CANADA

DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA

CONTROL OF POLLUTANT EMISSION AND SULPHURIC ACID CORROSION FROM COMBUSTION OF RESIDUAL FUEL OIL

PART I: LOW-PRESSURE HEATING BOILERS WITH MECHANICAL ATOMIZING BURNERS

G.K. LEE, F.D. FRIEDRICH AND E.R. MITCHELL

FUELS RESEARCH CENTRE

DECEMBER 1968

Research Report R 195

Price $1.00

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Queen's Printer and Controller of Stationery
Ottawa, Canada
1969

FOREWORD

The role of the Mines Branch is to look forward and attempt to anticipate the problems of the Canadian mineral industry, and to conduct scientific investigations to help to create new industries, as well as to stimulate traditional activities in the mineral area.

A problem of widening scope - not only in the mineral industry but in the urban areas - is that of pollution. The Mines Branch recognizes the importance of combustion processes in producing atmospheric pollution, and has conducted research on the suppression of the emission of pollutants in the atmosphere from this source. Also, the corrosion effects of combustion products, and the estimation of the quantities of toxic substances produced as a function of the variables controlling combustion, have been studied.

In the analytical work, the Canadian Combustion Research Laboratory was aided by the intramural services of the Fuels Research Centre, as well as by the laboratories of the Occupational Health Division of the Department of National Health and Welfare. Their co-operation is hereby gratefully acknowledged, and we look forward to its continuation to alleviate this important problem, which affects the well-being of many Canadians.

John Convey,
Director,
Mines Branch.

Ottawa, September 1968

AVANT-PROPOS

Le rôle de la Direction des mines est de prévoir et d'essayer d'anticiper les problèmes de l'industrie minérale canadienne, d'entreprendre des recherches scientifiques pour aider à créer de nouvelles industries, et aussi de stimuler les activités traditionnelles dans le domaine minéral.

Un problème d'envergure grandissante, non seulement dans l'industrie minérale mais aussi dans les régions urbaines, est celui de la pollution. La Direction des mines reconnaît l'importance des procédés de combustion dans la création de pollution atmosphérique, et elle a fait des recherches sur la suppression d'émission d'agents de pollution dans l'atmosphère à partir de cette source. En outre, on a étudié les effets de corrosion des produits de combustion, ainsi que l'estimation des quantités de substances toxiques produites en fonction des variables contrôlant la combustion.

Pour les analyses, le Laboratoire canadien de recherche sur la combustion a été aidé par nos services du Centre de recherches sur les combustibles, et aussi par les laboratoires de la Division de santé professionnelle, au Ministère de la santé et du bien-être. Leur collaboration est ici appréciée avec reconnaissance, et nous comptons qu'elle continuera afin de soulager cet important problème, qui affecte le bien-être de nombreux Canadiens.

John Convey,
Directeur,
Direction des mines.

Decembre, 1968

Mines Branch Research Report R 195

CONTROL OF POLLUTANT EMISSION AND SULPHURIC ACID CORROSION FROM COMBUSTION OF RESIDUAL FUEL OIL

Part I: Low-Pressure Heating Boilers with Mechanical Atomizing Burners

by

G. K. Lee[*], F. D. Friedrich[**] and E. R. Mitchell[***]

ABSTRACT

The paper, first of a series, deals with the burning of residual fuel oil containing 2.5 per cent sulphur under conditions prevalent in heating boilers, to assess the effects of (a) boiler load, (b) excess combustion air, (c) mean residence time, and (d) a magnesia-alumina fuel oil additive, on the formation of noxious and corrosive products of combustion. Results show that the additive can be used as an effective substitute for low excess combustion air in reducing the emission of NO_x and SO_3. Furthermore, the additive neutralizes condensed H_2SO_4 and improves the electrical resistivity of soot particles to the point where electrostatic precipitation of soot is technically feasible. Detailed analyses of particulate matter samples taken from flames with untreated oil and oil treated with three different amounts of additive are described to elucidate the mechanism of acid soot neutralization and to obtain data on soot constituents that may contribute to atmospheric pollution. It is shown that the standard methods for measuring SO_3 concentrations in flue gas can give misleading results when soot or particulate matter is present.

Subsequent papers of the series will describe experiments of a broad research programme carried out in the same pilot-scale research boiler that provides control of boiler metal temperature (operating steam pressure) both below and above sulphuric acid dewpoint and provides flexibility in the selection of burner systems.

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Rapport de recherche de la Direction des mines R 195

CONTRÔLE D'ÉMISSION D'AGENTS DE POLLUTION ET DE CORROSION PAR L'ACIDE SULFURIQUE PROVENANT DE LA COMBUSTION DE MAZOUT RÉSIDUEL

Première partie: Chaudières à basse pression avec brûleurs à atomisation mécanique.

par

G. K. Lee*, F. D. Friedrich** et E. R. Mitchell***

RÉSUMÉ

Ce mémoire, le premier d'une série, traite de la combustion de mazout résiduel, contenant 2.5 pour cent de soufre, dans les conditions habituelles des chaudières de chauffage, afin d'évaluer les effets de (a) la charge de la chaudière, (b) l'excès d'air de combustion, (c) la durée moyenne de résidence, et (d) un additif pour le mazout constitué de magnésie-alumine.

Les résultats obtenus montrent que l'additif peut être utilisé comme substitut efficace pour un faible excès d'air de combustion dans la réduction d'émission de NO_x et SO_3. De plus, l'additif neutralise le H_2SO_4 condensé et améliore la résistivité électrique des particules de suie au point que la précipitation électrostatique de la suie est techniquement possible. Des analyses détaillées d'échantillons de particules pris dans les flammes d'huile non traitée et d'huile traitée avec trois quantités différentes d'additif sont décrites pour élucider le mécanisme de neutralisation des suies acides et obtenir des renseignements sur les constituants de la suie pouvant contribuer à la pollution atmosphérique. On montre que les méthodes classiques de mesure des concentrations en SO_3 dans les gaz de carneau peuvent induire en erreur lorsqu'il y a de la suie ou des particules.

Les rapports suivants de cette série décriront les expériences d'un large programme de recherche effectué avec la même chaudière de recherche à l'échelle pilote, fournissant le contrôle de la température du metal de la chaudière (à la pression de vapeur de fonctionnement) au dessous et au dessus du point de rosée de l'acide sulfurique, avec quelque flexibilité dans le choix des systèmes de brûleur.

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CONTENTS

FIGURES

FIGURES (Cont'd)

TABLES

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1. INTRODUCTION

The Canadian commercial and industrial heating industry, including as it does large numbers of small heating boilers burning high-sulphur residual oil, has become a major contributor to air pollution through the emission of acid soot. A parallel problem, widespread and expensive to fuel users, is the corrosion of boiler surfaces by sulphuric acid. This may occur in any steam generator where metal temperatures at the cold end fall below the typical acid dewpoint range of 250 to 290°F, but it is most serious in low-pressure heating boilers where temperature conditions frequently permit acid condensation in a furnace, within sight of the flame.

To overcome both the pollution and corrosion problems, a comprehensive research programme was undertaken at the Canadian Combustion Research Laboratory (CCRL) of the Mines Branch in Ottawa, the first part of which deals with operating conditions typical of low-pressure heating boilers, and is described in this paper. Two approaches were taken. The first was to control combustion conditions particularly by using low excess combustion air despite known limitations in boilers operating under cycling loads. The second was to neutralize chemically SO_3 and sulphuric acid by means of a fuel additive. The additive developed for this purpose by the CCRL is a magnesia-alumina formulation, described previously (1), and has advantages that are explained in this report.

Several hundred experiments, representing months of intensive research on a pilot-scale boiler burning untreated and additive-treated residual fuel oil, have (a) demonstrated that an inexpensive dosage of the aforementioned additive can have markedly beneficial results, and (b) indicated a mechanism of low-temperature corrosion somewhat different than that generally accepted to date. It was convenient to describe the test results under two main headings, Gas Phase Test Results and Particulate Matter Test Results, but in view of their strong interdependence each section must be considered in relation to the other.

2. RESEARCH OBJECTIVES

The aims of the research programme were:

1. To show how and to what extent oil combustion pollutants may be reduced at the source.
2. To chemically neutralize adsorbed SO_3 and sulphuric acid in soot so that it will be inert for safe emission to atmosphere.
3. To improve the electrical resistivity of soot, thereby increasing the efficiency of electrostatic precipitation.
4. To study mechanisms related to low-temperature corrosion in boilers.
5. To chemically neutralize condensed sulphuric acid, whether on furnace tubes or cold end surfaces, to protect boilers from acid corrosion.

An important part of the pollution study was an examination of the role of soot in removing SO_3 in gas phase, as well as an assessment of levels of nitrogen oxides, gas phase hydrocarbons, aldehydes, oily matter, carcinogens and vanadium emitted to the atmosphere.

In fulfilling these research aims, considerable emphasis was placed on a) the development and improvement of techniques for analyzing sulphuric acid in particulate matter, b) atomic absorption analyses for vanadium, magnesium, aluminum and iron in soot samples (2). The sampling procedures for SO_2 and SO_3 determinations have been modified to eliminate interferences that are not normally taken into consideration.

3. DESCRIPTION AND OPERATION OF RESEARCH BOILER

The research boiler is shown schematically in Figure 1, which also shows the location of the measuring stations used throughout the tests. Table 1 shows the calculated cumulative residence times in the boiler under

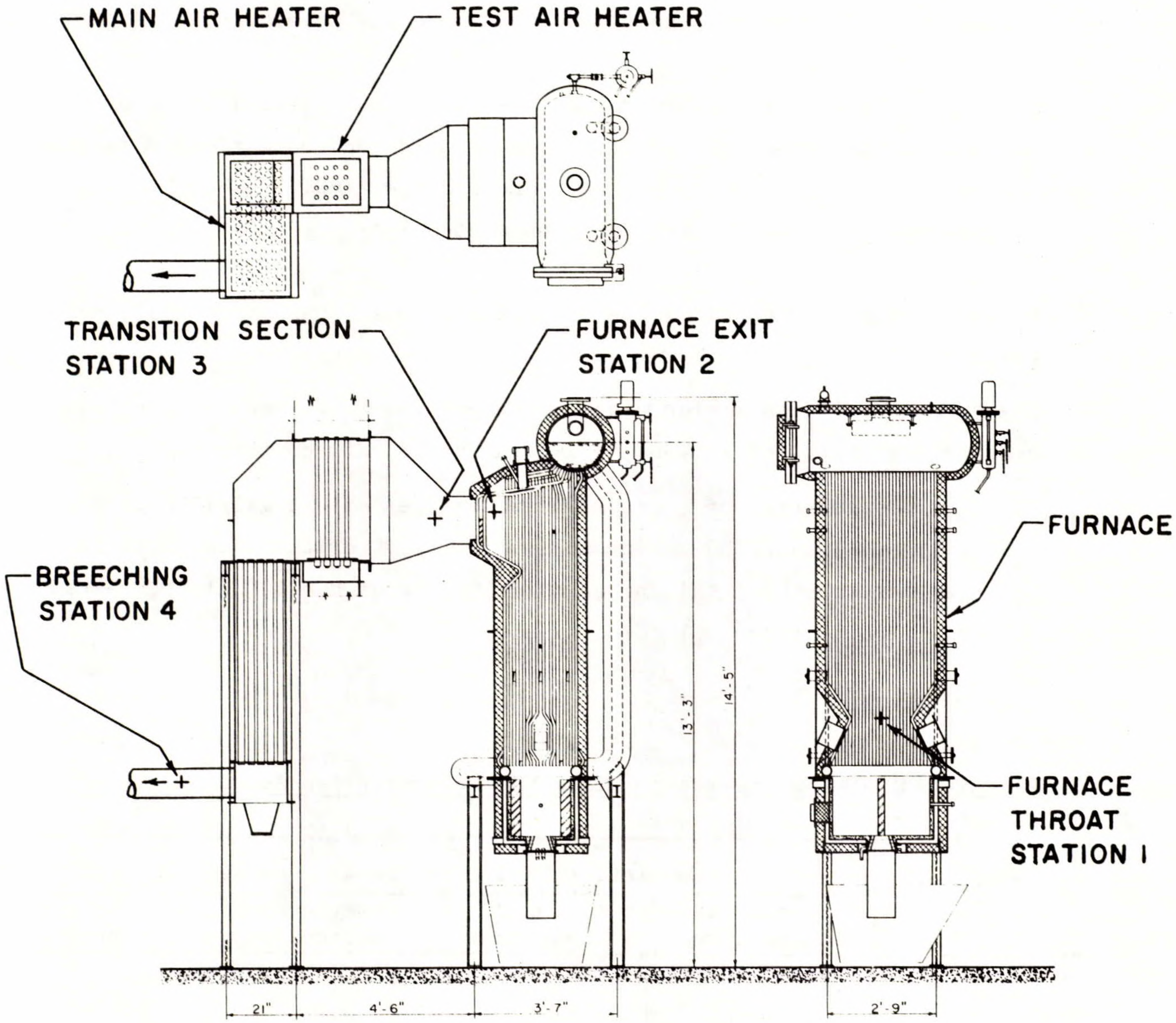


Fig. 1. Schematic view of combustion research boiler, showing location of sampling stations.

typical firing conditions. Since the boiler has been described elsewhere (3, 4), it need only be reiterated that for the present series of tests the steam pressure was nominally 15 psig, so that the furnace wall temperatures were below the acid dewpoint except at low excess air levels.

In Part I of the programme, both the No. 6 residual fuel oil and the magnesia-alumina fuel oil additive were considered to be fixed parameters having the properties given in Tables 2 and 3 respectively. The three variable parameters investigated are tabulated below:

1. O_2 in flue gas, which was varied stepwise from 1.0 per cent to 5.5 per cent.
2. Low, normal and high firing rates corresponding to furnace volumetric heat release rates of 27,600, 49,700 and 66,250 Btu/cu ft/hr.
3. Additive dosage rates of 1 gal/1000 gal of fuel oil, 1 gal/1500 gal of fuel oil, and 1 gal/2000 gal of fuel oil. For brevity, these will be referred to throughout this paper as 1/1000 treated oil, 1/1500 treated oil and 1/2000 treated oil respectively.

TABLE 1

Calculated Flue Gas Residence Times in the Combustion Research Boiler

Firing Rate	O_2, %	Cumulative Residence Times, seconds			
		Station 1 Furnace Throat	Station 2 Furnace Exit	Station 3 Transition Section	Station 4 Breeching
Low	1	0	2.38	3.06	10.54
	3	0	2.09	2.66	8.90
	5	0	1.87	2.35	7.69
Normal	1	0	1.25	1.55	4.75
	3	0	1.10	1.36	4.09
	5	0	0.98	1.20	3.59
High	1	0	0.90	1.10	3.26
	3	0	0.80	0.98	2.82
	5	0	0.72	0.88	2.51

TABLE 2

Analyses of No. 6 Residual Fuel Oil

Test	Range	Mean
Specific Gravity, 60/60°F	0.973 - 0.987	0.981
Kinematic Viscosity at 122°F, cS	458 - 473	468
Carbon, % wt	86.1 - 86.3	86.2
Hydrogen, % wt	11.2 - 11.3	11.3
Gross Calorific Value, Btu/lb	18,338 - 18,603	18,424
Sulphur, % wt	2.00 - 2.69	2.45
Vanadium, ppm wt	216 - 239	224
Sodium, ppm wt	15 - 22	18

TABLE 3

Fuel Oil Additive Properties

Property	Composition or Value
Chemical Composition*	MgO + Al_2O_3
Solids Content, %	55
Light Oil Carrier, %	45
Magnesium-Aluminum Ratio	9:1
Particle Size Range, µ	1-7
Specific Gravity, 70°F	1.45
Pour Point, °F	-10
Fire Point (COC), °F	220
Flash Point (PM), °F	162
Apparent Viscosity**, SSF at 80°F	20

*"Magnesia" and "alumina" in this report refer to partially dehydrated hydroxides of magnesium and aluminum.

**Thixotropic suspension.

4. ANALYTICAL PROCEDURES AND MEASUREMENTS

The following techniques were used to measure and evaluate the products of combustion during the experiments with both untreated and additive-treated oil:

1. CO_2, O_2 and CO in flue gas by Orsat at 15-min intervals; CO_2 and CO continuously by non-dispersive infrared analyzer, and O_2 continuously by both paramagnetic and combustion principle analyzers. Station 3.

2. Acid dewpoint and rates of acid buildup (RBU) measured in micro amperes/min (μA/min) by BCURA dewpoint meter, one traverse per run. Station 4.

3. SO_3 in flue gas by the Shell-Thornton hot water condensation method, one sample every 25 min. Stations 1 and 4, 2 and 4, 3 and 4.

4. SO_2 in flue gas by API Method 774-54 for total sulphur oxides. This apparatus was connected in series with the SO_3 condenser. Stations 1 and 4, 2 and 4, 3 and 4.

5. Gas-phase hydrocarbons in flue gas, measured continuously by flame ionization detector. Stations 3 and 4.

6. Total nitrogen oxides (NO_x) by ASTM Method D1608, one sample per run. Stations 3 and 4.

7. NO_2 by USBM Method RI 6790, one sample per run. Stations 3 and 4.

8. Aldehydes by USBM Method RI 4531, one sample per run. Stations 3 and 4.

9. Particulate matter in flue gas by means of a cyclone separator incorporating a filter arrangement that provides 100 per cent collection efficiency. One sample per run, extracted over a 60-90 min period. Stations 3 and 4.

10. Vanadium, magnesium, iron and aluminum in soot by atomic absorption technique (2).

11. Reacted SO_4 and free SO_4 in soot, by wet chemistry (2).

12. Total sulphur in soot, by ASTM Method D271.

13. Oily matter in soot, by benzene extraction.

14. Polycyclic aromatic hydrocarbons in soot, by cyclohexane extraction and UV spectrophotometry.

15. Electrical resistivity of soot, by a conductivity apparatus developed for this purpose as described in Appendix I.

16. Smoke in flue gas, measured continuously by a self-standardizing meter, of the photoelectric-cell type, mounted in the stack.

5. GAS PHASE TEST RESULTS

5.1 SO_3 Measurements with the Two-Burner System

In these tests, SO_3 measurements were made at stations 2 and 4, i.e. the furnace exit and the breeching. The normal firing rate (volumetric heat release rate = 49,700 Btu/cu ft/hr) was maintained in all tests, and three different fuels were used: untreated oil, 1/1500 treated oil, and 1/1000 treated oil. The results obtained with each fuel are shown respectively in Figures 2, 3 and 4. In these figures each measurement is represented by a horizontal line instead of a point, with the length of the line showing the variation in O_2 content of the flue gas during the sampling period.

In order to deal with the scatter of the results, the data were averaged using the method of least squares, assuming a straight line relationship. This reveals that untreated oil yields a higher level of SO_3 at the

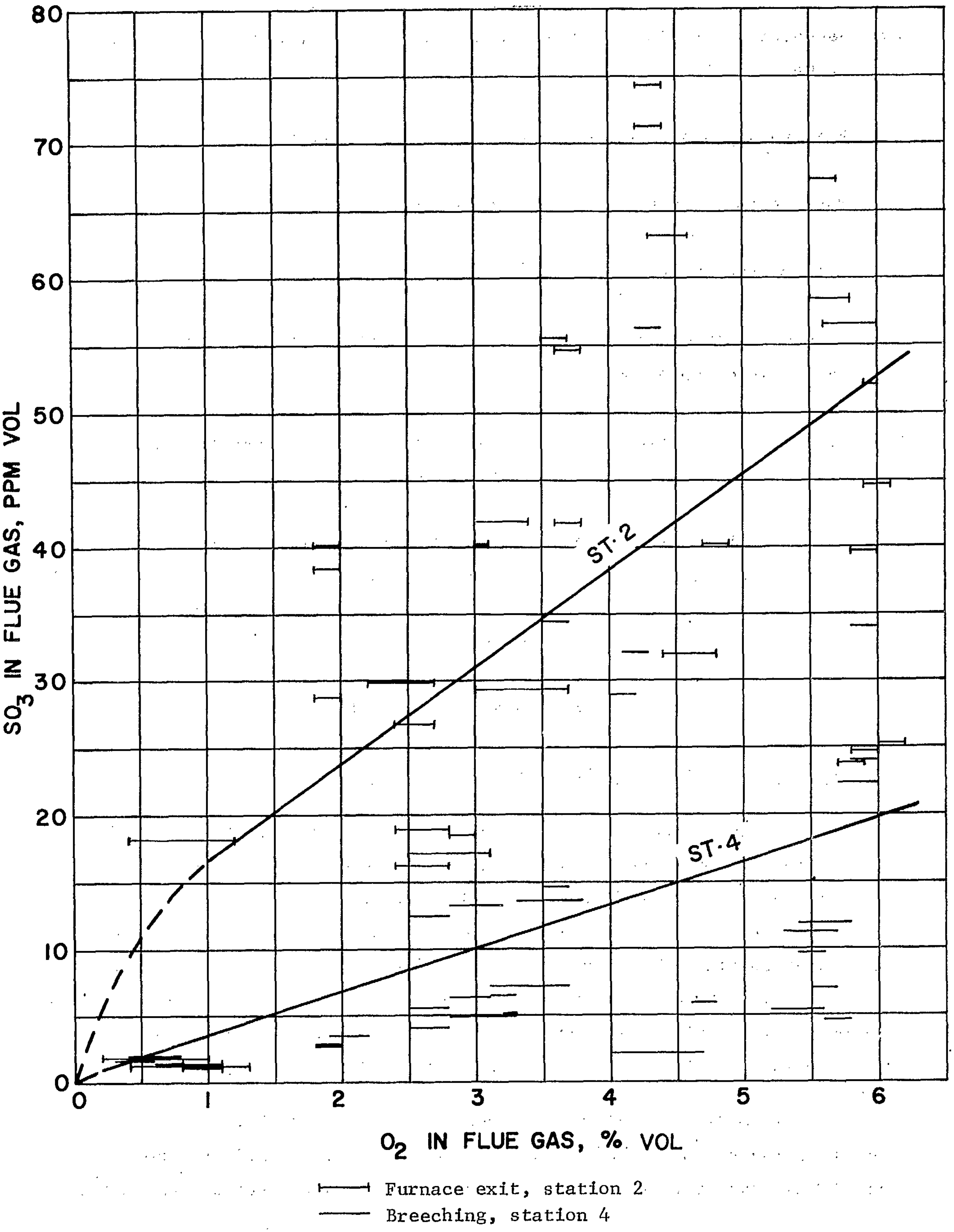


Fig. 2. SO_3 vs O_2 for untreated oil, two-burner system, normal firing rate.

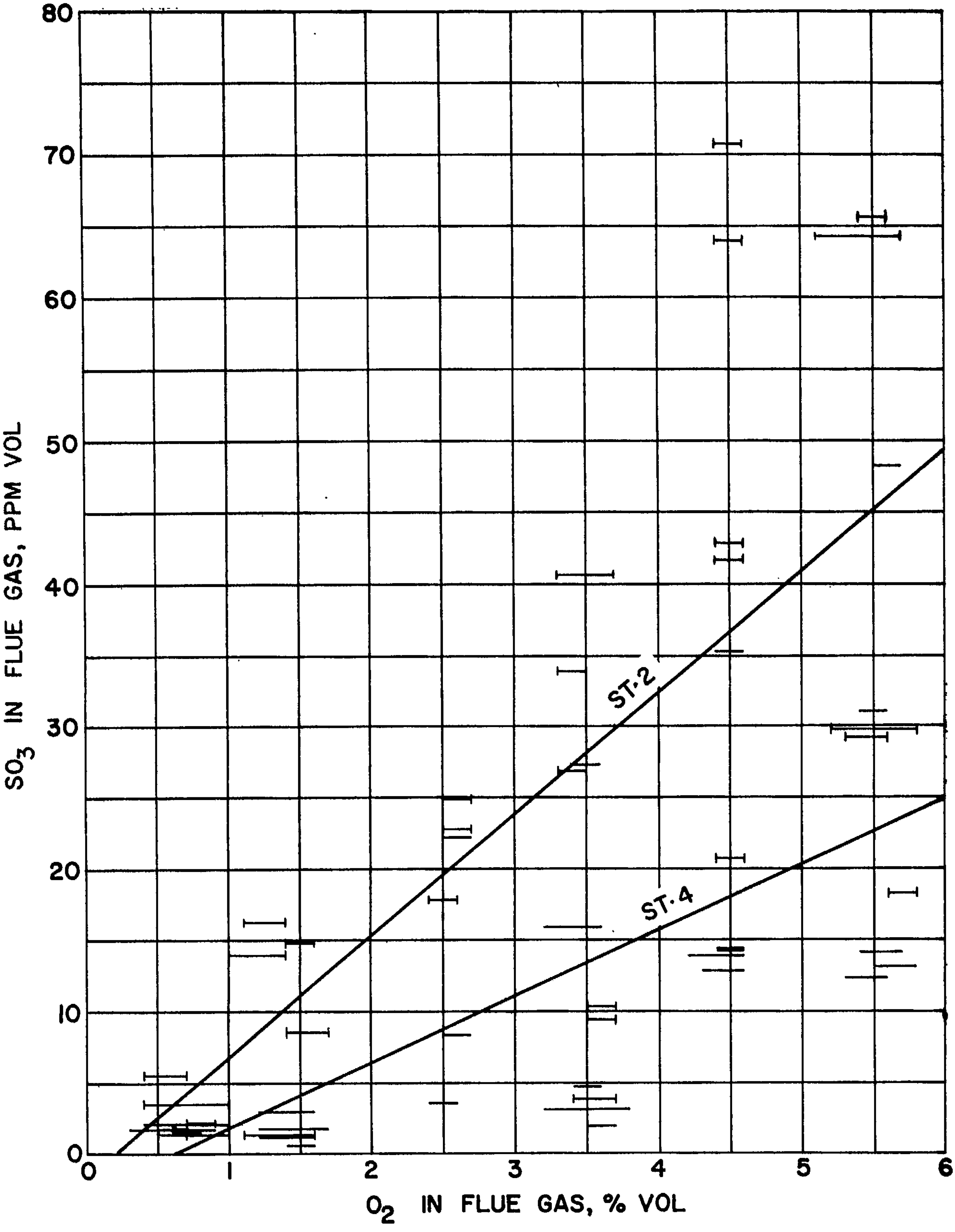
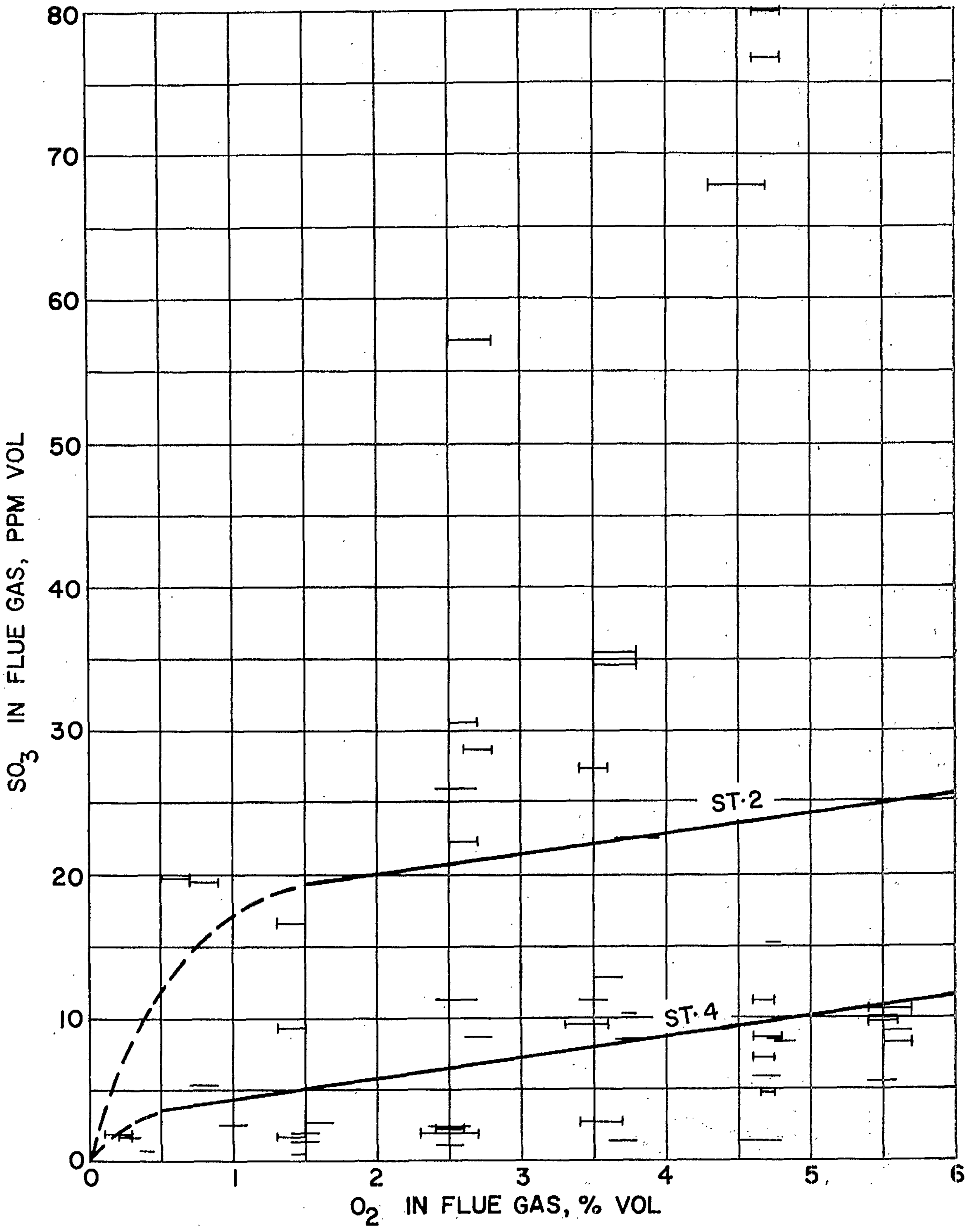


Fig. 3. SO_3 vs O_2 for 1/1500 treated oil, two-burner system, normal firing rate.



⊢—⊣ Furnace exit, station 2
—— Breeching, station 4

Fig. 4. SO_3 vs O_2 for 1/1000 treated oil, two-burner system, normal firing rate.

furnace exit than additive-treated oil, although untreated oil and 1/1500 treated oil give much the same SO_3 readings at the breeching. Figure 4 shows that 1/1000 treated oil has much lower average SO_3 levels, both at the breeching and at the furnace exit, than the other oils, although there were some high readings (80 ppm at the furnace exit).

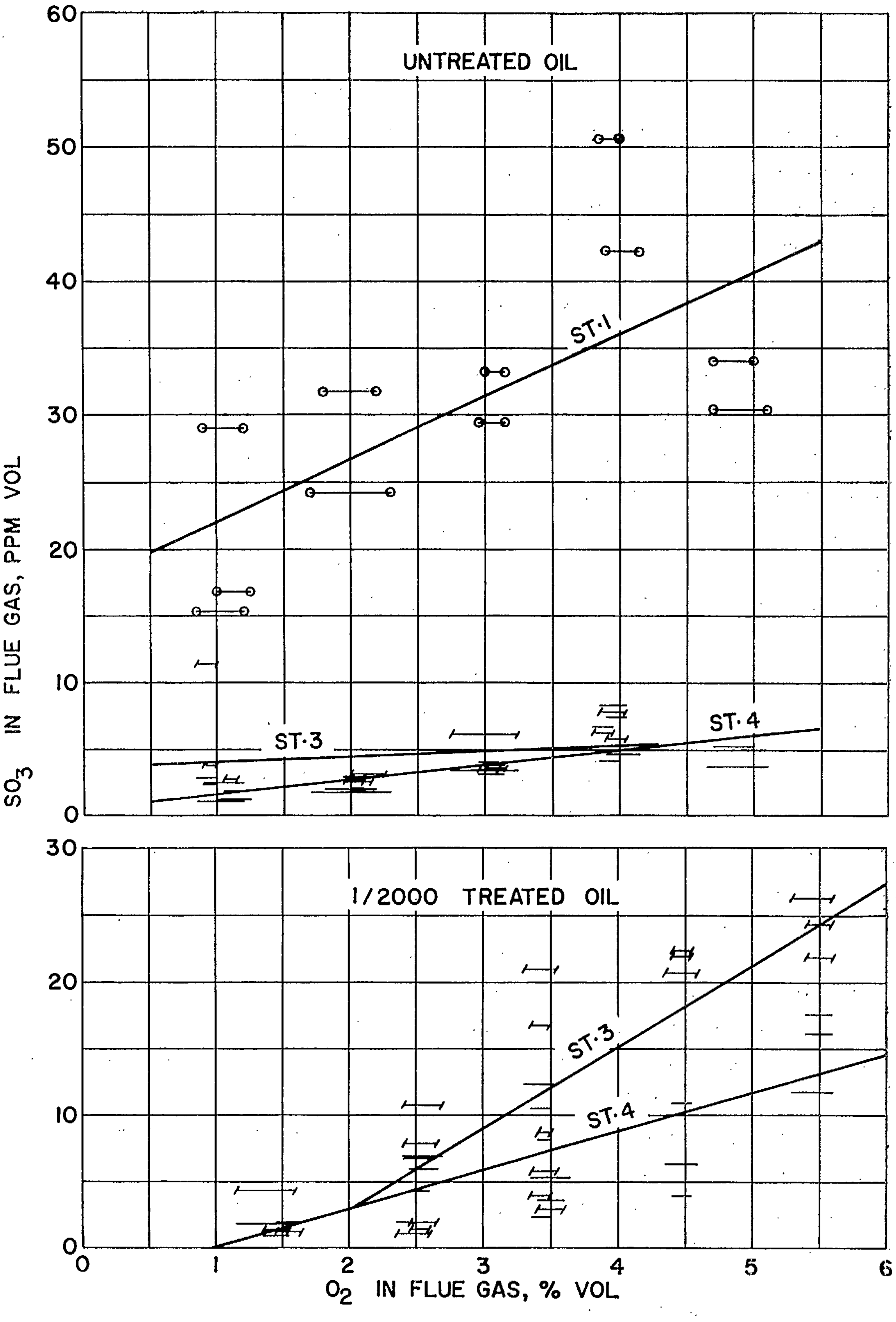
The scatter in the results is due in part to imbalance in the burner settings; that is to say, while the average O_2 in the flue gas was carefully controlled at 1 per cent, there was no way to establish whether both burners were getting equal amounts of the combustion air. Hence, reducing or oxidizing conditions may have existed locally, causing unrepresentative levels of SO_3 to be formed. For this reason the majority of the tests were carried out using a single burner, which provided more positive control of excess air, although flames were longer and more smoky due to decreased turbulence and more impingement on the cold walls of the furnace at high firing rates.

5.2 SO_3 Measurements with the Single-Burner System

Three different input variables were dealt with in these tests; firstly, fuel oil untreated and treated with additive at three dosage rates; secondly, firing rate, low, normal, and high; and thirdly, O_2 in the flue gas, which was varied from about 1 per cent to about 6 per cent.

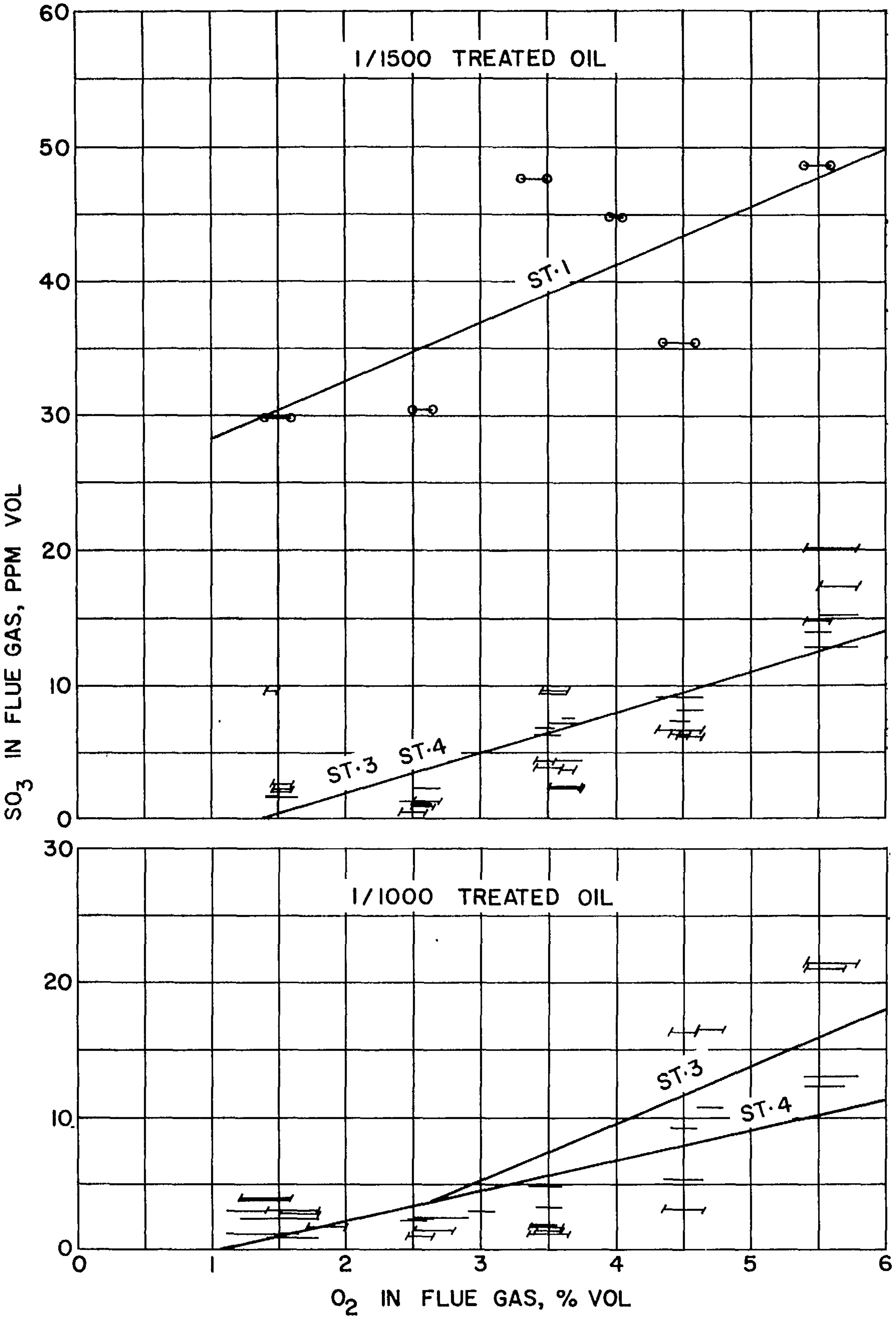
The results cannot be compared directly in all cases because sampling was carried out at different points. The asymmetrical path of the single flame, compared with two opposed flames, raised the possibility of stratification at the furnace exit; therefore, samples were taken a few feet further downstream in the transition section (Station 3). However, it was found that, except at high loads, SO_3 levels in the transition section were often close to those in the breeching (Station 4). Thus, sampling was carried out at the furnace throat (Station 1), rather than at the transition section, for subsequent tests.

Figures 5 and 6 show SO_3 vs O_2 at the normal firing rate for untreated oil and oil treated with additive at three dosage rates. Again, straight line average curves have been drawn, using the method of least squares. These curves show higher SO_3 levels in the furnace throat when



o——o	Furnace throat, station 1
⊢——⊣	Transition section, station 3
——	Breeching, station 4

Fig. 5. SO_3 vs O_2 for untreated oil and 1/2000 treated oil, single-burner system, normal firing rate.



o—o Furnace throat, station 1
⊢—⊣ Transition section, station 3
—— Breeching, station 4

Fig. 6. SO_3 vs O_2 for 1/1500 treated oil and 1/1000 treated oil, single-burner system, normal firing rate.

burning 1/1500 treated oil than when burning untreated oil. At the breeching, all treated oils show higher average SO_3 levels than untreated oil. The highest SO_3 level occurs with 1/2000 treated oil and there is a progressive decrease for 1/1500 and 1/1000 treated oil. Results from the transition section show a slightly different pattern: the treated oils again yield more SO_3 than untreated oil, and the 1/2000 treated oil yields the highest SO_3 levels, but the additive dosage of 1/1500 yields lower SO_3 levels than a dosage of 1/1000. This anomaly cannot be considered very significant in view of the scatter of the results. When burning 1/1500 treated oil there is no significant difference between SO_3 levels in the transition section and in the breeching, and both are much lower than the SO_3 levels in the furnace throat. There are three possible phenomena explaining the drastic reduction in SO_3 concentration beyond the furnace: (a) SO_3 may be condensing on the furnace walls which were below acid dewpoint except at low O_2 levels; (b) SO_3 may be adsorbed by the particulate matter in the flue gases as they pass through the air heater system together, and hence the SO_3 is filtered out before it reaches the condenser coil of the sampling system; and (c) decomposition of SO_3 to SO_2 may be occurring, because SO_3 levels in the furnace are generally on the high side of the SO_3/SO_2 equilibrium curve. At a temperature of about 1800°F, which would be encountered near the furnace exit, the existing SO_3/SO_2 ratio crosses the equilibrium curve and SO_3 should tend to increase, but this is a relatively slow reaction and it is unlikely that there is sufficient residence time in the air heaters for an increase to be noticeable. The results of tests on particulate matter samples, described in a later section, indicate that the second phenomenon has the greater influence.

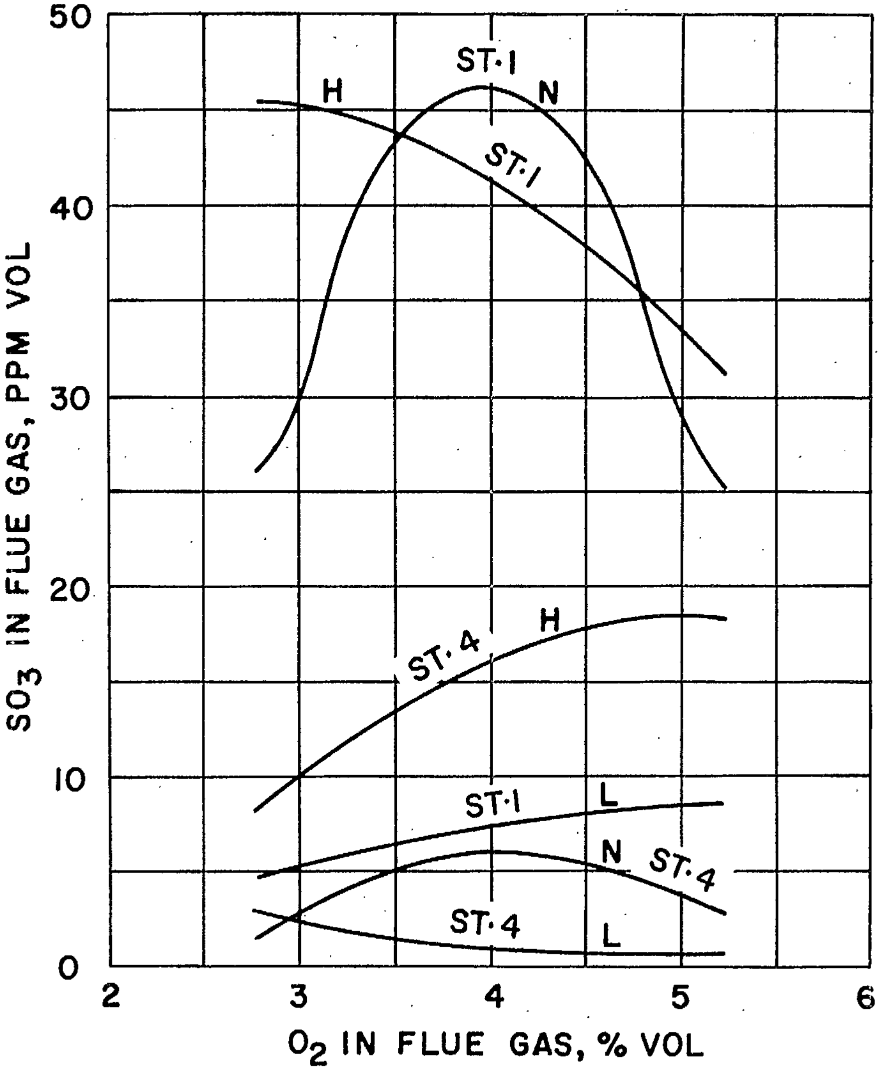
It will be noted that the results of the single-burner tests still demonstrate considerable scatter. The greatest single cause for this appears to be atomization; for example, it was observed that when the flame pattern began to deteriorate there was a slight buildup of coke on the nozzle. This resulted in slightly increased soot formation, and although there was virtually no measurable increase in smoke emission, the SO_3 concentrations dropped sharply. It was observed that the highest SO_3 levels occurred with the cleanest flames. A comparison of the single-burner system with the two-burner system shows that at the breeching the latter yields higher SO_3 levels when burning untreated oil and 1/1500 treated oil. When burning 1/1000 treated oil, SO_3 levels are comparable for both burner systems. The lower SO_3 levels with the single-burner system may be the result of condensation on the furnace walls brought about by the increased impingement of the asymmetrical flame. However, they are more likely the result of greater adsorption by particulate matter in the single-burner flame, which was found to have three to five times the particulate matter emission of the two-burner flame, as described in a later section.

Figures 7 and 8 demonstrate the very strong influence of heat release rate on SO_3 formation, and confirm the conclusions of Black et al. (5). Presumably the increase in SO_3 level with heat release rate is due to the increased temperature gradient at the edge of the flame envelope; that is to say, at high firing rates the flame is very near to, or impinges upon, the furnace walls, and the high SO_3 levels normally encountered in the flame envelope are fixed by chilling before they have opportunity to decay to SO_2. This phenomenon is described by Hedley (6). In these tests, SO_3 was measured in the furnace throat when burning untreated oil and in the transition section when burning 1/1500 treated oil; hence the results cannot be compared directly. However, it will be noted that at the high firing rate, when burning 1/1500 treated oil, the data show higher SO_3 levels in the transition section than in the furnace throat when burning untreated oil.

Generally, the results of the single-burner tests show higher SO_3 levels with additive-treated oil than with untreated oil, which is a desirable trend for control of pollution emission, as shown later in the context of the results on the particulate matter tests.

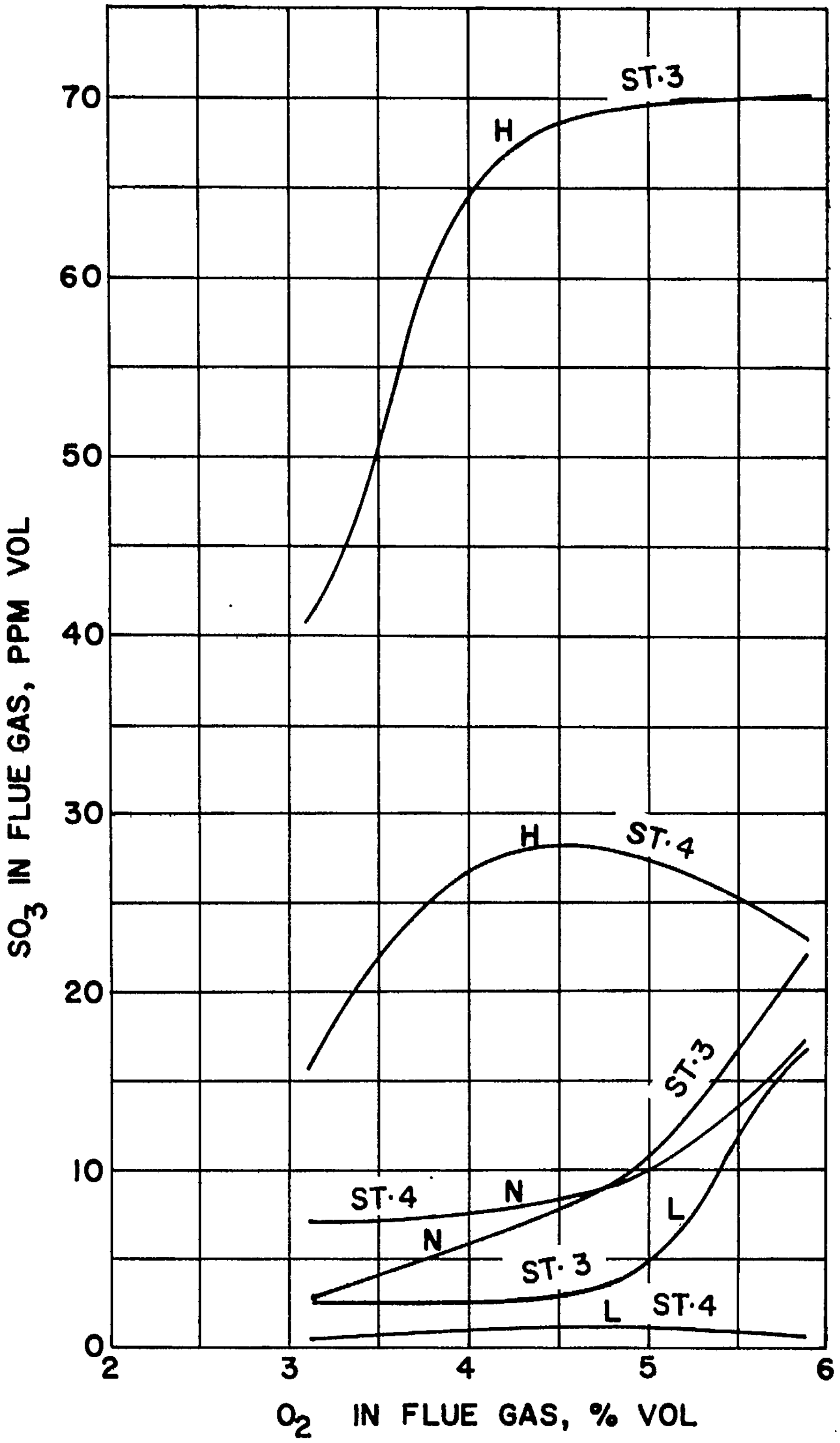
5.3 Acid Dewpoint and RBU Measurements

Figure 9 shows acid dewpoint and maximum RBU vs O_2 in the flue gas for untreated oil and 1/1500 treated oil when operating with two burners at normal load. It will be noted that the untreated oil yields a higher maximum RBU over the entire measured range of O_2. The untreated oil also has a higher acid dewpoint, except above 5 per cent O_2 where the acid dewpoint with both fuels is essentially the same. It will also be observed that for the untreated oil the acid dewpoint curve is essentially flat above 3 per cent O_2, while the maximum RBU curve rises sharply up to 4.5 per cent O_2. This



Station 1 - furnace throat
Station 4 - breeching
L - low firing rate
N - normal firing rate
H - high firing rate

Fig. 7. Effect of firing rate on SO_3 concentration when burning untreated oil, single-burner system.



Station 3 - transition section
Station 4 - breeching
L - low firing rate
N - normal firing rate
H - high firing rate

Fig. 8. Effect of firing rate on SO$_3$ concentration when burning 1/1500 treated oil, single-burner system.

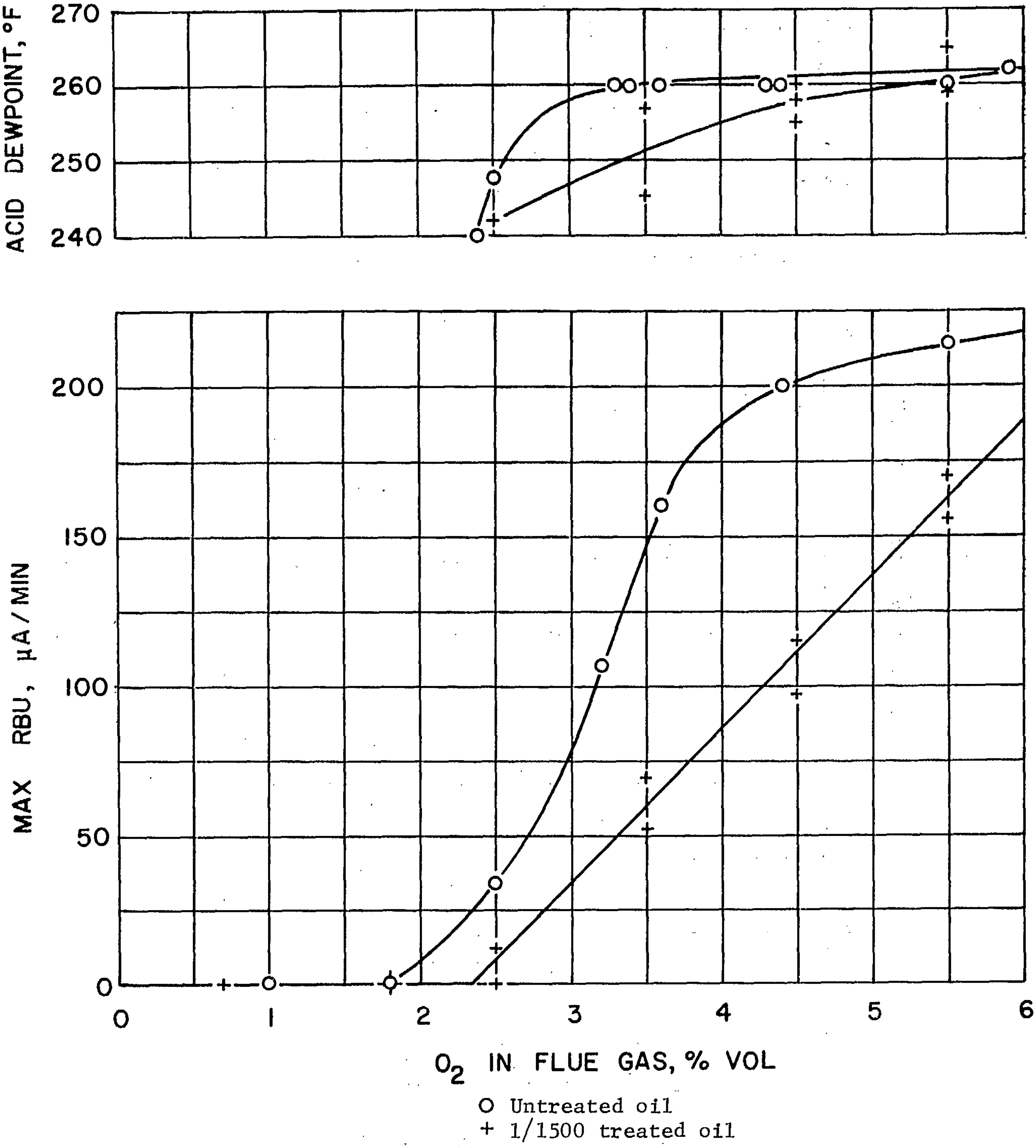


Fig. 9. Acid dewpoint and maximum RBU vs O_2 in the flue gases for untreated oil and 1/1500 treated oil, two-burner system, normal firing rate.

underlines the greater significance of RBU measurements over acid dewpoint measurements in establishing the corrosion potential of flue gas. If a rate of buildup of 100 μA/min is accepted as the beginning of serious corrosion, Figure 9 shows that using additive has the same effect as reducing O_2 from 4.3 per cent to 3.2 per cent. With the two-burner system, SO_3 measurements show the same trend as RBU measurements: both are higher with untreated oil than with additive-treated oil.

Figure 10 shows RBU vs surface temperature for 3 per cent, 4 per cent and 5 per cent O_2 in the flue gas when burning untreated oil at normal load, using the single-burner system. As would be expected, RBU increases sharply with O_2, although the acid dewpoint changes very little. It is an important point that the differential between the temperature at which maximum RBU occurs and the acid dewpoint becomes very small at high O_2 levels. This indicates that equipment having surface temperatures near the acid dewpoint can experience serious corrosion if the surface temperature drops or the acid dewpoint rises by as little as 10°F.

Figure 11 shows maximum RBU vs O_2 for the single-burner system at normal firing rates, burning untreated oil and fuel oil treated with additive at three dosage rates. Here again, the RBU data compare with equivalent SO_3 data, and show higher RBU with treated oil than with untreated oil, reversing the trend established in the tests with the two-burner system. As is the case in the SO_3 measurements, increasing additive dosage reduces RBU, with a dosage rate of 1/1000 giving somewhat similar RBU to untreated oil. A comparison of Figures 9 and 11 shows that, in the single-burner system, the RBU curve for 1/2000 treated oil is similar to the curve for untreated oil in the two-burner system, except that the former is shifted to the right by about 1 per cent O_2. In other words, at the normal firing rate all RBU in the single-burner system are less than the RBU for untreated oil in the two-burner system. It is believed that the possible explanations for the reduced RBU in the single-burner system are the same as those given previously for the reduced SO_3 levels in the single-burner system.

Figure 12 shows maximum RBU vs O_2 for three firing rates, each with untreated oil and 1/1500 treated oil, in the single-burner system. As would be expected from the comparable SO_3 data, there is a clear trend to higher RBU

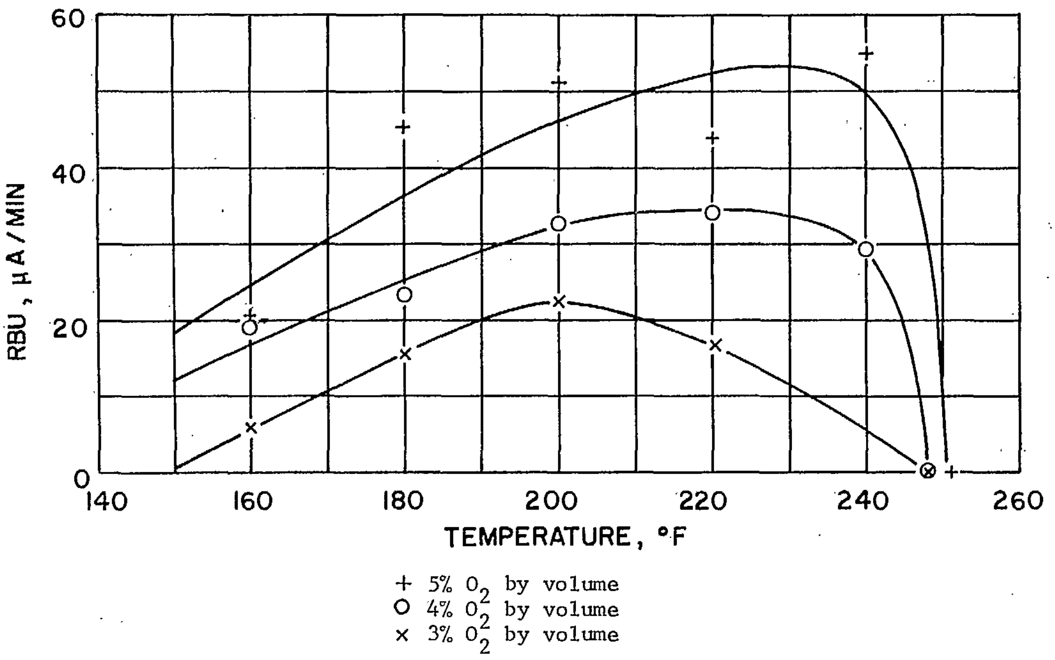


Fig. 10. RBU vs surface temperature for three levels of O_2 in the flue gas when burning untreated oil, single-burner system, normal firing rate.

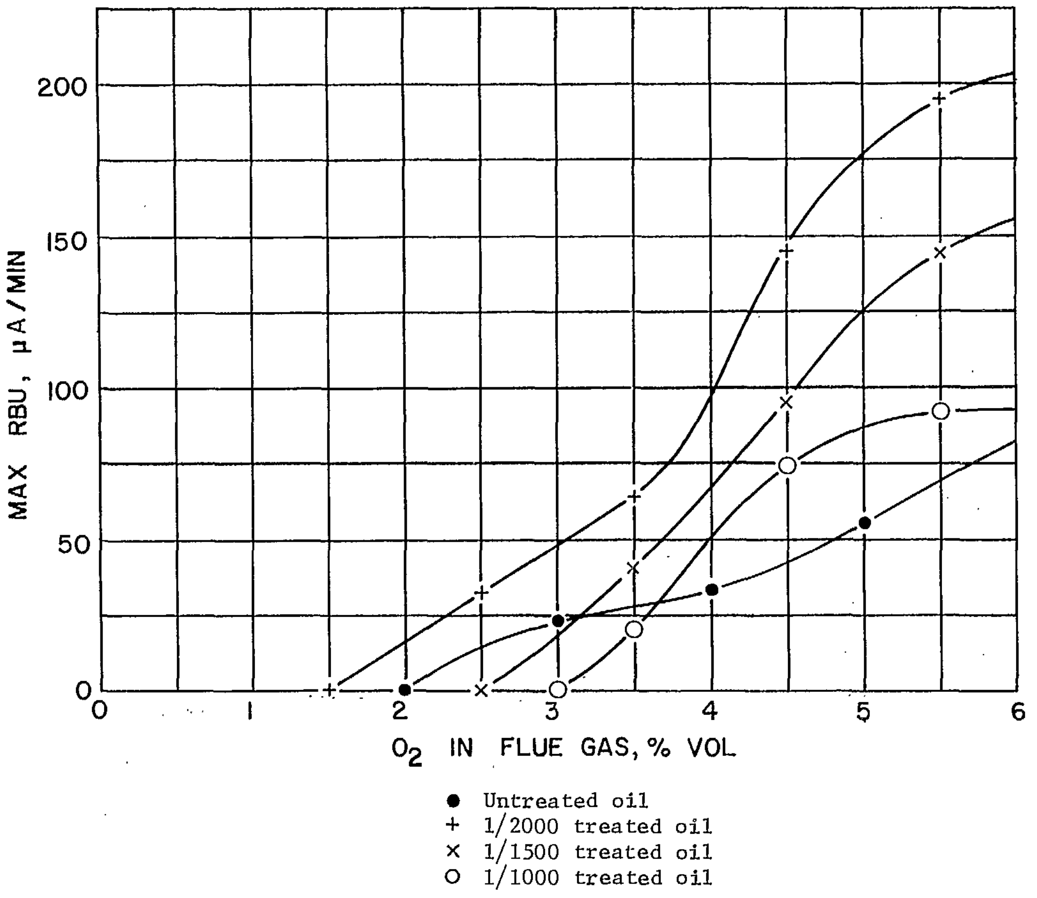


Fig. 11. Maximum RBU vs O_2 in the flue gas for untreated and treated oil, single-burner system, normal firing rate.

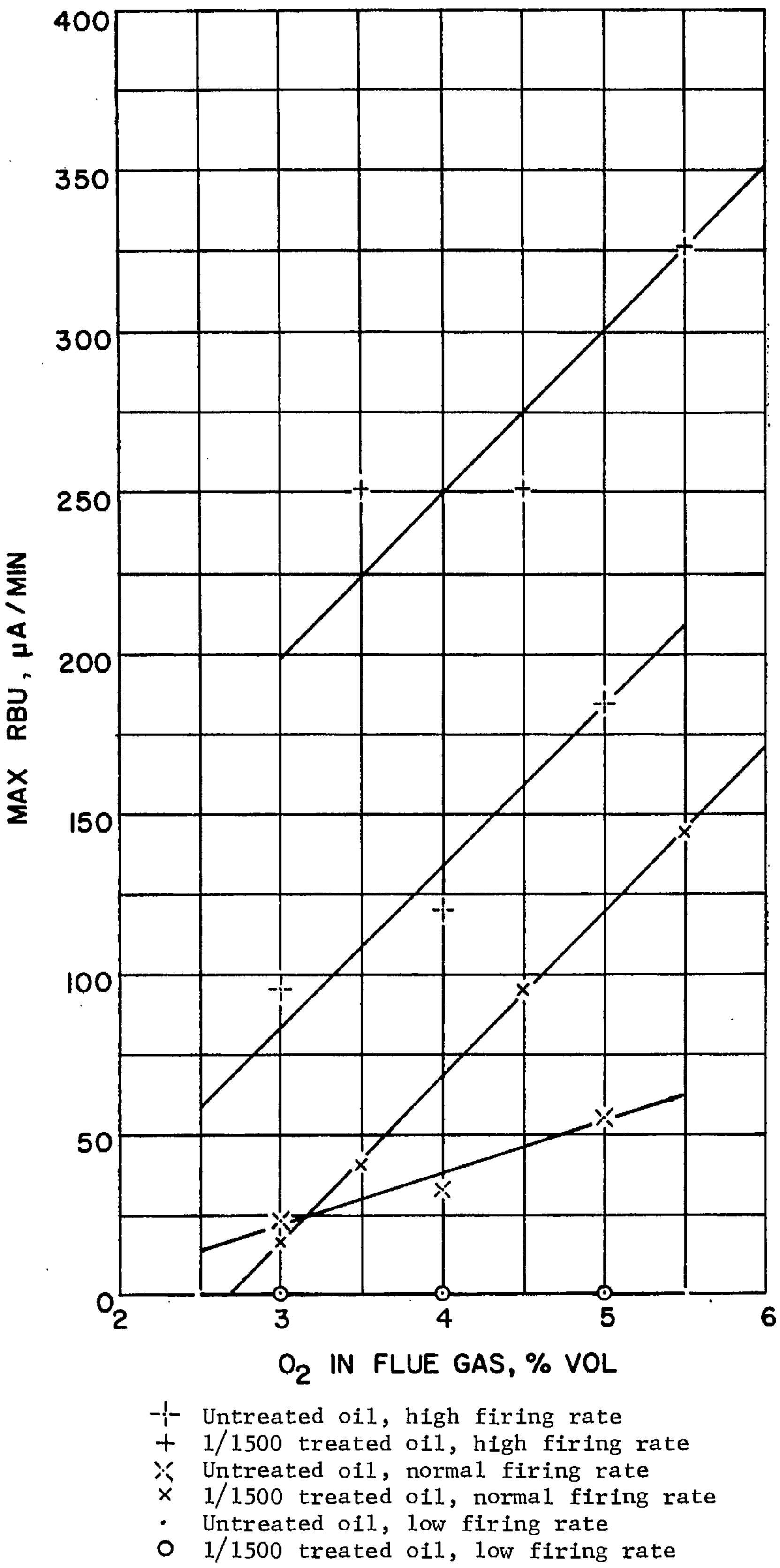


Fig. 12. Effect of firing rate on maximum RBU for untreated oil and 1/1500 treated oil, single-burner system.

with higher firing rates. At the low firing rate there was no RBU with either treated or untreated oil. At normal and high firing rates, measured RBU are higher with additive-treated oil than with untreated oil; which, in the context of particulate matter tests described later, demonstrates the unreliability of RBU measurements under some combustion conditions.

5.4 Nitrogen Oxide Measurements

Measurements of NO_2 and total nitrogen oxides (NO_x) were taken at the transition section and at the breeching, but there was found to be no significant difference due to location; hence, location is not indicated in Figures 13 and 14. Figure 13 shows NO_x and NO_2 concentrations vs O_2 in the flue gas for the two-burner system, burning untreated oil and 1/1500 treated oil. It can be seen that the additive reduces the formation of NO_x by about 50 ppm over the range of O_2 investigated, and reduces NO_2 by a lesser amount, about 25 ppm.

Figure 14 shows NO_2 and NO_x concentrations vs O_2 for the single-burner system using untreated oil and fuel oil treated with additive at three dosage rates. There is a fairly clear-cut reduction in NO_x with increasing additive dosage, but the NO_2 concentration, while decreasing with additive dosage, is at a higher level than with untreated oil until the dosage rate reaches 1/1000. This parallels the trends found in SO_3 and RBU measurements under comparable conditions. It may be noted that with regard to untreated oil, NO_x formation increases more rapidly with O_2 in the two-burner system than in the one-burner system. This may be the result of the higher flame temperatures achieved in the two-burner system, since the formation of NO increases with temperature. Hedley (6) indicates that nitrogen oxides will catalyze reduction or formation of SO_3 towards equilibrium, hence the presence of nitrogen oxides should tend to reduce SO_3 at temperatures above about 1800°F, and tend to increase SO_3 at lower temperatures. However, in the combustion research boiler any tendency to catalyze formation of SO_3 beyond the furnace exit was overridden by decomposition or adsorption processes; SO_3 levels downstream of the furnace exit were always lower than in the furnace. As would be expected, the NO_x and NO_2 curves in Figure 14 tend to converge at higher O_2 levels because the excess oxygen promotes the formation of the higher oxides of nitrogen.

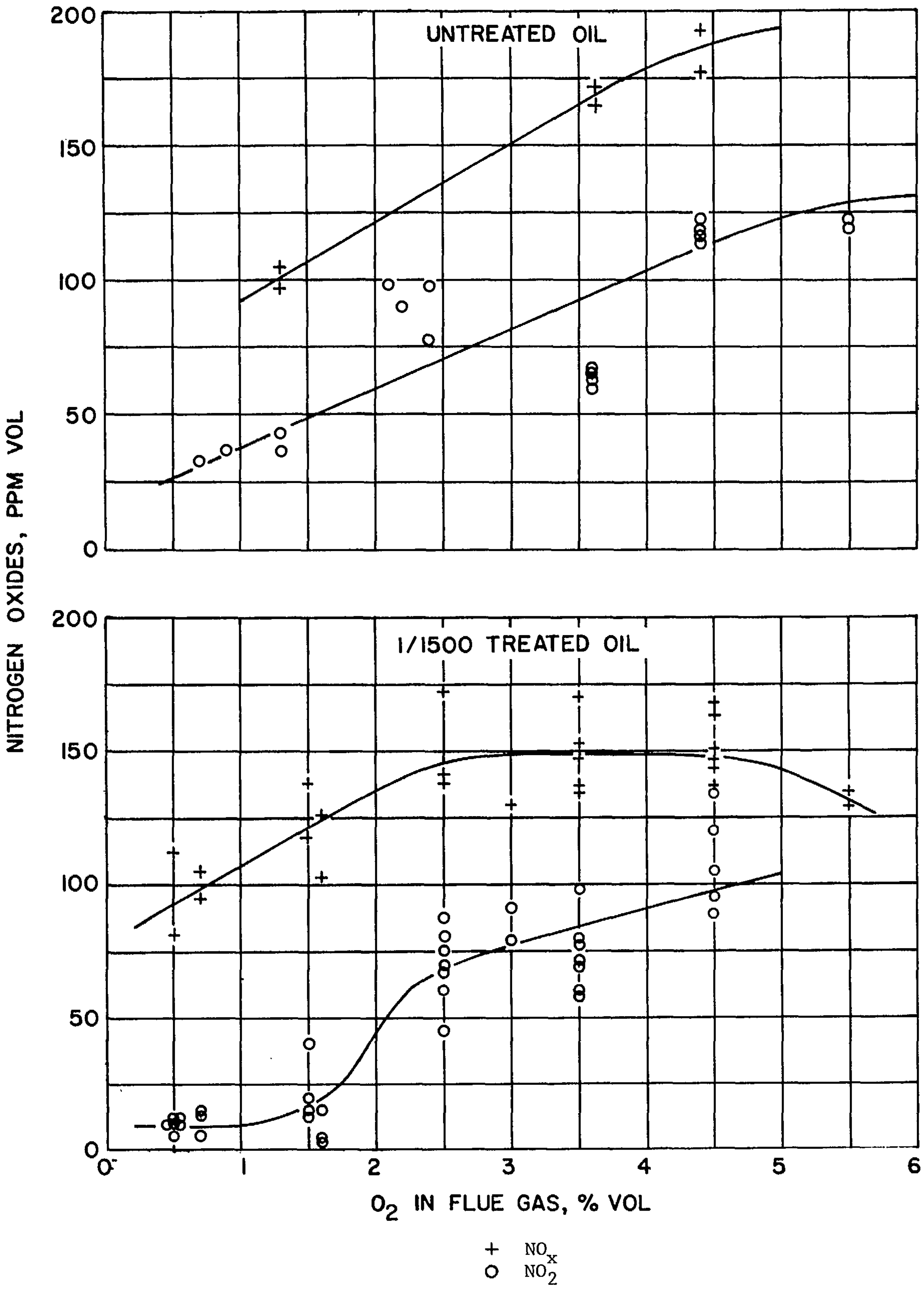


Fig. 13. Total nitrogen oxides (NO_x) and NO_2 vs O_2 in the flue gas for untreated oil and 1/1500 treated oil, two-burner system, normal firing rate.

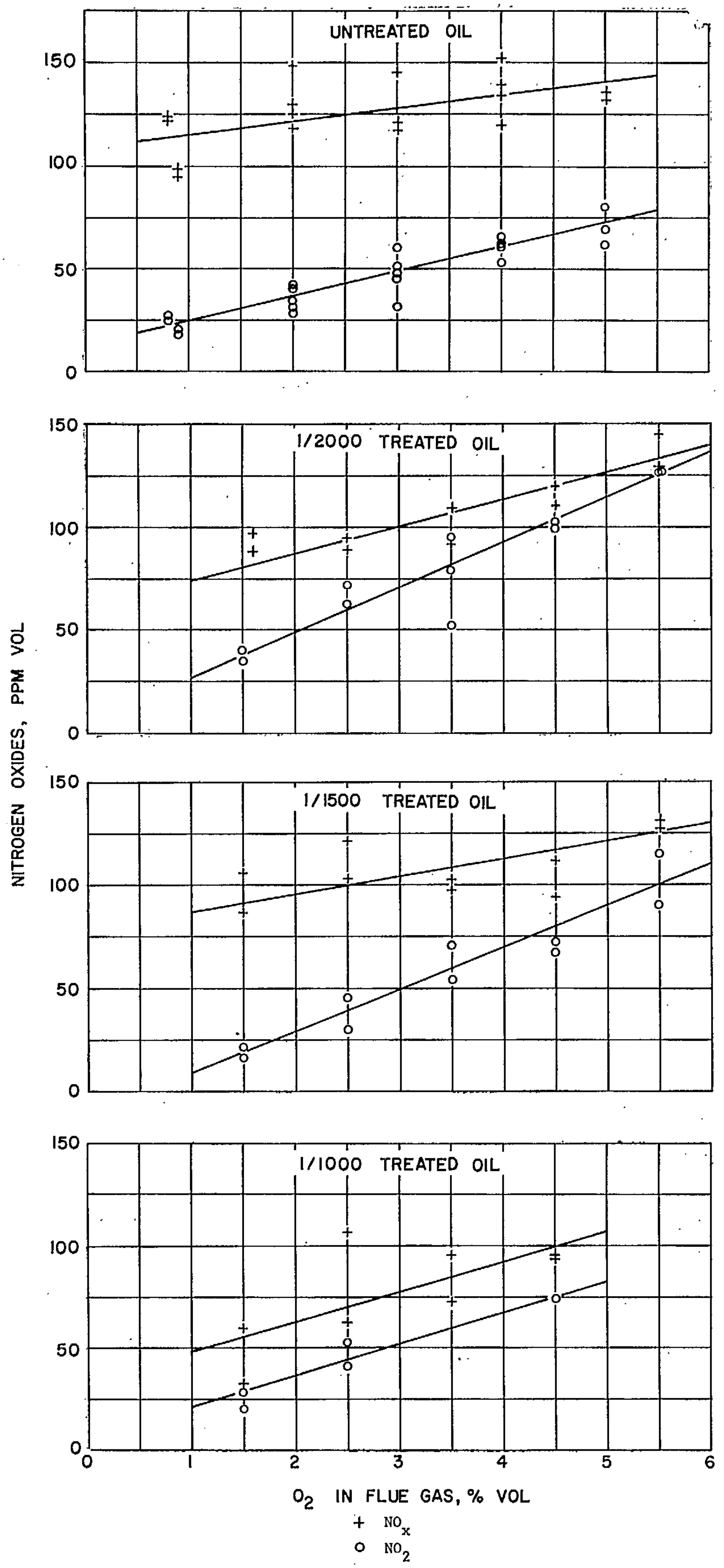


Fig. 14. Total nitrogen oxides (NO_x) and NO_2 vs O_2 in the flue gas for untreated oil and additive-treated oil at three dosage rates, single-burner system, normal firing rate.

5.5 Gas Phase Hydrocarbons and Aldehydes

The gas phase hydrocarbon and aldehyde levels in the flue gas were monitored during all of the single-burner tests with both untreated and additive-treated oil. Gas phase hydrocarbon levels, analyzed as methane, ranged from 5 to 12 ppm by volume for both untreated and additive-treated oil, whereas no aldehydes were detected by the analytical technique used.

5.6 Gas Phase Carcinogens

During normal load tests with untreated oil at 1 per cent and 3 per cent O_2 in the flue gas, it was found that soot-free flue gas contained no measurable carcinogens. Mukai et al. (7), in bench-scale experiments, also reported the absence of carcinogens in soot-free combustion gases. However, they demonstrated that any carcinogens produced were trapped in soot particles.

5.7 Abatement of SO_2, SO_3 and NO_x

It can be seen from Table 4 that the measured SO_2 values were sometimes higher and sometimes lower than the theoretical values calculated from the sulphur content of the fuel. API Procedure 774-54 for sulphur oxides is apparently susceptible to interferences by organic acids and nitrogen oxides; therefore, an adaptation of the USPHS West-Gaeke Method (8) will be used in future experiments.

Table 5 shows that, for selected combustion conditions, the fuel oil additive reduced SO_3 in gas phase by 30 to 78 per cent, SO_3 in particulate matter by 100 per cent, and NO_x by 8 to 11 per cent.

By means of a chemical mass balance, calculations show that a dosage rate of one gallon of additive per 1500 gallons of oil is sufficient to neutralize chemically about 2% of the sulphur in the oil or about 26 ppm of SO_3 in the flue gases. Therefore, when SO_3 levels in gas phase are below 26 ppm, unreacted additive will either deposit on boiler surfaces or commingle with the combustion gases. The net result, as shown in Table 5, is that the formation of acid soot is suppressed completely by the additive.

6. PARTICULATE MATTER TEST RESULTS

6.1 Control of Acid Soot and Low-Temperature Corrosion

As a result of the anomalies noted during the gas phase SO_3 measurements, detailed studies were undertaken to determine the role of soot

TABLE 4

Typical SO_2 Measurements in Flue Gases

Fuel	Firing Rate	O_2, % vol	SO_2, ppm vol	
			Measured	Theoretical
	Two-Burner System			
Untreated	Normal	1.0	1187 - 1276	1650
		6.0	734 - 1175	1230
1/1500 Treated	Normal	0.6	1988 - 2021	1695
		5.5	1218 - 1441	1270
1/1000 Treated	Normal	0.5	1267 - 1674	1695
		5.5	2668 - 2923	1270
	Single-Burner System			
Untreated	Low	3.0	1007 - 1316	1480
		5.0	1089 - 1312	1315
	Normal	1.0	1128 - 1446	1650
		5.0	921 - 1037	1315
	High	3.0	1052 - 1226	1480
		5.0	932 - 1172	1315
1/2000 Treated	Normal	1.5	1297 - 1400	1605
		5.5	900 - 1095	1270
1/1500 Treated	Low	3.5	1015 - 1204	1435
		5.5	972 - 1098	1270
	Normal	1.5	1169 - 3576	1605
		5.5	719 - 3316	1270
	High	3.5	996 - 1246	1435
		5.5	901 - 1087	1270
1/1000 Treated	Normal	1.5	1525 - 2688	1605
		5.5	3151 - 3211	1270

TABLE 5

Abatement of NO_x and SO_3*

Fuel Oil	Firing Rate	Heat Release Rate, Btu/cu ft/hr	Nitrogen Oxides		Free SO_3 in Gas Stream		SO_3 in Particulate Matter and Deposits*	
			Measured, ppm by vol	Neutralized by Additive, %	Measured, ppm by vol	Neutralized by Additive, %	Equivalent ppm by vol	Neutralized by Additive, %
Untreated	Normal	49,700	140	0	3.7	0	22.3	0
	High	66,250	150	0	27.0	0	25.0	0
1/1500 Treated	Normal	49,700	125	11	0.8	78	25.2	100
	High	66,250	139	8	19.0	30	23.0	100

*Data for 5.0 O_2 in flue gases.

particles in the sorption and subsequent removal of sulphuric acid from the gas stream. In these studies a single-burner system was used to investigate three input variables: (a) untreated oil and oil treated with additive at three dosage rates, (b) low, normal and high firing rates, and (c) O_2 levels in the flue gases ranging from 1 per cent to about 6 per cent.

6.1.1 Mechanism of Acid-Soot Formation in Low-Pressure Steam Boilers When Burning Untreated Oil

The following postulated mechanism, based on theoretical considerations (9) and the test results, indicates that high levels of acid soot can be produced within a boiler having furnace wall temperatures below acid dewpoint. Consequently, deposition and buildup of acid soot, rather than condensed acid, may be primarily responsible for low-temperature corrosion of furnace walls and convection surfaces.

The time-temperature history of a residual oil flame is such that any soot particles once produced are unlikely to burn. These particles are normally present in high enough concentrations to act as heterogeneous nucleation sites for condensation of supersaturated SO_3 (H_2SO_4) vapour in combustion gases below 350°F. Under ideal conditions, steep temperature gradients between clean combustion gases at high temperatures and tube surfaces operating below acid dewpoint will sustain supersaturated levels of acid vapour which will subsequently condense as a liquid. However, for soot-laden combustion gases, sulphuric acid will condense (in the vicinity of tube surfaces) on the large surface of the carbon particles due to their high surface area and porosity. A relatively rapid buildup of sticky, highly corrosive acid soot will then occur. The cumulative effect of these processes will be high rates of acid-soot deposition and corrosion in the furnace, with relatively low SO_3 and acid-soot concentrations in the combustion gases leaving the furnace. This explains the low measured values of SO_3 and RBU as reported under the gas phase test results for the single-burner tests with untreated oil. The particulate matter studies for the same series of tests revealed that any acid soot produced in the furnace remains damp and acidic throughout the air heater system, despite the fact that both the combustion gases and the heat exchange surfaces are above acid dewpoint. This phenomenon will be investigated further during forthcoming experiments with the furnace walls above acid dewpoint.

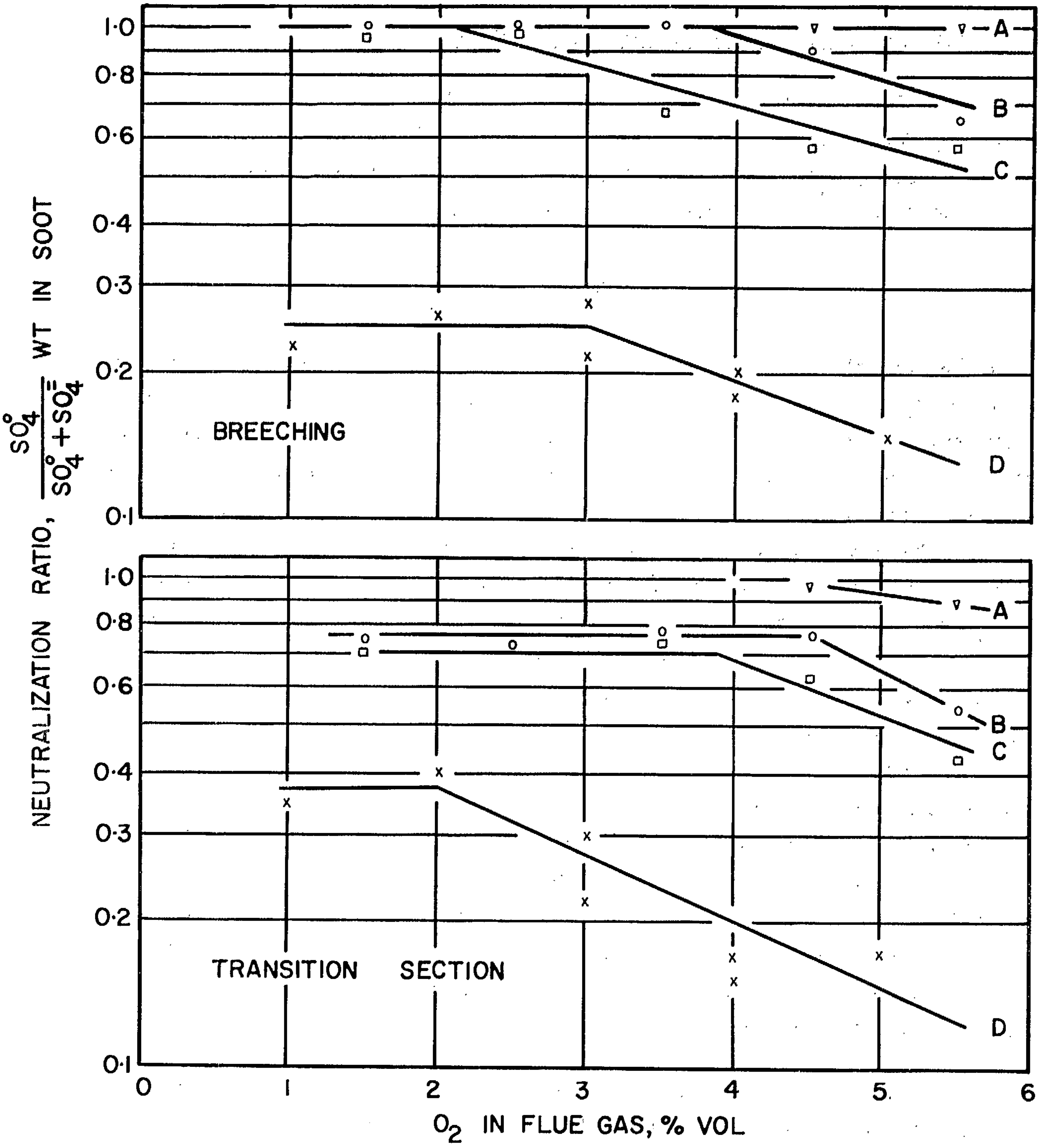
6.1.2 Neutralization Ratio of Soot in Flue Gas

Soot samples, collected at stations 3 and 4, were analyzed chemically for sulphates in the form of reaction products (SO_4°) and free sulphuric acid ($SO_4^{=}$), and the following ratio was used to assess the conversion of $SO_4^{=}$ to SO_4° under different combustion conditions:

$$\text{Neutralization Ratio} = \frac{SO_4^{\circ}}{SO_4^{\circ} + SO_4^{=}} .$$

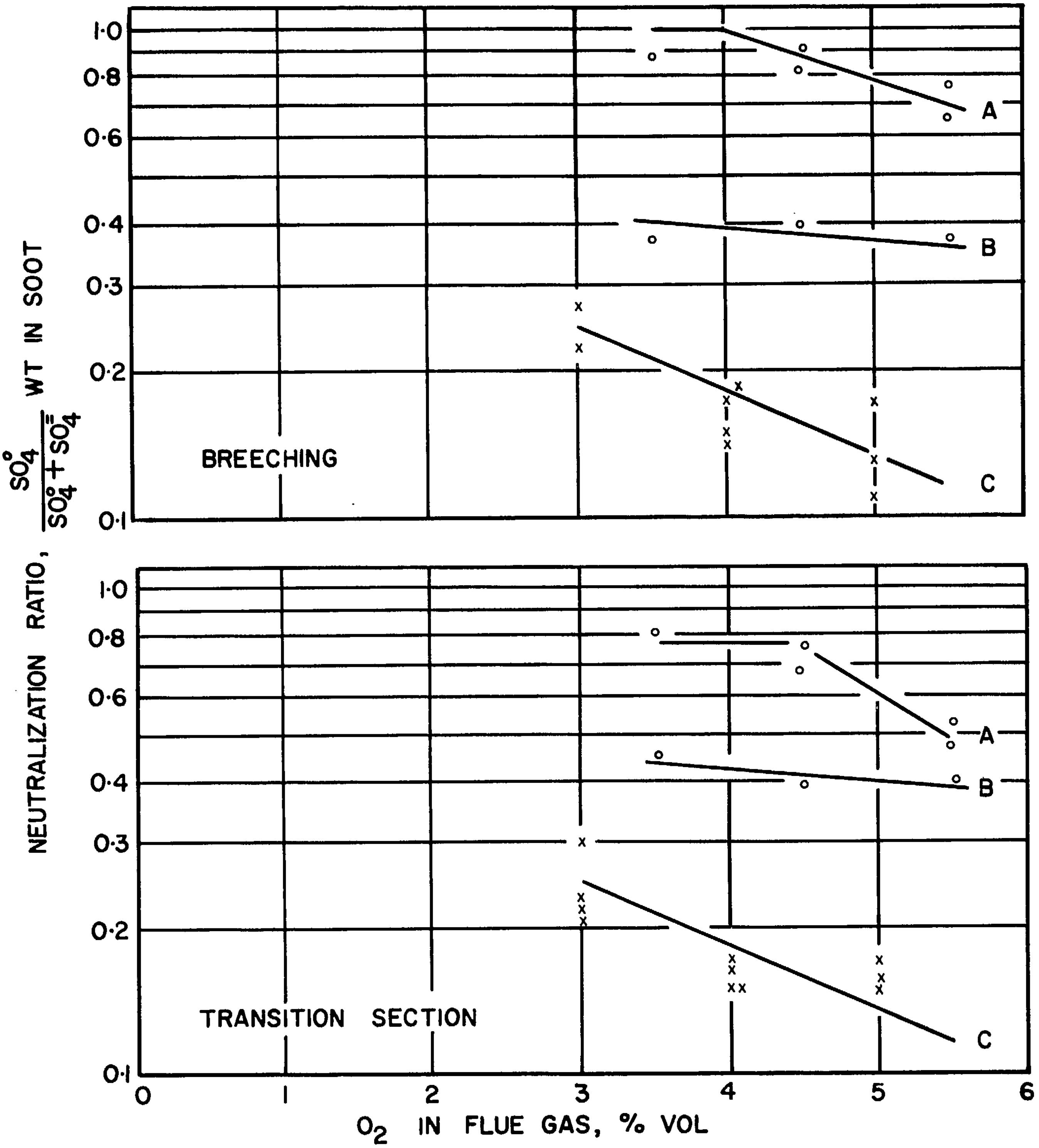
It can be seen that neutralization ratios below 0.5 are synonymous with high levels of acid sorption and at a neutralization ratio of unity no free acid is present. As shown in Figure 15, neutralization ratios at the transition section for normal firing rates are lowest for untreated oil and progressively increase with additive dosage rate. The same trends are found at the breeching, but the neutralization ratios relative to the transition section are lower for untreated oil and higher for additive-treated oil. These data show that soot from untreated oil adsorbs large amounts of free acid in the furnace and that acid continues to be adsorbed from the gas stream between the transition section and breeching. Also, very little neutralization of acid soot occurs when burning untreated oil, particularly at high O_2 levels. When using the additive, the soot likewise adsorbs large amounts of free acid but this is almost completely neutralized in the gas stream between the furnace and breeching. It is clear from Figure 15 that when operating at O_2 levels down to 1 per cent, the soot from 1/1500 treated oil contains little or no free acid while the soot from untreated oil is still relatively acidic. Therefore, in combustion systems where O_2 in flue gas cannot be reduced below 1 per cent, successful control of acid soot can be achieved by using the additive described in Table 2.

The influence of firing rate on the neutralization ratio of soot for untreated oil and 1/1500 treated oil is shown in Figure 16. In general, neutralization ratios are independent of firing rate, with one exception. At low firing rate with additive-treated oil, the neutralization ratio decreases appreciably with only about 40 per cent of the sulphate in the soot being neutralized. The neutralization ratios, being the same at both the transition section and breeching, suggest that if sufficient additive is present at low firing rates, acid-soot particles are rendered dry and non-corrosive by



A. 1/1000 treated oil
B. 1/1500 treated oil
C. 1/2000 treated oil
D. Untreated oil

Fig. 15. Neutralization ratio vs O_2 in flue gas for untreated and treated oil, single-burner system, normal firing rate.



A. 1/1500 treated oil at high and normal firing rate
B. 1/1500 treated oil at low firing rate, breeching
C. Untreated oil at high, normal and low firing rates

Fig. 16. Neutralization ratio vs O_2 in flue gas for untreated and 1/1500 treated oil, single-burner system.

physical dilution until chemical neutralization is complete. This method of acid inhibition is evident from Figure 18 described later.

6.1.3 Neutralization of Acidic Deposits on Boiler Surfaces

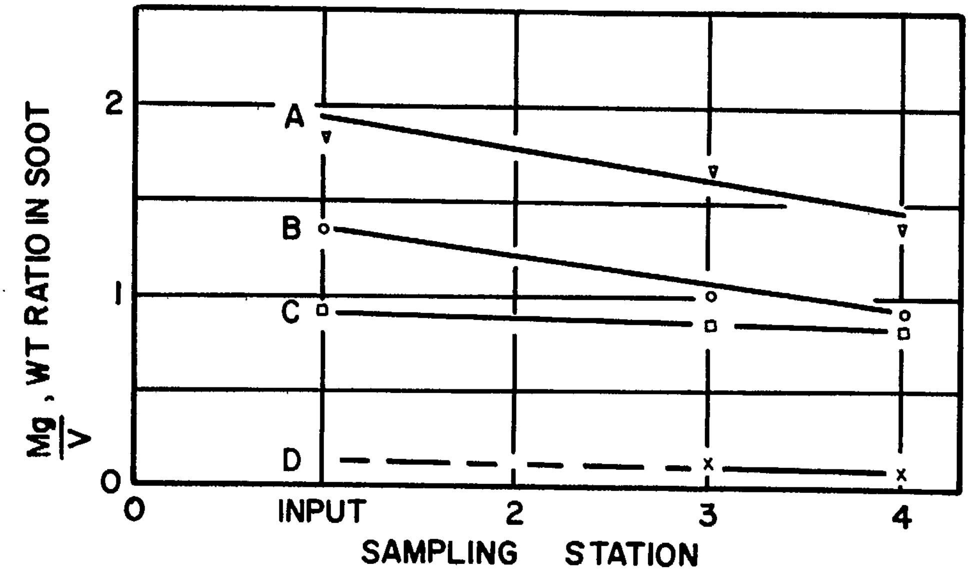
Studies of soot deposits suggest that any additive deposition on boiler surfaces occurs primarily by thermal diffusion. Furthermore, since this buildup remains dry, theoretical calculations show that deposition rates will continually decrease with time. The net result is a thin layer of powdery deposit that is self-cleaning. This phenomenon has been observed in both the research boiler and in power utility boilers when burning additive-treated oil. In utility boilers, powdery deposits of additive on cold end surfaces reached an equilibrium thickness and it was found that routine soot blowing in the air heater zone could be eliminated. Before additive treatment the air heaters were plagued by chronic blockage and corrosion problems. In the research boiler, the Mg/V ratio of soot decreased gradually with increases in residence time, when burning additive-treated oil, as shown in Figure 17. This selective deposition of additive, particularly on furnace walls, can be utilized in low-pressure steam boilers to prevent sulphuric acid and acid-soot corrosion within sight of flames.

Levy and Merryman (10) have demonstrated that MgO-coated iron reacts with SO_3 stoichiometrically to produce $MgSO_4$ which physically retards the contact of flue gas with iron.

6.1.4 Optimum Additive Properties and Dosage Rate

If the aforementioned mechanism of acid-soot formation (para 6.1.1) is valid, an additive to control SO_3 and H_2SO_4 in combustion products from oil-fired boilers should incorporate the following properties:

1. a chemical composition that neutralizes acid;
2. a particle physical structure that maximizes rates of acid sorption and chemical neutralization;
3. a particle size range that permits simultaneous deposition of additive with oil soot on boiler heat exchange surfaces; and



A. 1/1000 treated oil
B. 1/1500 treated oil
C. 1/2000 treated oil
D. Untreated oil

Fig. 17. Variation of Mg/V ratio in soot between sampling stations for untreated and treated oil, single-burner system, normal firing rate.

4. a method of application that results in intimate mixing between the additive and oil soot particles in the flame.

These properties are all inherent in the additive described in Table 2.

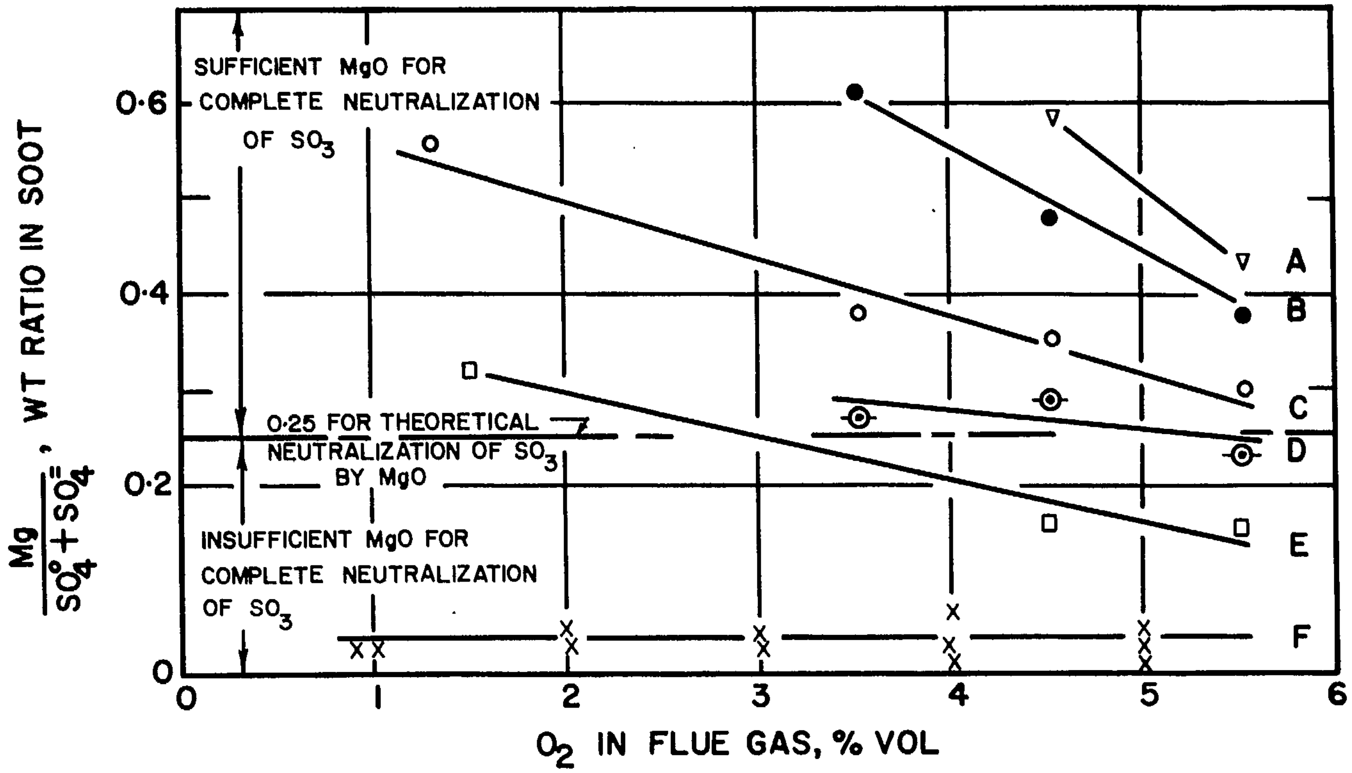
The minimum additive dosage rate for effective neutralization of acid soot was determined by plotting the ratio $Mg/[SO_4^{\circ} + SO_4^{=}]$ as a function of O_2 in the flue gas, firing rate and additive dosage rate. The results, shown in Figure 18, verify that an additive dosage rate of 1/1500 by volume is sufficient to neutralize acid soot produced under the combustion conditions selected. At O_2 levels below 2 per cent and at low firing rates, the additive dosage rate can be reduced by at least 33 per cent to compensate for corresponding reductions in SO_3 formation. These conclusions agree with observations made during additive trials in operational boilers, where additive treatment of oil effectively prevented cold-end corrosion and acid-soot emission.

6.2 Abatement of Particulate Pollutants

The influence of burner arrangement, combustion conditions and additive dosage rate on the production and emission of particulate pollutants was evaluated by (a) measuring soot concentrations in the flue gas, (b) examining the nature of the soot particles, and (c) determining the quantity and composition of selected toxic constituents in soot. These studies were all carried out on soot samples collected at the breeching.

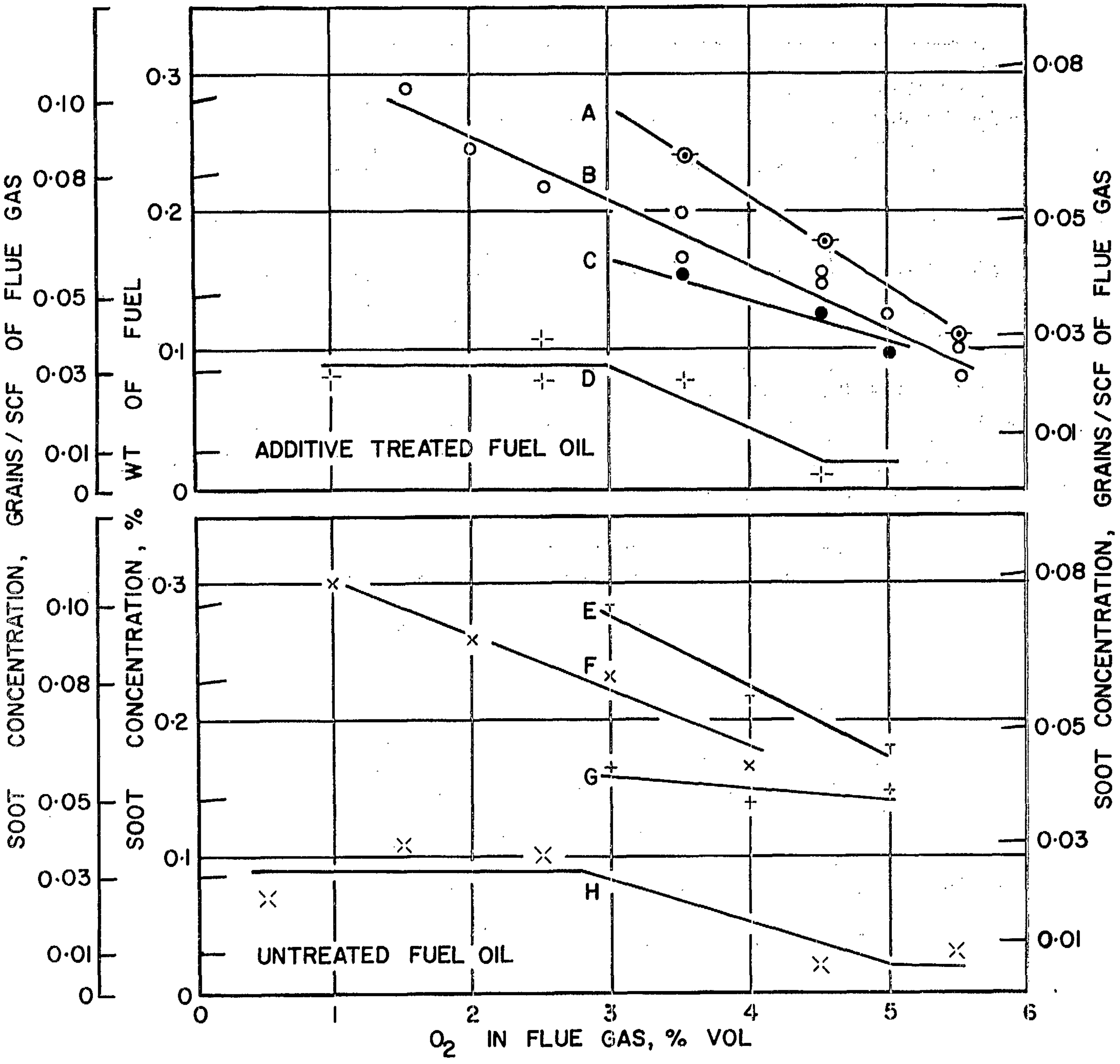
6.2.1 Soot Concentration

The soot concentration in the flue gas is shown in Figure 19 as a function of O_2 in flue gas, firing rate and burner arrangement when burning untreated oil, 1/1000 treated oil, 1/1500 treated oil and 1/2000 treated oil. Referring to the single-burner tests at normal firing rate, it is evident that soot concentrations increase with decreases in O_2, but are independent of additive treatment. Progressive increases in firing rate also increase soot concentrations, presumably because corresponding increases in flue gas velocity retard settling or deposition of soot in the boiler and because more soot may be formed through rapid chilling of flames impinging on furnace walls. In all tests the soot concentrations were less than 0.3 per cent weight of fuel, which compares favourably with a British Standard of 0.4 per cent weight (11)



A. 1/1000 treated oil at normal firing rate
B. 1/1500 treated oil at low firing rate
C. 1/1500 treated oil at normal firing rate
D. 1/1500 treated oil at high firing rate
E. 1/2000 treated oil at normal firing rate
F. Untreated oil at low, normal and high firing rates

Fig. 18. Effect of additive dosage rate, firing rate and O_2 in flue gas on magnesium/sulphate ratio in soot at the breeching, single-burner system.



A. 1/1500 treated oil at high firing rate, single burner
B. Composite curve, 1/1000, 1/1500 and 1/2000 treated oil at normal firing rate, single burner
C. 1/1500 treated oil at low firing rate, single burner
D. 1/1500 treated oil at normal firing rate, two opposed burners
E. Untreated oil at high firing rate, single burner
F. Untreated oil at normal firing rate, single burner
G. Untreated oil at low firing rate, single burner
H. Untreated oil at normal firing rate, two opposed burners

Fig. 19. Effect of additive dosage rate, firing rate and O_2 in flue gas on soot concentration at the breeching.

and North American Standards that range upward from 0.8 per cent weight of fuel (12, 13).

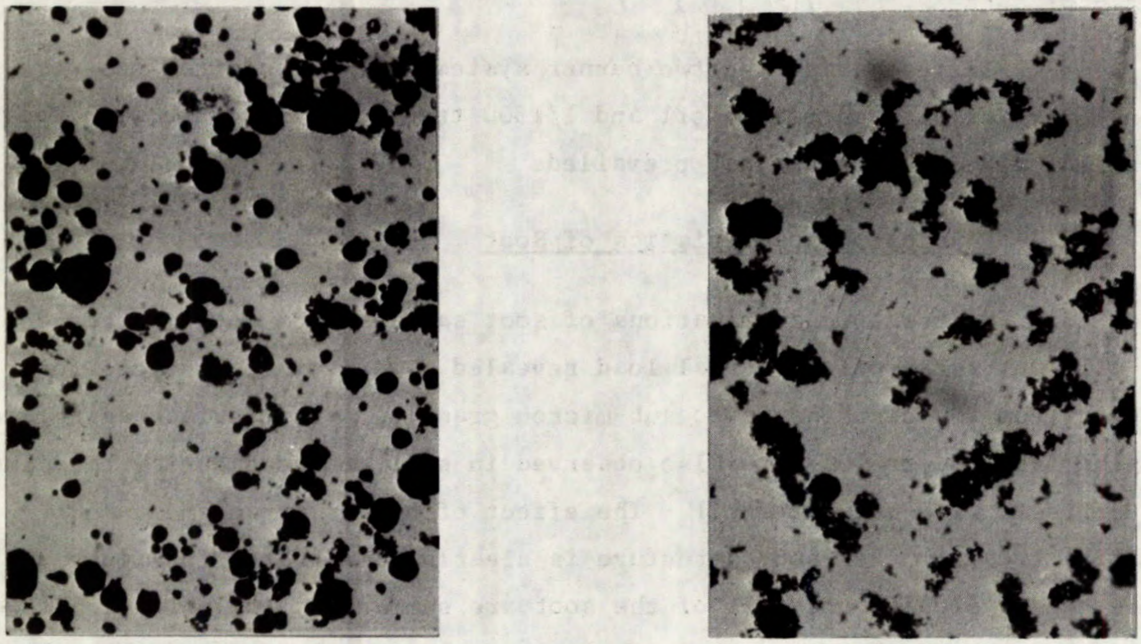
In tests with the two-burner system, soot concentrations were even lower for both untreated oil and 1/1500 treated oil because of highly turbulent air-fuel mixing that prevailed.

6.2.2 Physical Characteristics of Soot

Microscopic examinations of soot samples from both untreated oil and 1/1500 treated oil at normal load revealed a variety of particle forms ranging from 30μ cenospheres to sub-micron granules. Particulate aggregates ranging from 10μ to 70μ were also observed in soot produced during the single-burner tests with untreated oil. The effect of burner arrangement and additive treatment on soot structure is clearly illustrated in Figure 20, while the physical properties of the soot are summarized in Table 6. It was found that the two-burner system yields lower Loss on Ignition (LOI) values than the single-burner system, and that the corrosive, sticky soot typical of untreated oil is transformed into a dry, inert, free-flowing powder having improved electrical resistivity properties when the additive is used.

To illustrate the practical advantages of improvements in soot electrical resistivity, reference is made to Figure 19 which shows maximum soot concentrations at the breeching of about 0.3 per cent weight of fuel corresponding to 0.10 grains/SCF of flue gas. If an electrostatic precipitator efficiency of only 90 per cent can be assumed, although higher efficiencies may be possible with the improved resistivity and the free-flowing nature of soot from additive-treated oil, the maximum particulate emission to atmosphere would be about 0.03 per cent by weight of fuel, or 0.01 grains/SCF of flue gas. Such emission levels are far below those now common to residual oil firing, but the time may not be far off when such a limit may have to be enforced to solve air pollution by acid and acid soot.

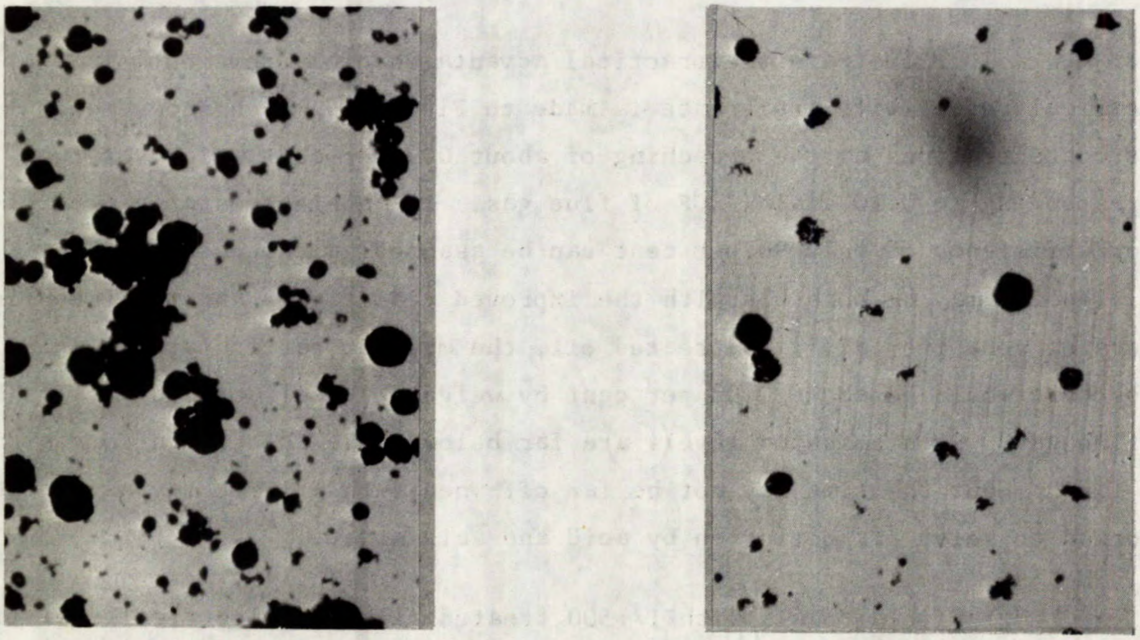
In field trials with 1/1500 treated oil, the electrical resistivity of soot particles was improved to the point where collection efficiencies of electrostatic precipitators were increased and current leakage across high-voltage insulators was prevented. Laboratory experiments will be carried out in a small electrostatic precipitator to study these and other related factors quantitatively.



Non-aggregated carbon particles, untreated oil

Powdery additive particles, 1/1500 treated oil

(a) Two opposed burners



Aggregated carbon particles, untreated oil

Carbon and powdery additive particles, 1/1500 treated oil

(b) Single burner

Fig. 20. Photomicrograph of soot particles for untreated and 1/1500 treated oil, normal firing rate. Magnification X160.

TABLE 6

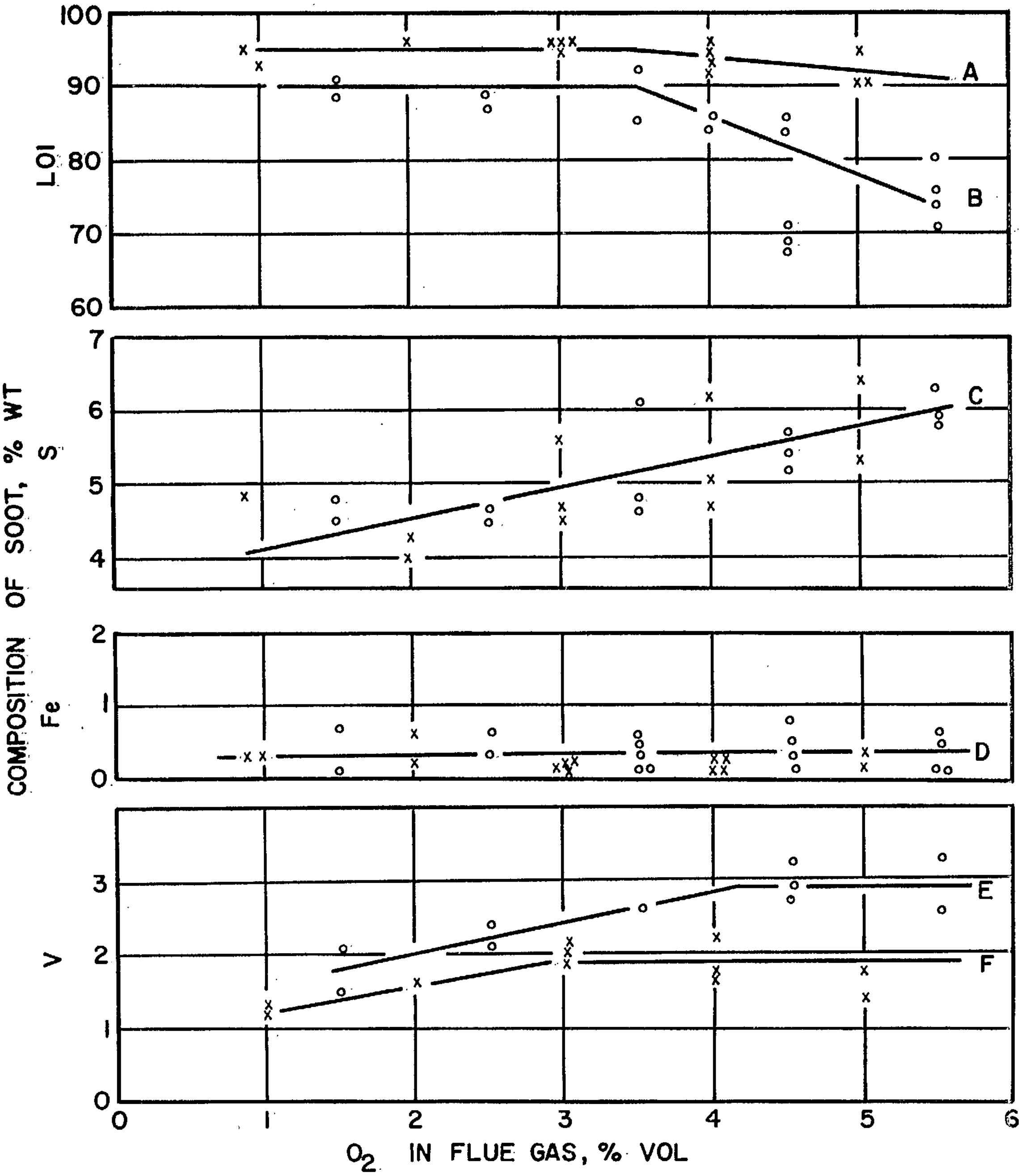
Physical Properties of Soot

Burner Arrangement	Fuel Oil	Soot Properties		
		Description of Particles	LOI, %	Electrical Resistivity, Ω/CM-ft
Two Opposed Burners	Untreated	Damp, non-aggregated	75-90	10^8 - 10^9
	1/1500 Treated	Dry, free flowing	65-80	10^{10} - ∞
Single Burner	Untreated	Wet, sticky aggregates	92-95	10^8 - 10^9
	1/1500 Treated	Dry, free flowing	75-90	10^{10} - ∞

6.2.3 Chemical Composition of Soot

Chemical analyses of soot produced during the single-burner tests were undertaken to determine the concentration of toxic and corrosive constituents present. The measurements of loss on ignition, sulphur, iron and vanadium in soot at the breeching are shown in Figure 21 for a range of O_2 levels at normal firing rate. The soot from additive-treated oil has lower Loss on Ignition values and higher vanadium contents than untreated oil, indicating a better degree of burnout at all O_2 levels. Consequently, additive-treated oil soot looks encouraging as a source of vanadium.

Figure 22 shows the neutralized sulphate and free acid content of soot at the breeching for both untreated oil and 1/1500 treated oil at low, normal and high firing rates. These results, in conjunction with the neutralization data discussed in section 6.1.2, confirm that wet, sticky, acid soot emissions from untreated oil are effectively modified and suppressed by applying the additive at a rate of one gallon per 1500 gallons of oil. It can also be seen that (a) the free acid content of soot from 1/1500 treated oil is much lower than soot from untreated oil, (b) the soot from 1/1500 treated oil has higher acid sorption and neutralization capacities than soot from untreated oil, and (c) at O_2 levels below 3.5 per cent the soot from 1/1500 treated oil is completely neutralized while the soot from untreated oil still contains free acid.



o Untreated oil

x Additive-treated oil

A. Loss on ignition, untreated oil
B. Loss on ignition, composite curve for 1/1000 treated oil, 1/1500 treated oil and 1/2000 treated oil
C. Sulphur, composite curve for untreated oil, 1/1000 treated oil, 1/1500 treated oil and 1/2000 treated oil
D. Iron, composite curve for untreated oil, 1/1000 treated oil, 1/1500 treated oil and 1/2000 treated oil
E. Vanadium, composite curve for 1/1000 treated oil, 1/1500 treated oil and 1/2000 treated oil
F. Vanadium, untreated oil

Fig. 21. Composition of soot at the breeching, for untreated and treated oil, single-burner system, normal firing rate.

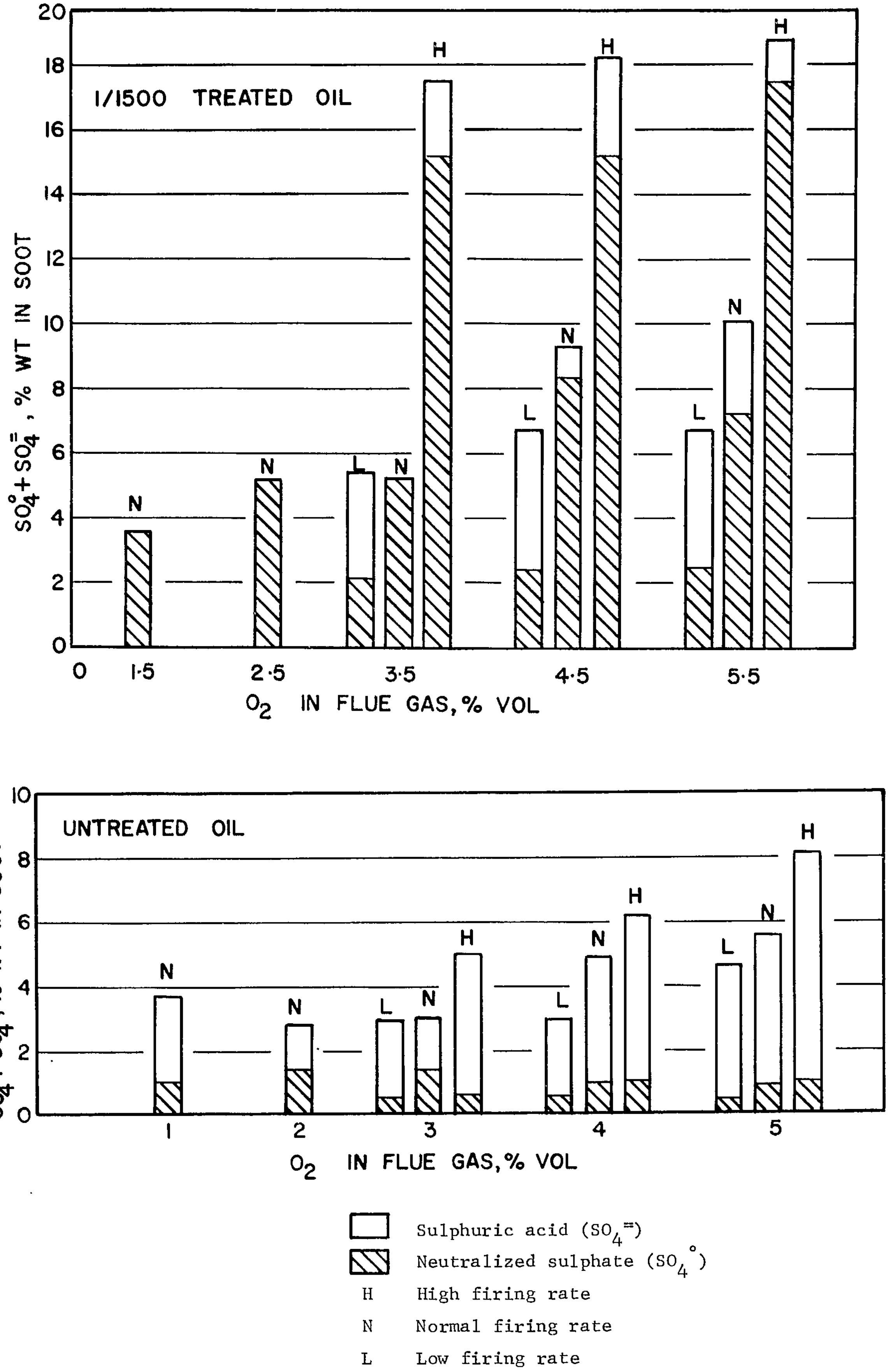


Fig. 22. Sulphate content of soot at the breeching, for untreated and 1/1500 treated oil, single-burner system, normal firing rate.

Table 7 shows results of oily matter determinations on selected samples of soot from untreated and additive-treated oil. The oily matter appears to be essentially unburned fuel oil, and tends to concentrate in superfine particles which comprise about 20 per cent by weight of the soot.

The carcinogenic fraction of the polycyclic aromatic hydrocarbons in soot from both untreated and additive-treated oil is extremely low. All samples tested, when expressed in µg/1000 Nm^3* of flue gas, were less than ambient air levels in Ottawa which range between 0.18 and 3.40 µg/1000 Nm^3 of air. These findings agree with data reported by Howe (14) who concluded that oil-fired combustion systems are unlikely to emit abnormal levels of carcinogenic irritants.

6.2.4 Retention of Sulphur and Vanadium in Soot

To assess the effect of both mean residence time of flue gas and variable soot concentrations on the chemical composition of soot, the analytical data for vanadium, sulphur and sulphate were recalculated using unit weight of fuel as a datum level. The recalculated data, shown in Figures 23 and 24 for untreated oil and additive-treated oil respectively at normal firing rates, are summarized below:

1. Less than 1 per cent of the sulphur in the oil is trapped in soot particles leaving the furnace, with sulphur levels for untreated oil being slightly higher than for additive-treated oil.

2. When burning untreated oil at O_2 levels between 1 per cent and 5 per cent, about 65 per cent of the sulphur is present in non-sulphate form and hence could initiate intergranular corrosion on high-temperature boiler surfaces.

3. When burning additive-treated oil, the sulphur in soot is progressively converted from non-sulphate to sulphate form as O_2 levels increase; therefore, the additive should minimize the risk of high-temperature corrosion due to localized sulphidation attack at O_2 levels over 3 per cent.

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* Standard cubic metres at 0°C and 760 mm mercury.

TABLE 7

Oily Matter Content of Soot

Fuel	Firing Rate	O_2 in Flue Gas % S	Sampling Station	Oily Matter, µg/g soot	
				+2µ Particles	-2µ Particles
1/1000 Treated	Normal	5.5	4	1027	N.D.
1/1500 Treated	Normal	1.5	4	756	N.D.
		2.5	4	998	998
		3.5	4	1107	2379
		4.5	4	1022	1372
		5.5	4	1718	3033
	Low	3.5	4	705	3854
		5.5	4	619	5278
	High	3.5	4	360	1948
		5.5	4	1453	1411
1/2000 Treated	Normal	1.5	4	1496	11573
		5.5	4	656	4008
Untreated	Normal	1.0	4	598	1103
		4.0	4	642	1165
	Low	3.0	3	913	2110
		5.0	3	759	1143
	High	3.0	3	720	980
		5.0	4	666	1347

N.D. - Not determined.

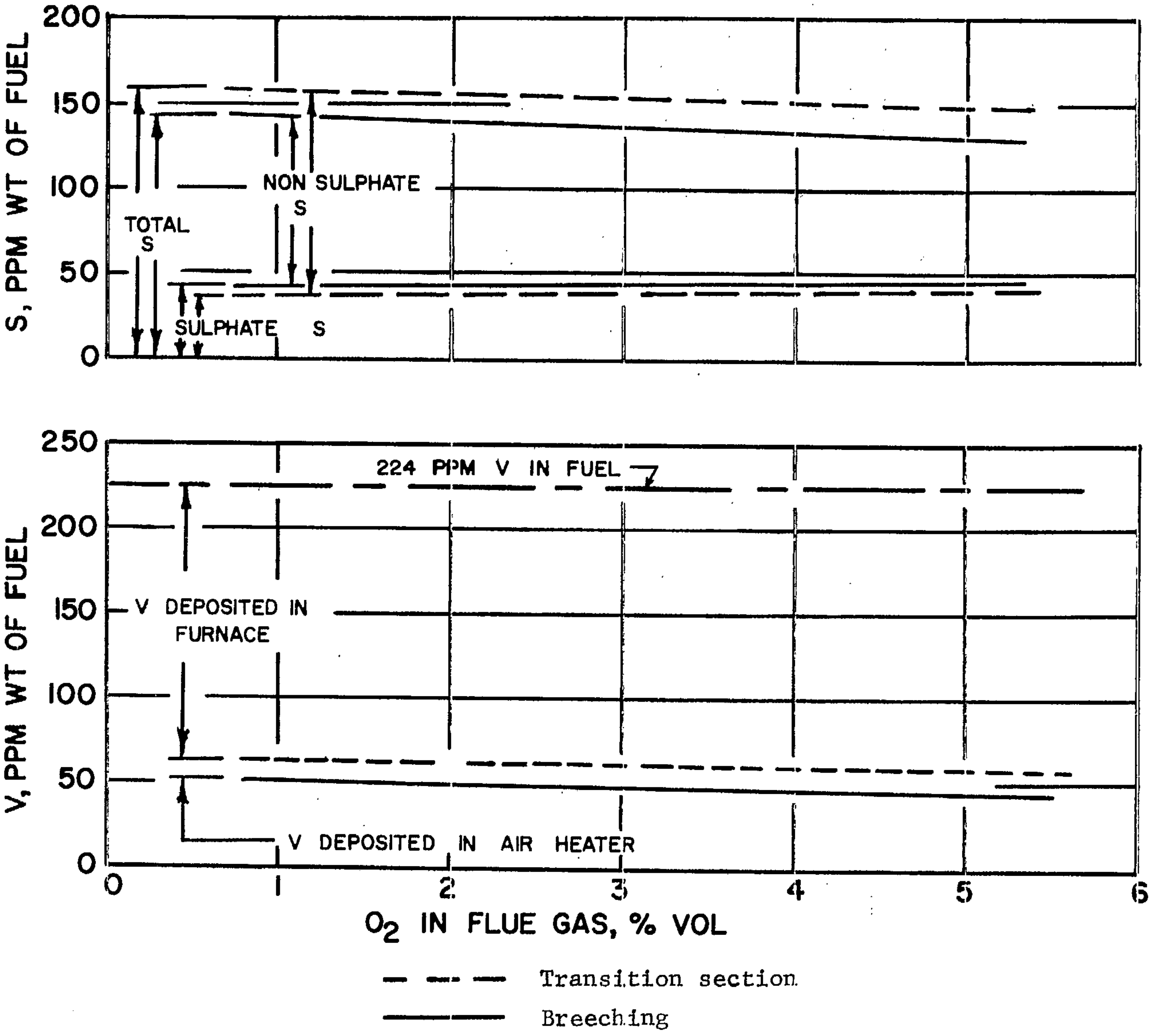

Fig. 23. Retention of sulphur and vanadium in soot for untreated oil, single-burner system, normal firing rate.

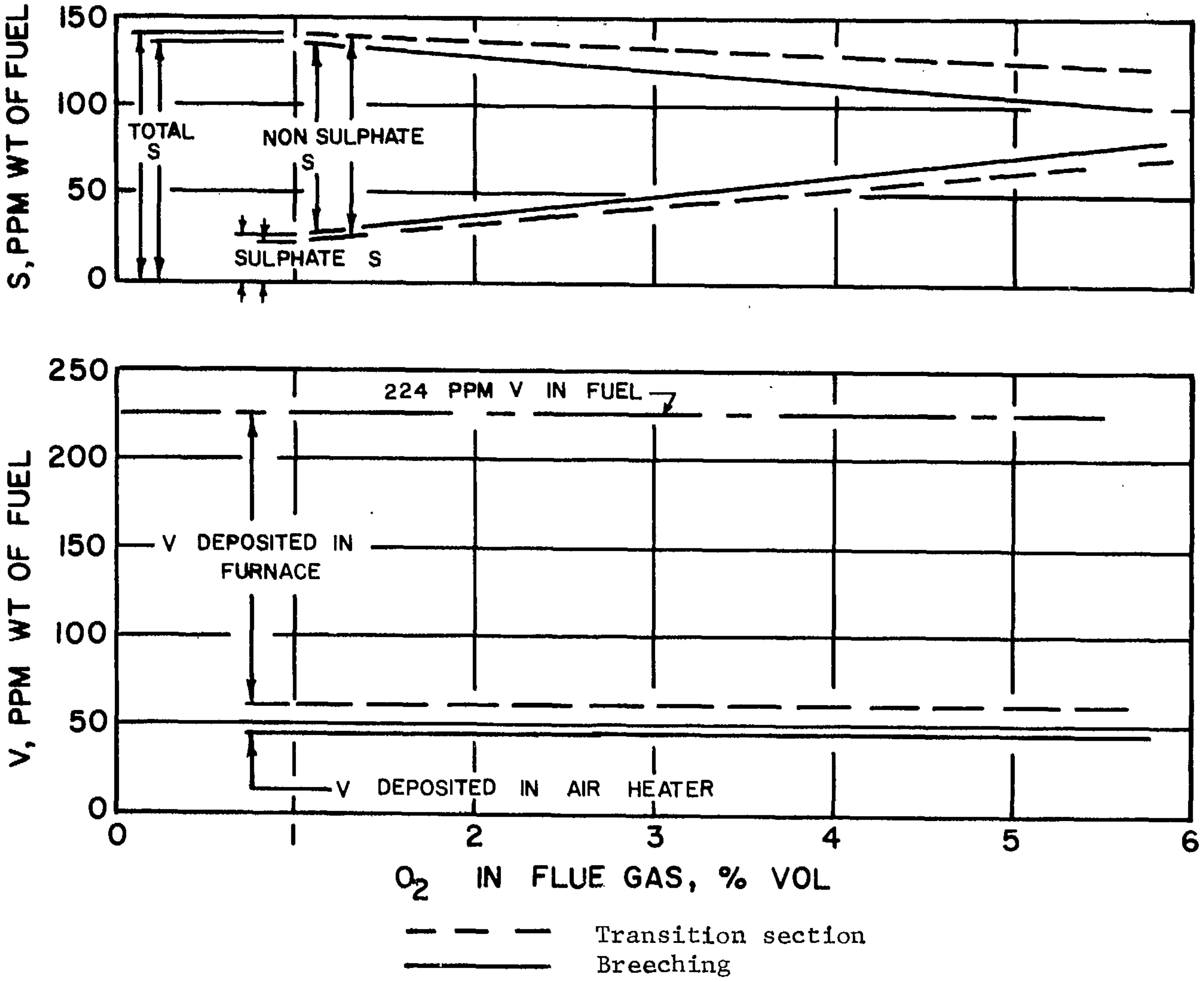

Fig. 24. Retention of sulphur and vanadium in soot for 1/1000 treated oil, 1/1500 treated oil, and 1/2000 treated oil, single-burner system, normal firing rate.

4. About 75 per cent of the vanadium in the oil is deposited in the furnace, with a further 5 per cent being deposited in the air heater system when either untreated or additive-treated oil is burned.

7. CONCLUSIONS

While the numerical levels of SO_3, RBU, NO_2 and other measurements made on the combustion research boiler may not necessarily be extrapolated directly to other firing systems or furnace configurations, nonetheless the trends will apply under similar conditions. It is considered safe to apply the following conclusions to industrial equipment burning untreated oil or oil treated with the magnesia-alumina additive described in Table 2:

1. (a) The H_2SO_4 content of soot from burning untreated oil decreases gradually with decreasing O_2 levels in the flue gas; however, the soot still contains free acid at an O_2 level of 1 per cent. With additive-treated oil, any H_2SO_4 in soot is physically and/or chemically inhibited at all O_2 levels up to 5 per cent.

   (b) Additive treatment of the oil removes NO_x and SO_3 from flue gas by physical adsorption and/or chemical reaction.

   (c) Gas-phase hydrocarbons and aldehydes in flue gas from both untreated and additive-treated oil are relatively low.

   (d) Carcinogens in soot from both untreated and additive-treated oil are present in less than trace amounts.

2. Adsorbed SO_3 and condensed H_2SO_4 in soot are effectively neutralized by the additive in the gas stream. The additive transforms sticky, corrosive, acid soot into a dry, inert powder that can be readily collected for sale as a source of vanadium.

3. Additive treatment of the oil improves the electrical resis-

tivity of soot particles to the extent that collection efficiency of electrostatic precipitation is improved.

4. A dominant mechanism in the initiation of low-temperature corrosion appears to be one of acid sorption on soot particles in the vicinity of boiler surfaces that are below acid dewpoint, followed by an inevitable deposition of acid soot.

5. (a) In low-pressure steam boilers the deposition of acid soot on furnace walls will result in relatively low SO_3 and RBU readings in flue gas farther downstream. Therefore, any assessment of corrosion potential in this type of equipment must be analyzed with respect to both furnace and combustion conditions.

(b) The additive successfully controls chronic fouling and corrosion problems due to acid and acid soot deposits on low-temperature heat exchange surfaces.

(c) With both untreated and additive-treated oil, SO_3 and RBU levels increase sharply with increasing firing rate.

8. REFERENCES

1. Lee, G.K., Mitchell, E.R., Grimsey, R.G., and Benn, D.H. Formation of Oil Ash Deposits on Boiler Surfaces and Control by an Additive. Proc. of the American Power Conference, 1966, Vol XXVIII, pp 613-631.

2. Dubois, L., Teichman, T., Baker, C.J., Zdrojewski, A., Jeffrey, R.K., and Monkman, J.L. The Analytical Chemistry of Pollutants from Controlled Combustion of High Sulphur Fuel Oil, in print.

3. Lee, G.K., Friedrich, F.D., and Mitchell, E.R. Effect of Fuel Characteristics and Excess Combustion Air on Sulphuric Acid Formation in a Pulverized-Coal-Fired Boiler. Jour. Inst. Fuel, Vol XL, No. 320, Sept. 1967, pp 397-405.

4. Fouhse, R.G. A Pilot Scale Research Boiler at the Canadian Combustion Research Laboratory, in preparation.

5. Black, A.W., Stark, C.F., and Underwood, W.H. Dewpoint Measurements in Boiler Flue Gases, ASME Paper 60-WA-285.

6. Hedley, A.B. Factors Affecting the Formation of Sulphur Trioxide in Flame Gases. Jour. Inst. of Fuel, Vol XL, No. 315, April 1967, pp 142-151.

7. Mukai, M., Thomas, J.F., and Tebbens, B.D. The Fate of Airborne Benzo(a)pyrene. Symposium on Photochemical Aspects of Air Pollution, 152nd National ACS Meeting, New York, Sept. 1966.

8. U.S. Department of Health, Education and Welfare. Selected Methods for the Measurements of Air Pollutants, Public Health Service, Division of Air Pollution, Cincinnati, Ohio, 1965.

9. Mason, B.J. Nucleation of Water Aerosols. Disc. Faraday Society, No. 60, 1960, pp 20-37.

10. Levy, A., and Merryman, E.L. Interactions of Sulphur Oxide - Iron Oxide Systems, ASME Paper No. 66-WA/CD-3.

11. Report of the Working Party on Grit and Dust Emissions, HMSO, London, 1967.

12. City of New York. N.Y. Air Pollution Control Code, Article 9, Oct. 1964.

13. The Municipality of the City of Toronto. Draft By-Law entitled "To Control Air Pollution in Metropolitan Toronto", Sept. 1966.

14. Howe, E.L. Sampling for 3:4 Benzpyrene from Continuous Combustion Appliances Fired by Petroleum Fuels. National Society for Clean Air, Harrogate Conference, England, 1960.

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APPENDIX

A Method for Determining the Relative Electrical Resistivity of Soot Particles Emitted from Residual Oil Flames

Field trials with utility boilers demonstrated qualitatively that use of the magnesia-alumina fuel oil additive improved the efficiency of electrostatic precipitators. In order to obtain quantitative data, a bench-scale apparatus was designed by the authors to measure the electrical resistivity of soot particles under static conditions. By taking measurements on soot particles from both untreated oil and additive-treated oil, their relative electrical resistivity can be compared, and any improvement due to additive treatment can be correlated to increases in electrostatic precipitator efficiency.

The apparatus for measuring the electrical resistivity of soot particles developed in this research program is illustrated in Figure 25. It consists of a sectional lucite cylinder containing two brass pistons between which a given volume of air-dried soot is compressed to a constant thickness at room temperature. The pistons also serve as electrodes to permit the passage of d-c current through the compressed sample. By selecting an emf of 1 volt or 10 volts, the current between the electrodes can be controlled between 0 and 1000 microamperes. The apparatus yields reproducible data from which the electrical resistivity of soot can be calculated within an order of magnitude for particles less than 30μ.

The equation for the electrical resistivity of a conductor (or insulator) is given by $R = \rho\frac{L}{A}$ where p = resistivity, Ω/CM-ft (ohms/circular mil-ft)

E = potential difference, volts

I = current, amperes

A = cross-sectional area of the conductor, circular mils (CM) = 62500 CM

L = length of conductor, ft = 0.021 ft

Resistivity values for the apparatus described above are therefore given by the following equation:

$$\rho = \frac{E}{\mu\ I} \times 3 \times 10^{12} \quad \Omega/\text{CM-ft}$$

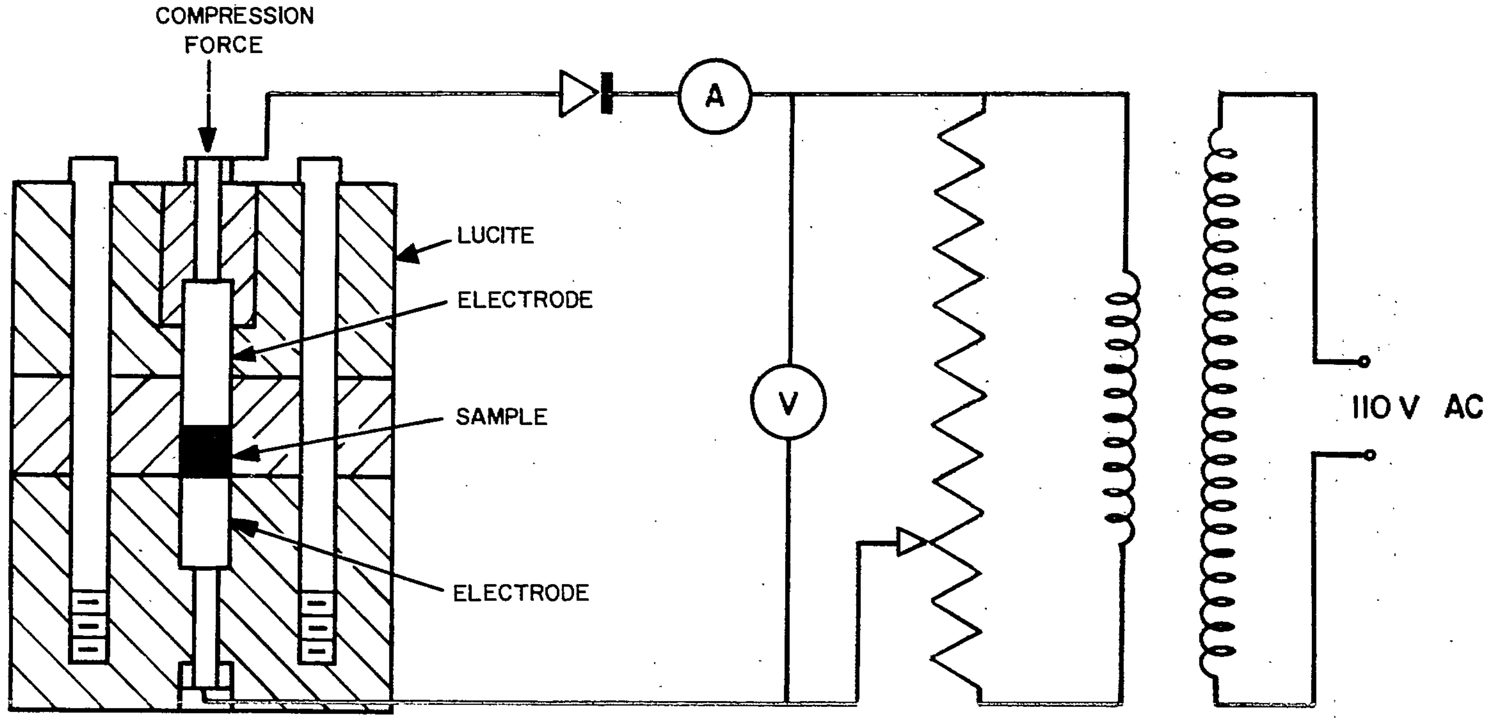

Fig. 25. Electrical resistivity apparatus.