der Bildung von Stickoxyden wird besprochen, wie auch die gegenwärtigen Veröffentlichungen über die Menge von Stickoxyden in Verbrennungseinrichtungen. Die zahlreichen Möglichkeiten für irreführende Ergebnisse als Folge von sich gegenseitig beeinflussenden Faktoren, und die massgebenden Einflüsse, die in dem vorgeschlagenen Programm untersucht werden sollen, werden besprochen.

INTRODUCTION

Canadians are fortunate that their generally cold climate is more than adequately compensated for by the large fuel resources at their disposal. In this technological age, fuel is a basic requirement for a high standard of living but, if we are to enjoy the 'good life', solutions must be found to the pollution problems without delay.

Calculations show that the fuel-source pollution problem in Canada is extensive. Since the purpose of the Canadian Combustion Research Laboratory (CCRL) is to assist industry through research, it is logical that we should consider our research on flame phenomena and combustion-source pollution as inseparable disciplines. It is in this context that our relationship with the International Flame Research Foundation (IFRF) has developed in adapting and extending the work of the Foundation to meet the requirements of Canadian industry. More precisely, the work of the Foundation has demonstrated that aerodynamic considerations tend to dominate both the chemical kinetics and the heat transfer. Therefore, the CCRL is attempting to produce minimal-pollution flames by controlling burner aerodynamics. Sufficient information is already available to indicate that, though this approach offers little potential for reduc-

ing SO_2 , it offers considerable potential for reducing other pollutants. For example, measurements on blue-flame burners operating on light oil have shown that unburned hydrocarbons and soot are virtually non-existent and nitric oxide concentrations are half of those measured in equivalent yellow flames.

On this basis, the CCRL is undertaking a broad research program aimed at rationalizing combustion-source air pollution, from all fossil fuels, as fully as possible. As a tool for this research, we are now completing a fairly sophisticated tunnel furnace which, together with the first phase of our program, is described in the following. It is hoped that this paper will stimulate critical comment on both our facilities and our program.

ESTIMATED FUEL-SOURCE POLLUTANT EMISSION IN CANADA

Some fairly simple calculations, based on Canadian fuel consumption statistics for 1968 and on a number of reasonable assumptions (1, 2), have demonstrated that fuel use in Canada results in the dumping of over 300 million tons of pollutants into the atmosphere annually. These pollutants are in the form of CO_2 , NO , CO , particulates, gas-phase hydrocarbons, SO_2 , and SO_3 . Table 1 gives a breakdown of fuel

TABLE 1 Breakdown of Thermal Energy from Fossil Fuels in Canada, Based on 1968 Fuel Consumption Statistics

Fuel	Consumption	Calorific Value	Btu
Natural Gas			
3.1 Domestic	214.6 x 10 ⁹ cu ft	(1007 Btu/cu ft)	216 x 10 ¹²
4.1 Commercial	144.0 x 10 ⁹ cu ft	(")	145 x 10 ¹²
5.1 Industrial	407.2 x 10 ⁹ cu ft	(")	410.05 x 10 ¹²
Oil			
Total Btu from natural gas: 771.05 x 10 ¹²			
3.2 Light furnace oil	27302 x 10 ⁶ lb	19590 Btu/lb	534.85 x 10 ¹²
3.3 Kerosene & stove oil	5566 x 10 ⁶ lb	19745 Btu/lb	109.90 x 10 ¹²
4.2 Diesel fuel	12765 x 10 ⁶ lb	19600 Btu/lb	250.19 x 10 ¹²
4.3 Motor gasoline	39256 x 10 ⁶ lb	20276 Btu/lb	795.96 x 10 ¹²
5.2 Heavy fuel oil	33843 x 10 ⁶ lb	18320 Btu/lb	620.00 x 10 ¹²
Coal			
Total Btu from oil: 2310.9 x 10 ¹²			
Commercial			
4.4 Can. bit coal	469 x 10 ⁶ lb	14031 Btu/lb	6.58 x 10 ¹²
4.5 Can. sub-bit coal	273.25 x 10 ⁶ lb	11653 Btu/lb	3.18 x 10 ¹²
4.6 Can. lignite	84.68 x 10 ⁶ lb	10960 Btu/lb	0.93 x 10 ¹²
4.7 Imported anthracite	194.8 x 10 ⁶ lb	13350 Btu/lb	2.60 x 10 ¹²
4.8 Imported bit coal	966.73 x 10 ⁶ lb	14310 Btu/lb	13.83 x 10 ¹²
Industrial			
5.3 Can. bit coal	8031 x 10 ⁶ lb	14031 Btu/lb	112.68 x 10 ¹²
5.4 Can. sub-bit coal	3783.4 x 10 ⁶ lb	11653 Btu/lb	44.09 x 10 ¹²
5.5 Can. lignite	2474 x 10 ⁶ lb	10960 Btu/lb	27.12 x 10 ¹²
5.6 Imported anthracite	572.24 x 10 ⁶ lb	13350 Btu/lb	7.64 x 10 ¹²
5.7 Imported bit coal	31468 x 10 ⁶ lb	14310 Btu/lb	450.3 x 10 ¹²
		Total Btu from coal: 668.95 x 10 ¹²	% from gas: 20.56
		Grand total Btu : 3750.9 x 10 ¹²	% from oil: 61.61
			% from coal: 17.83

TABLE 2 Breakdown of Pollution Emission from Fossil Fuels in Canada, Based on 1968 Fuel Consumption Statistics

Weight of Pollutant Emitted, lb x 10⁶

Fuel	CO ₂	NO	CO	Part.	SO ₂	SO ₃
Natural Gas						
3.1 Domestic	25670.	8.588	15.41	—	—	—
4.1 Commercial	17230.	24.93	10.34	—	—	—
5.1 Industrial	48710.	70.49	29.24	—	—	—
Sub-totals:	91610.	104.008	54.99	—	—	—
Total for natural gas:	Incl. CO ₂ : 91768.998		Excl. CO ₂ :	158.998		
Oil						
3.2 Light furnace oil	86110.	35.11	43.68	68.26	374.6	9.556
3.3 Kerosene & stove oil	17540.	7.169	8.917	13.92	32.73	0.835
4.2 Diesel fuel	40260.	192.8	119.9	16.56	153.2	—
4.3 Motor gasoline	91430.	846.8	19470.	12095.	23.55	—
5.2 Heavy fuel oil	106400.	249.8	51.81	84.61	1692.	42.30
Sub-totals:	341740.	1331.679	19694.307	12278.35	2276.08	52.691
Total for oil:	Incl. CO ₂ : 377373.107		Excl. CO ₂ :	35633.107		
Coal						
Commercial						
4.4 Can. bit coal	1339.	2.716	0.564	3.972	8.208	0.201
4.5 Can. sub-bit coal	684.5	1.320	0.274	2.235	2.869	0.072
4.6 Can. lignite	206.9	0.395	0.082	0.951	1.101	0.028
4.7 Imp. anth.	607.4	1.128	0.234	1.948	1.364	0.034
4.8 Imp. bit coal	2855.	5.772	1.197	5.955	11.12	0.278
Industrial						
5.3 Can. bit coal	22930.	46.52	9.648	34.01	140.5	3.512
5.4 Can. sub-bit coal	9477.	18.27	3.79	15.47	39.73	0.993
5.5 Can. lignite	6044.	11.54	2.393	13.89	32.16	0.804
5.6 Imp. anth.	1784.	3.313	0.687	2.861	4.006	0.100
5.7 Imp. bit coal	92920.	187.9	38.96	96.92	361.9	9.046
Sub-totals:	138847.9	278.874	57.829	178.212	602.958	15.068
Total for Coal:	Incl. CO ₂ : 139980.741		Excl. CO ₂ :	1132.941		
Grand Total:	Incl. CO ₂ : 609122.741		Excl. CO ₂ :	36925.046		
			Incl. CO ₂	Excl. CO ₂		
	% from gas		15.07	0.43		
	% from oil		61.95	96.5		
	% from coal		22.98	3.07		

usage, while Table 2 gives a breakdown of pollutant emission.

Whether CO₂ should be treated as a pollutant is still a matter of controversy. On the one hand, it is a non-poisonous product which is necessary to healthy vegetation; on the other hand it consumes and dilutes the oxygen necessary for life and can alter the heat balance of the earth with respect to space. If we exclude CO₂ from the list of pollutants, then our fuel-source pollutant emission amounts to

about 18.5 million tons per year. Analysis of Table 2 shows that our transportation fuels (gasoline and diesel oil) are at present responsible for nearly 90% of this figure. However, because of the massive efforts now being put forth by the automotive and oil industries to reduce pollution from internal combustion engines, we anticipate a reduction in their total emissions despite the projected increase in the consumption of gasoline and diesel oil. On the other hand, a projection of the current trends in non-trans-

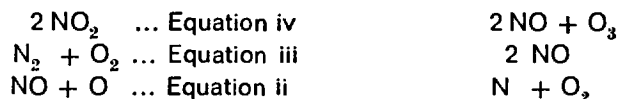
port consumption of fuel indicates a threefold increase by the year 2000. Thus, unless ways are found to reduce emissions, we can expect a substantial increase in pollution from stationary sources, both in terms of absolute quantity and in relation to transportation sources of air pollution.

NITROGEN OXIDE AS A POLLUTANT

One pollutant produced by the combustion of all fossil fuels is nitric oxide, or NO. It presently comprises only 4.6 % of the total pollution, excluding CO₂, from combustion sources in Canada but it is known to be a serious pollutant, primarily, because of its role in the formation of smog. Unfortunately, this fact was recognized only a decade ago; hence, research efforts directed at its causes and effects have been relatively small compared to, for example, the research on combustion-source sulphur oxides. Therefore, it seemed timely for the CCRL to begin its program of rationalizing combustion-source pollution with a study of means for reducing NO formation in flames.

The Chemistry of Nitrogen Oxides Formation

The mechanisms by which nitrogen oxides are formed high temperature air or combustion products are not completely understood, but it is generally agreed that an important part is played by atomic oxygen and nitrogen, formed by dissociation at high temperature. Therefore, in a flame, the following reactions may occur (3):



Most of the nitrogen oxides in flue gas are in the form of NO, but in the atmosphere it oxidizes fairly rapidly to NO₂, probably, through combination with ozone which is always present in trace quantities, according to the reaction (4):



The rates at which the reaction of formation and decomposition progress and the equilibrium concentrations ultimately reached vary with a number of factors. Many of these have not been fully investigated, but it is recognized that temperature and oxygen concentration are of primary importance (3) and that pressure is of secondary importance (5). Sufficient information exists to calculate equilibrium concentrations for various mixtures of gases. As a simple example, Figure 1 shows what happens as air is heated (6). At a temperature of 2000° R (1111° K), out of one million molecules of nitrogen (N₂) and oxygen (O₂), about one hundred have dissociated into atoms of nitrogen (N) and oxygen (O),

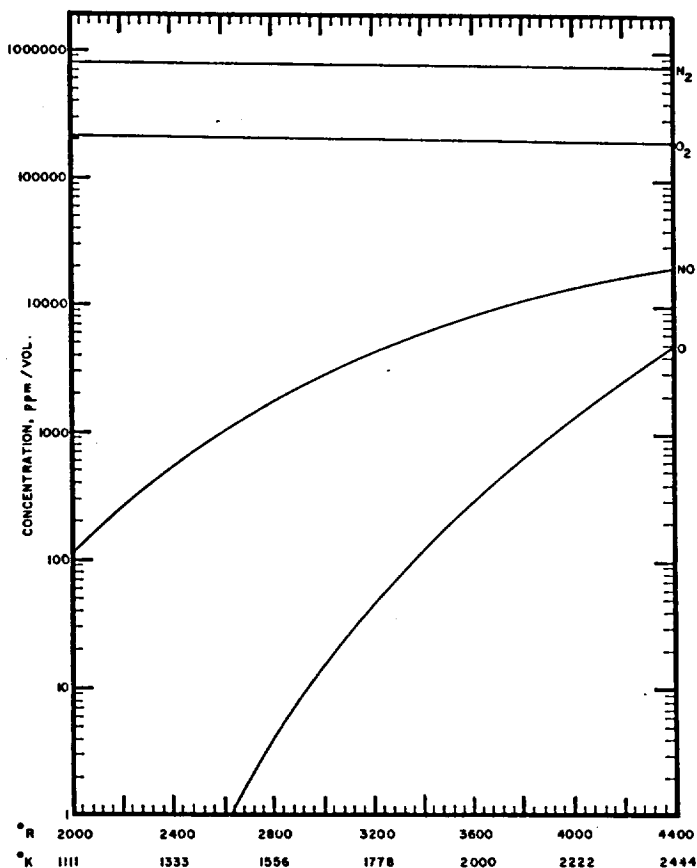


FIG. 1. Equilibrium concentrations of NO and O in heated air, from Table 6, p. 11, U.S. Bureau of Mines R.I. 6958 (Ref. 6)

which in turn have combined to form about one hundred molecules of nitric oxide (NO). At 3000° R (1667° K), a greater degree of dissociation has occurred, resulting in about 2700 ppm of NO plus 14 ppm of atomic oxygen. At 4400° R (2444° K), dissociation has further increased by a factor of about 10, resulting in about 20,000 ppm NO and 4800 ppm of atomic oxygen. Dissociation has now noticeably reduced the concentrations of N₂ and O₂.

Figure 2 shows calculated equilibrium concentrations for NO in products of combustion from propane-air flames at different fuel-air ratios (6). The stoichiometric fraction F is defined as propane concentration, vol %, divided by 4.03. Thus F = 1 represents a stoichiometric mixture, F > 1 represents a propane-rich mixture, and F < 1 represents a propane-lean mixture. The curves clearly demonstrate that NO concentration tends to increase rapidly both with increasing temperature and increasing excess air.

To clarify what these curves represent, consider a stoichiometric mixture (F = 1) of propane and air, burning under near-adiabatic conditions, that cools slowly enough that the NO formation and decomposition mechanisms achieve equilibrium. At maximum flame temperature, 4000° R (2222° K), sufficient N₂ and O₂ will dissociate and combine with each other

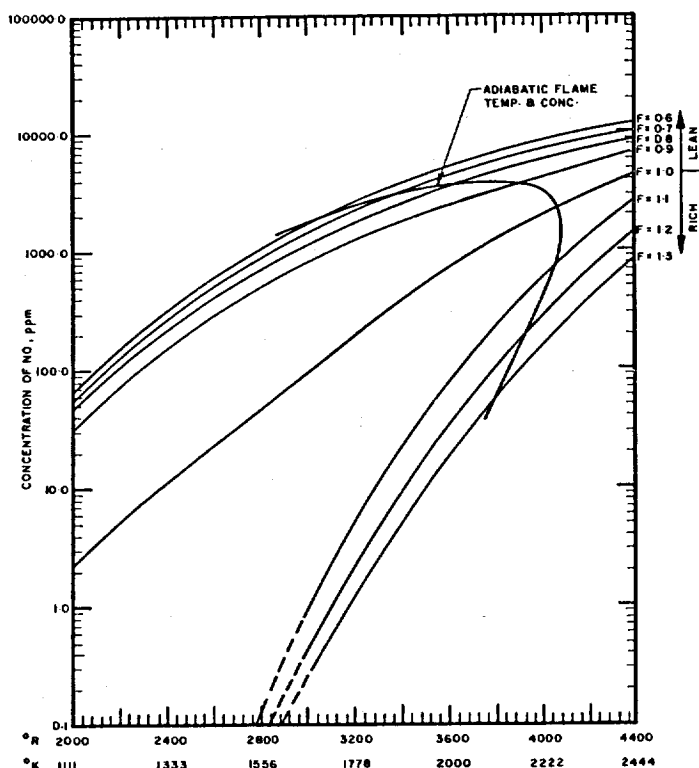


FIG. 2. Equilibrium concentrations of NO in products of combustion of propane-air mixtures at various temperatures, from Table 4, p. 10, U.S. Bureau of Mines R.I. 6958 (Ref. 6).

to form 2000 ppm of NO, according to Equations i and ii. Further formation of NO will be counterbalanced by decomposition of NO according to Equation iii. As the products of combustion slowly cool, equilibrium shifts in favour of the decomposition reaction so that NO is decomposing more rapidly than it is formed. Thus, at 3000° R (1667° K), about 99 ppm of NO remain and, at 2000° R (1111° K), only about 2 ppm of NO remain.

It is very important to remember that calculated equilibrium concentrations are only a guide to what can happen in a flame. This is because it takes time for the reactions of formation and decomposition of NO to reach equilibrium. As previously stated, the rate of reaction varies primarily with temperature and concentration of the reacting species and, though the reaction may proceed quite rapidly at high temperature, the rate will usually decay according to some exponential function as the concentration of the reacting species is reduced through reaction. Table 3 gives some idea of the rates of reaction for NO formation and decomposition (7). It can be seen that, at a temperature as high as 3060° R (1700° K), the formation of equilibrium composition would take several hours. In an industrial furnace or boiler, the average residence time, from fuel or air entering the burner to flue gas leaving the stack, is a matter of a few seconds; during this time, the mean temperature of the components rises from near ambient to flame temperature and, then, drops back to the stack temperature. These temperature fluctuations are too rapid for the NO reactions to achieve equilibrium, so what is most likely to happen is roughly shown in Figure 3.

Again, assume a stoichiometric mixture of propane and air such that the equilibrium values from the $F = 1$ curve of Figure 2 apply; but assume that it takes 0.1 sec from time of ignition for the mixture to reach the maximum temperature of 4000° R (2222° K) and that the gases then cool linearly with respect to time to 2000° R (1111° K) in an additional 2 sec. Then, at time $t = 0.1$ sec, the gas temperature is 4000° R (2222° K) and the corresponding NO equilibrium concentration is about 2000 ppm but, though NO is being formed rapidly, there has not been sufficient time for the actual concentration to reach the equilibrium value and perhaps only about 30 ppm of NO have actually formed. Thereafter, the gas tem-

TABLE 3
Variation with Temperature of the Half-life Period of Formation and Decomposition of Pure Nitric Oxide *

Temperature		Time for formation of half of equilibrium NO	Time for decomposition of half of pure NO
°K	°R		
900	1620	—	123 hr
1000	1800	81 years	—
1500	2700	30 hr	3 min
1700	3060	1 hr	15 sec
1900	3420	2 min	1 sec
2000	3600	5 sec	0.07 sec
2300	4140	0.2 sec	0.005 sec
2500	4500	0.01 sec	—
2900	5220	0.00003 sec	—

* From Table 5, p. 149, Journal of the Institute of Fuel, April 1967 (Ref. 7).

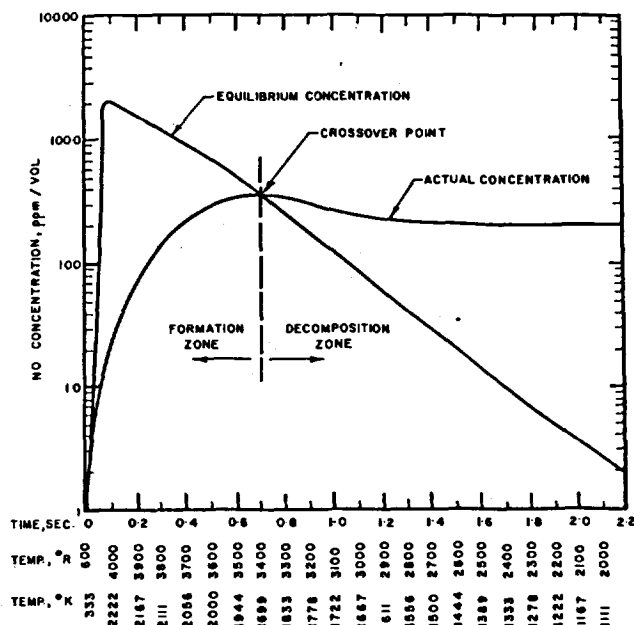


FIG. 3. Possible history of NO formation and decay in a flame.

perature begins to drop and the equilibrium concentration drops correspondingly. Since the actual concentration is still below the equilibrium value, the formation of NO continues but the rate of reaction is steadily decreasing, partly because the temperature is dropping and partly because the actual concentration is getting closer to the equilibrium value. At some point, perhaps when $t = 0.7$, the equilibrium concentration drops to the actual concentration, equi-

librium is momentarily achieved at a level of perhaps 360 ppm of NO, and no additional NO is formed. The temperature and the corresponding equilibrium concentration continue to drop rapidly and, since the actual concentration is now above equilibrium, NO begins to decompose, but not rapidly enough to maintain equilibrium. Thus, at $t = 1.1$ sec, the equilibrium concentration is about 100 ppm, but the actual concentration has dropped to only about 250 ppm. As the temperature continues to drop, the equilibrium concentration rapidly approaches zero (approx. 2 ppm at 2000° R, or 1111° K) but the temperature is now in a region where the decomposition reaction proceeds relatively slowly, hence, at $t = 2.1$ sec, the actual concentration may still be about 200 ppm. As the gas temperature continues to drop toward ambient, the decomposition reaction virtually grinds to a halt, and the flue gas leaves the chimney with the actual NO concentration essentially fixed at a level well above the equilibrium concentration corresponding to stack temperature.

It should be emphasized that the foregoing is an oversimplified illustration of the manner in which the NO reactions may proceed. The values given, while probably typical, are not actual measurements. Using data published by Zeldovitch (8), Singer et al (6) derived equations for the rate of NO formation in propane-air flames and, then, calculated NO concentrations using residence times and temperatures measured in an experimental (bench-scale) burner. These calculated concentrations of NO were then compared with concentrations measured in the same burner, and some of the results are given in Table 4. It is clear that, even when information is available

TABLE 4
Experimental and Predicted Nitric Oxide Concentrations in Lean, Stoichiometric, and Rich Propane-Air Flames *

* From Table 10, p. 16, U.S. Bureau of Mines R.I. 6958 (Ref. 6)

Distance above burner, inches	Propane-Air Concentrations, Fraction of Stoichiometric					
	0.86		1.04		1.23	
	Experimental	Predicted	Experimental	Predicted	Experimental	Predicted
	Nitric oxide concentrations, ppm					
0.16	—	0	—	0	—	0
1	—	25.5	—	11.0	—	3.9
2	91	42.5	99	33.0	32	6.9
3	—	51.3	—	39.5	—	8.3
4	—	57.3	—	44.0	—	9.2
5	—	61.8	—	46.5	—	9.6
6	118	65.0	105	47.6	61	10.0
7	—	67.0	—	48.3	—	10.1
8	—	67.6	—	48.5	—	10.2
9	111	67.8	174	48.7	72	10.2
14	—	67.8	84	48.7	64	10.2

on temperature and residence time, the method of prediction is not very reliable and that, in combustion systems (large boiler furnaces) where patterns of temperature and residence time are complex, it will be necessary to carry out actual measurement of NO concentration until such time as the methods of prediction are substantially refined.

Measured Levels of Nitrogen Oxides from Combustion Equipment

Published data giving measured concentrations of NO and NO₂ in flue gas from industrial processes are surprisingly limited. In 1960, Sensenbaugh and Jonakin (9) published the results of NO measurements on power-station boilers, burning oil and natural gas, with both tangential firing and front-wall horizontal firing. Some of their data are reproduced in Table 5.

TABLE 5

NO Concentrations Measured in Power Station Boiler Operating at Full Load with Different Fuels and Firing Systems *

Plant	Fuel	Firing System	Avg. NO, ppm
El Segundo	Oil	Horizontal	685
A	Oil	Horizontal	567
B	Oil	Horizontal	505
C	Oil	Horizontal	482
E	Oil	Tangential	362
F	Oil	Tangential	309
G	Oil	Tangential	209
El Segundo	Gas	Horizontal	520
A	Gas	Horizontal	290
B	Gas	Horizontal	319
D	Gas	Horizontal	226
E	Gas	Tangential	164
F	Gas	Tangential	157

* From Table 1, p. 3, ASME Paper No. 60-WA-334 (Ref. 9).

In 1964, Orning et al (10) published measured data on NO_x concentrations in large pulverized-coal-fired boilers. Measurements were taken at several locations on four boilers; therefore, the complete data became too voluminous to reproduce here but Table 6 summarizes measurements, in the breeching, of the NO_x concentrations emitted to atmosphere.

Austin and Chadwick report that measurements on a variety of boiler designs and fuels showed NO concentrations, in the stack gas, ranging from 650 to 1450 ppm from coal-fired boilers, 190 to 1350 ppm from natural-gas fired boilers, and 310 to 945 ppm from residual-oil fired boilers (11).

Lee, Friedrich, and Mitchell, working on a pilot-scale model of an opposed-fired utility boiler, found NO_x levels of 181 to 260 ppm while burning residual fuel oil (12) and 414 to 743 ppm while burning Canadian lignite (13), NO_x being defined as NO + NO₂. While gas turbines account for only a small portion of Canada's total fuel consumption, some idea of their nitrogen oxide emission may be of interest. Smith et al report that concentrations measured on aircraft turbojet engines ranged from 100 to 350 ppm, adjusted to stoichiometric conditions, whereas concentrations measured on a 60-hp industrial-gas turbine, while burning either jet fuel or diesel oil, were less than 50 ppm, adjusted to stoichiometric conditions (14).

A recent review by Cadorn (15) collates considerable information on nitrogen oxides and includes some of the aforementioned references.

TABLE 6

Nitrogen Oxide Concentrations Measured in the Breechings of Large Boilers Fired by Pulverized Coal *

Type of Furnace	Load	Excess air, %	NO _x Conc., ppm
Vertically fired, dry-bottom	Full	14	480
	Full	18	340
	Full	18	240
	3/4	13	240**
	3/4	22	270
Front-wall fired, dry-bottom	Full	14	620**
	Full	17	720
	Full	18	740
	3/4	10	470
	3/4	21	610
Corner fired, dry-bottom	Full	19	430
	Full	20	500
	3/4	19	320
	3/4	22	360
Turbo-fired, wet-bottom	Full	17	370
	Full	28	460
	Full	28	330
	Full	34	360
	3/4	24	400
	3/4	26	370

* From Table 3, p. 4, ASME Paper No. 64-WA/FU-2 (Ref. 10).

** These items are single observations. Others are averages of two or more observations.

POSSIBLE METHODS OF REDUCING NITROGEN OXIDE FORMATION

A. Control of Temperature History

The pattern of NO formation and decay shown in Figure 3 suggests that, if the time taken up by the formation zone could be reduced and if the gas temperature in the formation zone could be kept lower, the actual concentration of NO would peak at a lower level. Furthermore, if the gas temperature in the decomposition zone dropped more slowly, the actual concentration could decay to a lower level. Theoretically, then, what is desired is a very rapid ignition and combustion, of the fuel, accompanied by high rates of heat transfer to minimize flame temperature up to the crossover point of the equilibrium concentration and actual concentration curves. Beyond the crossover point, rates of heat transfer should be kept fairly low at least until the gas reaches a temperature of 3000° R (1667° K). Below this temperature, the rate of NO decomposition becomes so slow that most combustion processes cannot conveniently accommodate it.

It is very likely that optimized aerodynamics, to provide rapid mixing and combustion, coupled with high heat-transfer rates, in the vicinity of the flame envelope, can reduce the formation of NO. However, the point at which rapid heat transfer should be replaced by slow heat transfer, to facilitate NO decomposition, cannot be readily determined because the crossover point is not known, will likely change from system to system, and shift with different firing conditions in a particular system.

Some pragmatic experiments along these lines have been carried out. Sensenbaugh and Jonakin (9) show that some reduction in NO emission can be achieved by varying the manner in which air is admitted to the burners; this may improve the combustion aerodynamics. They also show that a reduction of NO emission of 22 to 45 % can be achieved with a two-stage combustion system, in which about 90 % of stoichiometric air (85 % total combustion air) is introduced through the burners, while the remaining combustion air (15 %) is introduced through ports above the burners. Similar results with a two-stage combustion system were reported by Austin and Chadwick (11).

B. Reduction of Flame Temperature

It is clear from the equilibrium data that reducing flame temperature tends to reduce NO formation. Essentially, this approach emphasizes one facet of controlling the temperature history and it appears to offer a good chance of success because of its simplicity.

One way to reduce flame temperature is to increase the level of excess air. However, the benefits are usually offset by the increased amount of oxygen available for formation of NO, and increased excess air is undesirable from the viewpoint of overall ef-

iciency of the combustion system. Increasing excess air may in fact increase emission of NO, as shown in the data of Sensenbaugh and Jonakin (9).

A more attractive approach to reducing flame temperature is to dilute the combustion air with flue gas. This avoids both an increase in available oxygen and a decrease in system efficiency. The limited research that has been carried out using this approach has shown encouraging results. Sensenbaugh and Jonakin show a 15 % reduction in NO concentration with 15 % gas recirculation (9), and Singer et al, on the basis of extensive calculations, predict that recycling cold flue gas into lean propane-air mixtures will reduce nitrogen oxide formation even though it will increase carbon monoxide emission (6).

Flame temperature can also be reduced by the injection of water or steam. The former has been used with some success in diesel engines but a boiler's efficiency would be impaired and its susceptibility to corrosion would be increased.

C. Firing with Low Excess Air

To minimize formation of NO using this technique, it is usually necessary to approach stoichiometric conditions. A moderate reduction in excess air, say from 30 to 20 %, may be accompanied by an increase in NO formation because of higher flame temperatures. However, Sensenbaugh and Jonakin (9) observed that NO concentration dropped as excess air was reduced, even at high excess air levels. The data of Fernandes (16) indicate a drop of NO_x of about 60 % while excess air is reduced from 15 to 3 %. The data of Andrews (17), obtained from oil-fired equipment, show a reduction in NO_x emission of 80 % while excess air is reduced from 50 to 20 % and while, simultaneously, 50 % of the flue gas is recirculated.

D. Chemical Neutralization

The possibility of removing NO from flue gas streams by chemical means has received only limited attention, usually in connection with removal of SO₂. Haagen-Smit concluded that it is technically possible to remove about 75 % of the NO and 90 % of the SO₂ from fuel-oil flue gas by-passing the gas through a vanadium catalyst at high temperature, introducing ozone, and electrostatic precipitation (11). However, this system was found to be economically infeasible. Lee et al found that a magnesia-alumina additive, normally employed to neutralize SO₃ in oil-fired systems, also neutralized 13 to 30 % of the nitrogen oxides at the dosage rate normally employed for complete acid neutralization (12).

Cadorin (15) outlines several methods of removal, including catalytic reduction, absorption of NO_x by solids, and absorption of NO_x by liquids. However, most experiments along these lines are still at the bench-scale stage.

A PROPOSED CCRL PROGRAM FOR STUDYING NITROGEN OXIDES

Pilot-Scale Research

What has been said in the preceding pages should make one point abundantly clear: there is a great deal yet to be learned before NO emission from combustion processes can be substantially and feasibly reduced. Opinions, on what information is most necessary and how best to obtain it, will range from those of the engineer, who wants to vary whatever parameters he can control in a full-size plant while measuring emission levels, to those of the pure scientist, who wants to fully explore the formation and decomposition mechanisms on a bench scale before attempting any extrapolation to practical combustion systems. Both extremes have serious disadvantages. On the other hand, the authors have had gratifying success with pilot-scale equipment, a compromise between the two extremes. How faithfully a pilot-scale rig simulates the equipment it is supposed to represent depends largely on the ingenuity of its design. With sufficient thought and experience, the results of pilot-scale research, in many cases, have been shown to apply quantitatively to full-scale equipment and, in most other cases, have done no worse than to point in the right direction. This has been well demonstrated by the research of the IFRF.

A pilot-scale rig (tunnel furnace) suitable for research on the formation of nitrogen oxides in flames was designed by F. D. Friedrich and constructed by the staff of the CCRL. The following is devoted to a description of it, to a description of the probes and pollutant monitoring gear that have been acquired for studying combustion and combustion-source pollution, and to an outline of an investigation of NO_x formation in relation to combustion aerodynamics.

THE CCRL TUNNEL FURNACE

Although the tunnel furnace is being used first for a study of nitrogen oxide formation, it was conceived as a versatile facility for the study of combustion aerodynamics, of burner performance, of the character of pollutants in relation to flame properties, and of heat transfer from flames; all of this relates to commercial and industrial combustion equipment.

After much discussion, consultation with a number of authorities in the field, and first-hand experience with the furnaces of the IFRF, the following features were incorporated in the design of the CCRL tunnel furnace:

1. The furnace is capable of firing pulverized coal, fuel oil, and natural gas or propane using a wide variety of interchangeable burners.
2. To be comparable to commercial and industrial equipment, the furnace has 'cold' rather than refractory walls. However, to permit reliable measure-

ment of SO_3 in the flue gas, the furnace walls are kept hotter than the acid dewpoint.

3. It is possible to add refractory to the furnace walls at will.
4. It is possible to measure the pattern of heat absorption in the furnace.
5. Since one purpose of the furnace is to study combustion aerodynamics, a round tunnel configuration was chosen so as to minimize the furnace influence on both flame shape and gas-flow patterns.
6. There is a continuous access slot along the furnace through which measuring probes may be introduced.
7. To permit the furnace to be operated independently, the heat generated is wasted without any attempt at utilization.
8. External flue-gas recirculation has been incorporated both for controlling excess air levels and minimizing nitrogen oxide formation.
9. It is possible to operate with a moderate pressure in the furnace.

To permit convenient and fairly accurate measurements and within a strict budget, the furnace was designed for a fuel firing rate of two million Btu/hr (0.504 million kcal/hr). Since one purpose of the furnace is to study swirling flames which tend to be bushy, a furnace diameter of 1 meter (39 in.) was settled upon. Since furnace length was deemed less important, it was felt that 4.25 meters (14 ft) would be long enough to permit the development of any flow patterns of interest. With these dimensions, the heat release rates work out to 14,000 Btu/sq ft/hr, (38,000 kcal/m²/hr) or 17,000 Btu/cu ft/hr (151,000 kcal/m³/hr).

The first five features were made possible by assembling circular segments, flanged together on a horizontal axis, much like a row of doughnuts. One end is left free for mounting any desired form of burner.

As previously stated, furnace walls are cooled, but maintained hotter than the acid dewpoint. This is no problem for natural-gas firing, but, for most coals and residual fuel oil, this means that the surface temperature should not fall below 300° F (149° C). Steam cooling was not practical with the chosen configuration. Instead, a commercial heat-transfer liquid known as Therminol FR-1 was selected. It is a non-toxic, fire-resistant, chlorinated biphenyl which remains stable, in liquid phase at atmospheric pressure, over the temperature range from 32 to 6000° F (0 to 316° C).

To accommodate the addition of refractory to the furnace walls, the furnace segments were designed as interchangeable units. This enables one or more segments to be taken out and to be replaced by segments having a refractory lining of the same diameter.

It was decided to have each furnace segment form a separate cooling circuit, each being supplied in

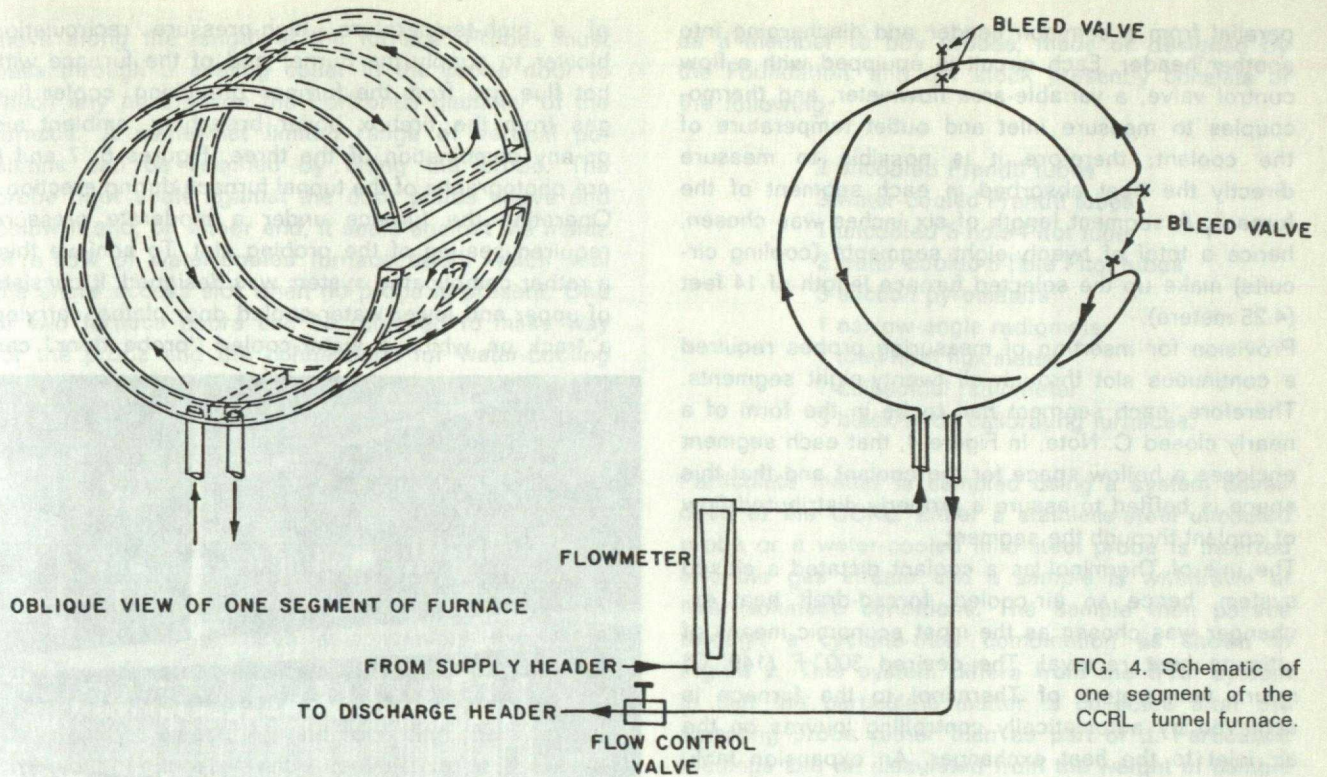


FIG. 4. Schematic of one segment of the CCRL tunnel furnace.

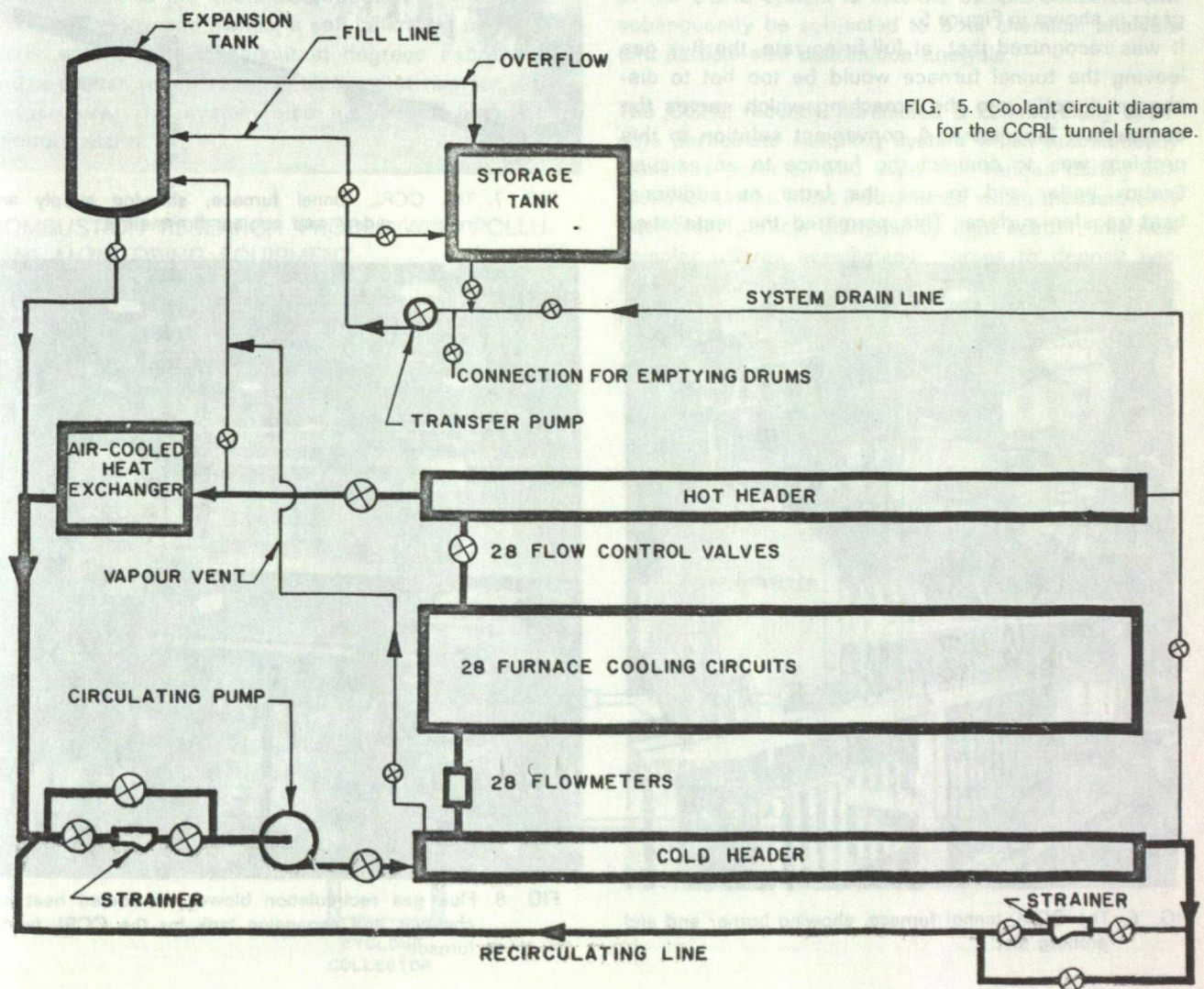


FIG. 5. Coolant circuit diagram for the CCRL tunnel furnace.

parallel from a common header and discharging into another header. Each circuit is equipped with a flow control valve, a variable-area flowmeter, and thermocouples to measure inlet and outlet temperature of the coolant; therefore it is possible to measure directly the heat absorbed in each segment of the furnace. A segment length of six inches was chosen, hence a total of twenty-eight segments (cooling circuits) make up the selected furnace length of 14 feet (4.25 meters).

Provision for insertion of measuring probes required a continuous slot through all twenty-eight segments. Therefore, each segment had to be in the form of a nearly closed C. Note, in Figure 4, that each segment encloses a hollow space for the coolant and that this space is baffled to assure a properly distributed flow of coolant through the segment.

The use of Therminol as a coolant dictated a closed system, hence an air-cooled, forced-draft heat exchanger was chosen as the most economic means of ultimate heat removal. The desired 300° F (149° C) return temperature of Therminol to the furnace is achieved by automatically controlling louvres on the air inlet to the heat exchanger. An expansion tank, storage tank, circulating pump, and transfer pump complete the coolant circuit. The coolant flow diagram is shown in Figure 5.

It was recognized that, at full-firing rate, the flue gas leaving the tunnel furnace would be too hot to discharge directly into the breeching which serves the combustion laboratory. A convenient solution to this problem was to connect the furnace to an existing firebox boiler and to use the latter as additional heat-transfer surface. This permitted the installation

of a high-temperature, high-pressure recirculation blower to supply the burner end of the furnace with hot flue gas from the furnace breeching, cooler flue gas from the firebox boiler breeching, ambient air, or any combination of the three. Figures 6, 7 and 8 are photographs of the tunnel furnace during erection.

Operating the furnace under a moderate pressure required sealing of the probing slot. To achieve this, a rather complicated system was designed. It consists of upper and lower water-cooled door plates, carrying a track on which a water-cooled "probe door" can

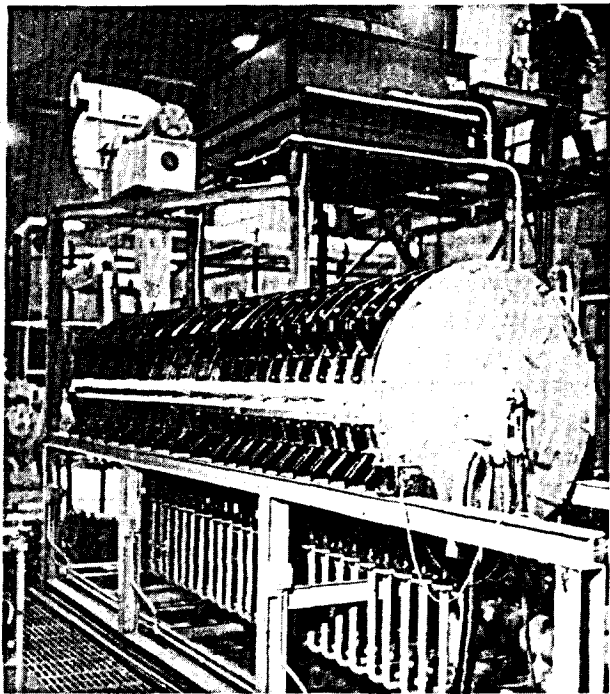


FIG. 6. The CCRL tunnel furnace, showing burner end and probing slot.

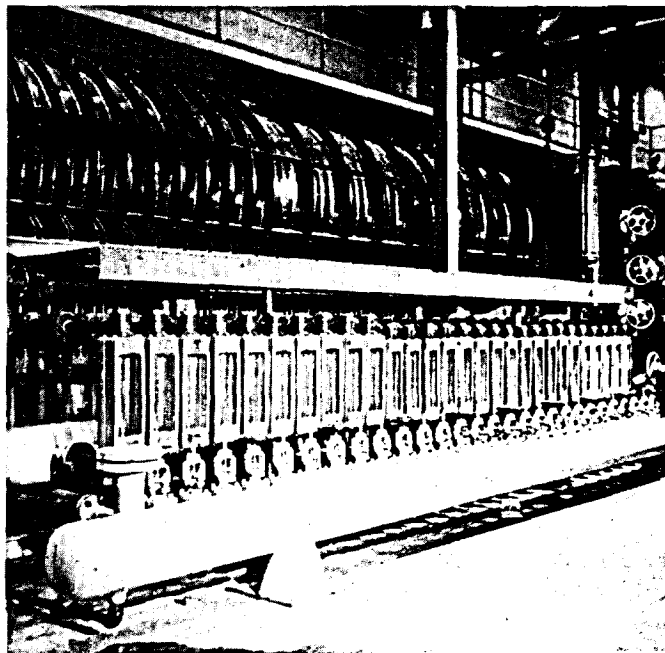


FIG. 7. The CCRL tunnel furnace, showing supply and return headers and coolant flowmeters.



FIG. 8. Flue gas recirculation blower, air-cooled heat exchanger, and expansion tank for the CCRL tunnel furnace.

move along the length of the furnace. Probes must pass through a sealing collar in the probe door to reach any position on the horizontal diameter of the furnace. A somewhat limited range of vertical positions can be reached by tilting the probe. The probe door seals against the door plates above and below it and, on either end, it seals against the inside of a row of water-cooled furnace doors which seal the entire access slot when no probe is present. One or two furnace doors can be removed to make way for the probe and the connections for water-cooling the probe doors and, still, a seal can be maintained on the furnace.

A complication arises from the fact that the furnace segments, being shaped somewhat like bourdon tubes, tend to straighten out under a combination of heat and pressure, widening the slot which the doors are designed to seal. This is controlled by a large beam running the length of the furnace above the doors. The beam also provides a convenient fixture for mounting the headers and hoses which provide cooling water to the doors.

A system for measuring and recording the inlet and outlet temperature of each coolant circuit has been installed. It consists of 56 thermo-couples, cemented and strapped to the inlets and outlets of the circuits, a 60-point motorized switch, a self-balancing potentiometer with a digital readout in degrees Fahrenheit, and a printer which records time, point number, and temperature. The system also includes a high-temperature alarm.

COMBUSTION RESEARCH PROBES AND POLLUTANT MONITORING EQUIPMENT

The CCRL depends heavily on the Foundation's leadership in the development of probes for combustion research. We have made good use of our privilege

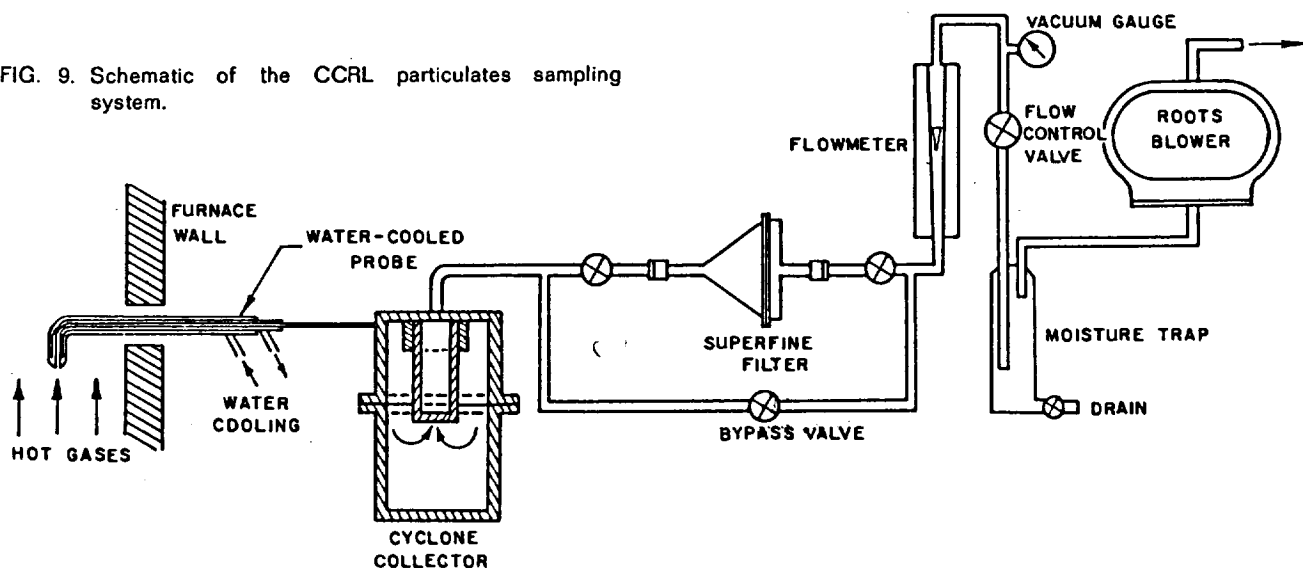
as a member to buy probes, made or designed by the Foundation, and our stock presently consists of the following:

- 2 uncooled Prandtl tubes
- 2 water-cooled Prandtl tubes
- 1 uncooled 5-hole Pitot tube
- 2 water-cooled 5-hole Pitot tubes
- 3 suction pyrometers
- 1 narrow-angle radiometer
- 1 total heat flux meter
- 1 ellipsoidal radiometer
- 3 black-body calibrating furnaces.

Particulate matter is sampled using a system developed at the CCRL. Either a stainless-steel uncooled probe or a water-cooled mild-steel probe is inserted into the gas stream and a sample is withdrawn at near-isokinetic conditions. The sample then passes through a cyclone-filter combination as shown in Figure 9. This system differs from the IFRF system in that the particulate matter is collected after the sampling probe rather than as part of it. Particulate loadings can be calculated from the weight of sample collected and from the gas flow rate. An advantage of the CCRL system is that the sample collected can subsequently be subjected to both chemical analysis and particle-size distribution analysis.

The CCRL recently purchased a commercially available particulate sampling system which automatically classifies particles into eight size ranges during collections. Unlike most instruments, which measure only equivalent particle diameter by light scatter, this new sampler utilizes aerodynamic forces to deposit particles according to size on a series of collection plates. These particles suffer little or no degradation during quiescent deposition and are recoverable for further analytical work.

FIG. 9. Schematic of the CCRL particulates sampling system.



MONITORING OF COMBUSTION-SOURCE POLLUTANTS

The scarcity of definitive information on the formation and evolution of pollutants in industrial flames is, to a large degree, due to the difficulties inherent in collecting representative samples of hot flue gas that are normally laden with dust, moisture, and acid. For example, during sample collection the gas, vapour, and solid components of flue gas must be prevented from reacting with each other and with materials of the sampling system. In addition, if filters are used ahead of gas and vapour absorbers, precautions must be taken to ensure that both the filter medium and the accumulated particles do not remove or alter any of the pollutants of interest. After the sampling problems have been overcome, practically all pollutants of interest can be accurately determined using adaptations of methods developed for ambient-air analyses. During the past few years, over 50 constituents in flue gas have been determined in experiments conducted at CCRL including CO_2 , CO , O_2 , gas-phase hydrocarbons, SO_2 , NO , NO_2 , and a wide variety of particulate matter. Traditionally, these components are monitored intermittently by analyzing batch samples of flue gas. However, the usefulness of such samples is limited because either fuel quality or combustion conditions may change significantly between the time that the sample is taken and the time of completing the analyses. It follows that continuous, selective, and automated analytical methods are the most reliable for measuring pollutant levels in flue gas. Using this approach, two monitoring systems, one for CO , CO_2 , gaseous hydrocarbons, and O_2 and one for SO_2 , NO , and NO_2 have been assembled at CCRL using commercially available instruments. Both systems incorporate specially designed modules that continuously sample, filter, and dehumidify the flue gas prior to its analysis.

The first system, which is essentially an automated Orsat, incorporates non-dispersive, infrared analyzers for CO , CO_2 , and gaseous hydrocarbons respectively and a thermomagnetic sensor for O_2 . Infrared analyzers are based on the principle that every gaseous compound absorbs radiation at unique wavelengths that are specific to the compound of interest. Therefore, an instrument that is sensitized to absorb radiation at wavelengths where no superposition occurs can be used to selectively monitor most compound gases. In the case of gaseous hydrocarbons, the instrument is calibrated in terms of hexane.

The thermomagnetic sensor for O_2 utilizes the combined effect of a magnetic and a thermal gradient which forces oxygen-bearing gases to flow in the direction of the magnetic field. The magnitude of the flow produced is proportional to the oxygen content of the flue gas sample. A photograph of the automated Orsat system is shown in Figure 10. With this system, the time lag between the sample probe and the re-

order readout is less than 5 seconds because only about 2% of the total gas sample passes through the analyzers.

The second system employs three parallel-connected, automated, wet-chemical analyzers to continuously monitor SO_2 , NO_2 , and NO . It incorporates a sampling and preparation module, designed by CCRL, which provides the pollutant absorption columns with a continuous flow of dust- and moisture-free flue gas diluted with dry nitrogen. This dilution stage reduces the SO_2 , NO_2 , and NO levels of the sample stream to less than 1 ppm and thus permits the use of methodologies previously developed for ambient-air analyses. The West-Gaeke method is used for SO_2 analysis while a modified Saltzman reagent is used for both NO and NO_2 analyses. A photograph of the assembled system for monitoring SO_2 , NO_2 , and NO is shown in Figure 11.

Particulate matter is sampled isokinetically, as previously described, and, depending on the information required, representative fractions of the gross sample are analyzed for a variety of constituents, often by using facilities available in other parts of the Mines Branch. Typical analyses may include:

- (a) organics by solvent extraction followed by fluorescence spectrometry or electron capture;
- (b) combustible matter by low-temperature ashing in a plasma furnace or by high-temperature ashing in a muffle oven;
- (c) mineral components by X-ray diffraction analysis;

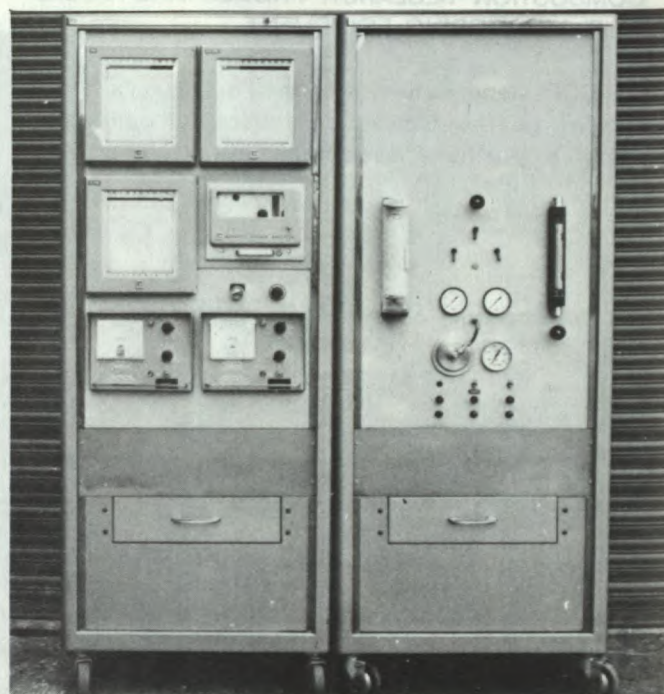


FIG. 10. Panel-mounted, automatic, flue gas sampling and analyzer system (Orsat).

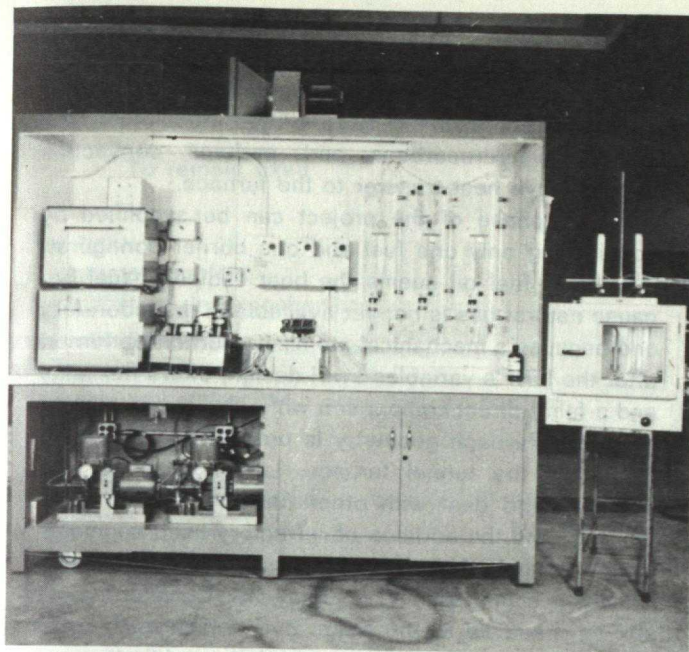


FIG. 11. Cabinet-mounted, SO₂, NO₂ and NO monitoring system.

- (d) elemental composition by electron microprobe analysis;
- (e) particle shape and mineral distribution by petrographic examination;
- (f) particle size distribution by Coulter Counter;
- (g) particles per unit volume by light scatter;
- (h) porosity by mercury infusion;
- (i) metal cations by AAS; and
- (j) anions by ion exchange and titration.

MAJOR PARAMETERS FOR THE CCRL FLAME RESEARCH PROGRAM

A few minutes of reflection on the factors governing NO formation in flames will demonstrate that it is not a simple matter to specify the independent variables in terms of what is actually under the in-

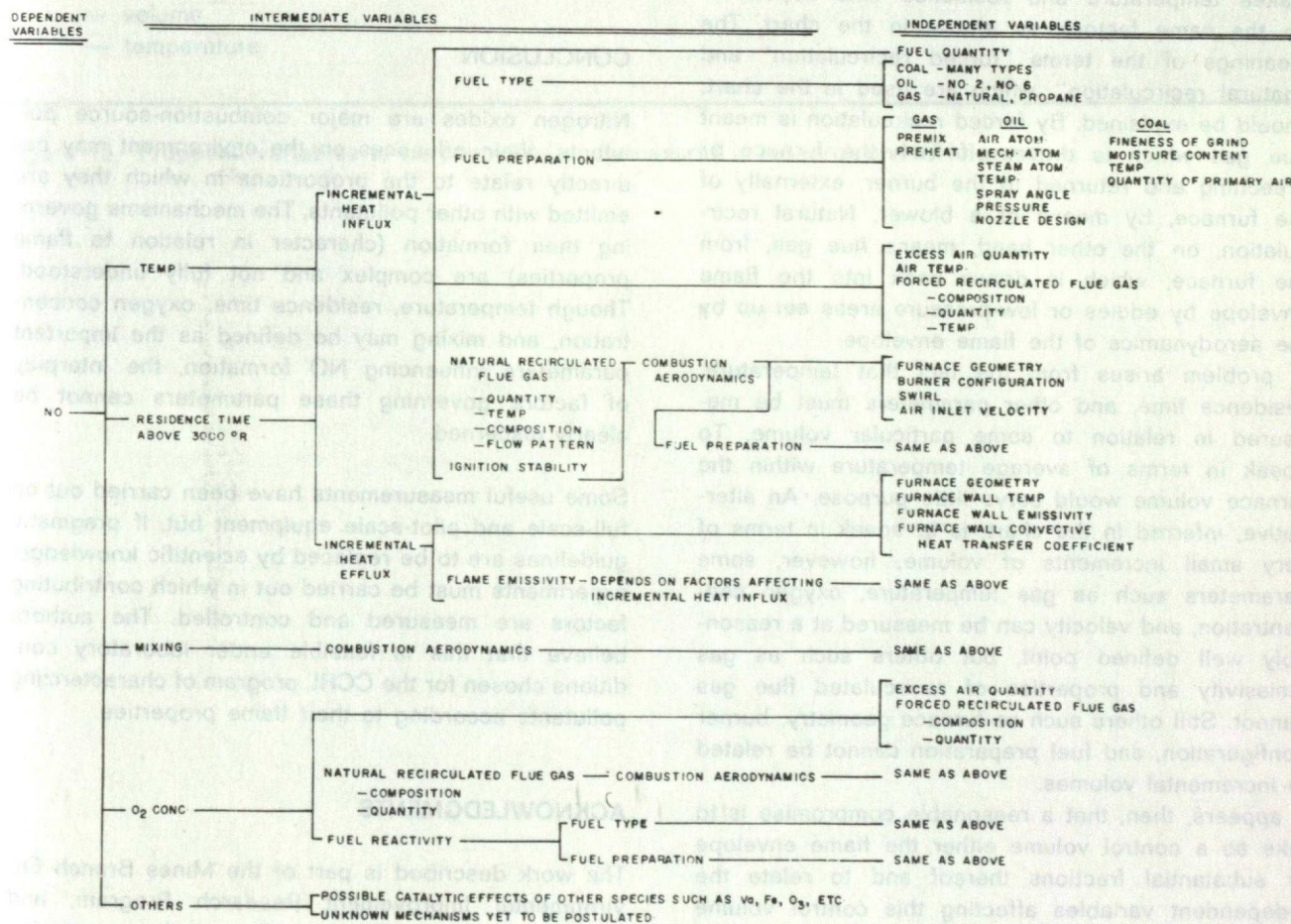


Figure 12. Relationship of independent, intermediate and dependent variables in the formation of NO.

investigator's control. Admittedly, NO concentration can be said to depend on four major factors: temperature, residence time, mixing, and oxygen concentration plus, perhaps, some other yet unknown factors, possibly activation by other materials present. But what are the factors that control flame temperature at any given point in the flame envelope? Obviously, the temperature of a given unit of mass depends on the difference between the rate of heat input and the rate of heat output, but these rates in turn depend upon many other factors such as fuel (quantity, type, and preparation), excess air (quantity and temperature), combustion aerodynamics, furnace geometry, furnace wall (temperature, emissivity), and flame radiation. The picture is further complicated by the tremendous potential for interactions. For example, temperature, residence time, and mixing are all affected by furnace geometry.

In an attempt to clarify the situation, the variables have been categorized as independent, intermediate, and dependent; and the relationships between them have been charted as shown in Figure 12. Since, in practical terms, temperatures below 3000° R (1667° K) have no effect on NO formation, it was convenient to define residence time as the time during which a given volume of gas is above 3000° R (1667° K). This makes temperature and residence time dependent on the same factors, as shown in the chart. The meanings of the terms "forced recirculation" and "natural recirculation", which are used in the chart, should be explained. By forced recirculation is meant flue gas which is drawn off from the furnace or breeching and returned to the burner, externally of the furnace, by means of a blower. Natural recirculation, on the other hand, means flue gas, from the furnace, which is drawn back into the flame envelope by eddies or low-pressure areas set up by the aerodynamics of the flame envelope.

A problem arises from the fact that temperature, residence time, and other parameters must be measured in relation to some particular volume. To speak in terms of average temperature within the furnace volume would serve little purpose. An alternative, inferred in the chart, is to speak in terms of very small increments of volume; however, some parameters such as gas temperature, oxygen concentration, and velocity can be measured at a reasonably well defined point, but others such as gas emissivity and properties of recirculated flue gas cannot. Still others such as furnace geometry, burner configuration, and fuel preparation cannot be related to incremental volumes.

It appears, then, that a reasonable compromise is to take as a control volume either the flame envelope or substantial fractions thereof and to relate the independent variables affecting this control volume to the concentrations of NO and NO₂ in the stack gas. Also, much can be learned by concurrently measuring intermediate variables, particularly tem-

perature and gas compositions, at many points within the flame envelope. At the same time, since little extra effort is involved, other dependent variables can be measured, such as SO₂, SO₃, particulates, CO, gas-phase hydrocarbons, and, perhaps, convective and radiative heat transfer to the furnace.

The first phase of the project can be simplified by considering only one fuel and one burner configuration. No. 2 fuel oil seems the best choice of fuel because natural gas is not yet available in the laboratory and because a mechanical-atomizing burner, patterned after the IFRF's variables-swirl design, offers flexibility and a fairly direct comparison with others in published research. Furnace geometry is presently fixed by the design of the tunnel furnace. Later phases of the project could deal with other fuels, different burner designs, and the addition of refractory-lined segments to the furnace. The proposed outline of the first phase is shown schematically in Figure 13. Decisions must still be made as to the range over which each parameter will be varied and as to what combinations of parameters will be tested, because there are too many for a factorial approach. However, such decisions are best left fairly flexible because preliminary results may show that certain parameters are too insignificant to warrant detailed study.

CONCLUSION

Nitrogen oxides are major combustion-source pollutants; their influences on the environment may not directly relate to the proportions in which they are emitted with other pollutants. The mechanisms governing their formation (character in relation to flame properties) are complex and not fully understood. Though temperature, residence time, oxygen concentration, and mixing may be defined as the important parameters influencing NO formation, the interplay of factors governing these parameters cannot be clearly discerned.

Some useful measurements have been carried out on full-scale and pilot-scale equipment but, if pragmatic guidelines are to be replaced by scientific knowledge, experiments must be carried out in which contributing factors are measured and controlled. The authors believe that this is feasible under laboratory conditions chosen for the CCRL program of characterizing pollutants according to their flame properties.

ACKNOWLEDGMENTS

The work described is part of the Mines Branch Environmental Improvement Research Program, and thanks are due to Dr. John Convey for permission to publish this paper. Thanks are also due to Mr. K. M. Brown for reviewing the manuscript.

Independent Variables	Intermediate Variables to be Measured	Dependent Variables to be Measured
To remain fixed	In breeching	In breeching and at points in furnace
Fuel type: No. 2 oil Fuel temp: ambient Type of atomizing: mechanical Furnace geometry Furnace wall temp. Furnace wall emissivity Burner configuration	Flue gas temp. O_2 CO_2	CO SO_2 SO_3 NO_2 NO_x Particulates Unburned hydrocarbons
To be varied	At points in furnace	
Nozzle design Nozzle spray angle Nozzle pressure Fuel quantity Excess air quantity Air temp. Air velocity Swirl Forced recirculated flue gas <ul style="list-style-type: none"> — composition — volume — temperature 	Natural recirculated flue gas <ul style="list-style-type: none"> — composition — volume — temp. — flow pattern Flue gas temp. O_2 CO_2 Flame radiation Gas flow pattern	

Figure 13. Proposed variables to be controlled and measured in research on NO formation.

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