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*CONTROL OF SO<sub>3</sub> IN LOW-PRESSURE  
HEATING BOILERS BY AN ADDITIVE*

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FUELS RESEARCH CENTRE

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# Control of SO<sub>3</sub> in low-pressure heating boilers by an additive

This paper deals with the burning of residual fuel oil containing 2.5% sulphur under conditions prevalent in heating boilers to assess the effect of boiler load, excess combustion air, mean residence time and the use of 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 oxides of nitrogen and SO<sub>3</sub>. Furthermore, the additive neutralizes condensed H<sub>2</sub>SO<sub>4</sub> 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<sub>3</sub> concentrations in flue gas can give misleading results when soot or particulate matter is present.

## 1. Foreword

Because air pollution and its control cut across many engineering and scientific disciplines, they require ever-broader collaboration between research agencies. In this case, as always, the Combustion Research Laboratory has received valuable analytical support from other groups in the Fuels Research Centre and the Mines Branch, especially the Petroleum and Gas Laboratory. For the work described in this paper the Occupational Health Division of the Department of National Health and Welfare provided additional collaborative support, not only in the analysis of carcinogenic irritants but in the development of a technique for measuring free sulphuric acid in particulate matter.

## 2. 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, the first phase of which deals with operating conditions typical of low-pressure heating boilers with mechanical atomizing burners, and is described in this paper. Two approaches were made. The first was to control combustion conditions particularly by using little excess combustion air, the advantages of which are well documented in the technical literature but which has been found to have severe limitations in heating boilers or boilers operating under cycling loads. The second was to neutralize (chemically) SO<sub>3</sub> and sulphuric acid by means of a fuel additive. The additive selected is a Mg:Al formulation, described previously,<sup>1</sup> which is preferred to magnesia or alumina separately because it forms a spinel structure in the flame, resulting in a friable and porous deposit having more chemically active surface exposed to

SO<sub>3</sub> and sulphuric acid than if either ingredient were used separately.

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 from that generally accepted hitherto. 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.

## 3. Research objectives

The objectives of the research programme were:

1. to show how and to what extent oil combustion pollutants may be reduced at the source;
2. to neutralize chemically adsorbed SO<sub>3</sub> and sulphuric acid in soot so that it will be inert for safe emission to the 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; and
5. to neutralize chemically 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 to examine the role of soot in removing SO<sub>3</sub> in gas phase as well as to assess the levels of nitrogen oxides, gas phase hydrocarbons, aldehydes, oily matter, carcinogens and vanadium emitted to the atmosphere.

In fulfilling these objectives considerable emphasis was placed on the development and improvement of techniques for analysing sulphuric acid in particulate matter and on atomic absorption analyses for vanadium, magnesium, aluminium and iron in soot samples.<sup>2</sup> The sampling procedures for SO<sub>2</sub> and SO<sub>3</sub> determinations have been modified to eliminate interferences that are not normally taken into consideration.

## 4. Description and operation of research boiler

The research boiler is shown schematically in Fig. 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 typical firing conditions. Since the boiler has been fully described elsewhere<sup>3,4</sup> it need only be reiterated here that for the

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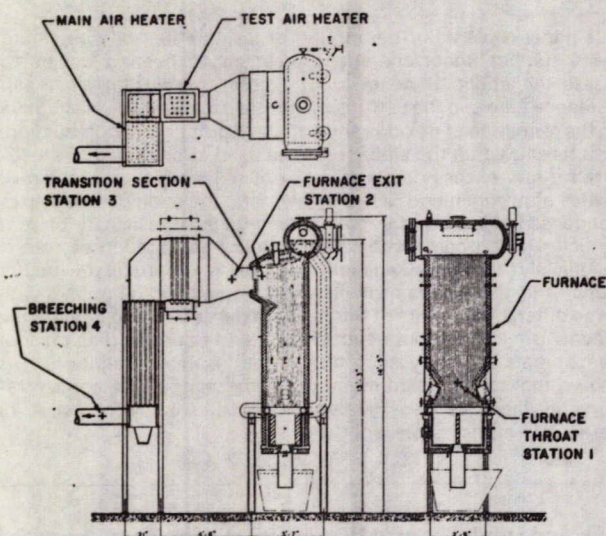


FIG. 1 Schematic view of combustion research boiler showing location of sampling stations.

TABLE 1 Calculated flue gas residence times in the combustion research boiler

Firing rate	O <sub>2</sub> , %	Cumulative residence times, seconds			
		Station 1 Furnace throat	Station 2 Furnace exit	Station 3 Transition section	Station 4 Breecing section
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

present series of tests, steam pressure was about 15 p.s.i.g., which meant that the furnace walls were below the acid dewpoint except at low excess air levels.

In this phase 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 were:

1. O<sub>2</sub> in flue gas which was varied stepwise from 1.0% to 5.5%;
2. low, normal and high firing rates corresponding to furnace volumetric heat-release rates of 27 600, 49 700 and 66 250 Btu/ft<sup>3</sup> h;
3. additive dosage rates of 1 gal/1000 gal of fuel oil, 1 gal/1 500 gal of fuel oil, and 1 gal/2 000 gal of fuel oil. For brevity these will be referred to throughout this paper as 1/1000 treated oil, 1/1 500 treated oil and 1/2000 treated oil respectively.

Continuous injection of the additive in the oil ahead of the burner was achieved by an infinitely adjustable slurry type metering pump.

## 5. 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<sub>2</sub>, O<sub>2</sub> and CO in flue gas by orsat at 15-min intervals; CO<sub>2</sub> and CO continuously by non-dispersive infra-red analyser and O<sub>2</sub> continuously by both para-

magnetic and combustion principle analysers. Station 3.

2. Acid dewpoint and rates of acid buildup (R.B.U.) measured in microamperes/min ( $\mu$ A/min) by B.C.U.R.A. dewpoint meter, one traverse per run. Station 4.

3. SO<sub>3</sub> 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<sub>2</sub> in flue gas by A.P.I. Method 774-54 for total sulphur oxides. This apparatus was connected in series with the SO<sub>3</sub> 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<sub>x</sub>) by A.S.T.M. Method D 1608, one sample per run. Stations 3 and 4.

7. NO<sub>2</sub> by U.S.B.M. Method RI 6790, one sample per run. Stations 3 and 4.

8. Aldehydes by U.S.B.M. 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% collection efficiency. One sample per run, extracted over a 60-90 min period. Stations 3 and 4.

10. Vanadium, magnesium, iron and aluminium in soot by atomic absorption technique.<sup>2</sup>

11. Reacted SO<sub>4</sub> and free SO<sub>4</sub> in soot by wet chemistry.<sup>2</sup>

12. Total sulphur in soot by A.S.T.M. Method D 271.

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 the Appendix.

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

TABLE 2 Analysis of No. 6 residual fuel oil

Test	Value	
	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 <sub>2</sub> O <sub>3</sub>
Solids content, %	55
Light oil carrier, %	45
Magnesium-aluminium ratio	9:1
Particle size range, $\mu$	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

\*Thixotropic suspension

\*\*"Magnesia" and "alumina" in this paper refer to partially dehydrated hydroxides of magnesium and aluminium.

TABLE 4 Average SO<sub>3</sub>, acid dewpoint, R.B.U., NO<sub>2</sub>, NO<sub>x</sub> and SO<sub>2</sub> measurements in flue gases

Fuel	Firing rate	O <sub>2</sub> , % vol	SO <sub>3</sub> , ppm vol				Acid Dewpoint °F	RBU Maximum µA/min	NO <sub>x</sub> ppm	NO <sub>2</sub> vol	SO <sub>2</sub> , ppm vol		
			Station 1	2	3	4					Measured	Theoretical	
Untreated	Two-burner system												
	Normal	1.0		17		4	< 150	0	90	37	1 187-1 276	1 650	
1/1 500 treated	Normal	6.0		53		20	262	220	200	130	734-1 175	1 230	
		0.6		3		0	< 150	0	90	10	1 988-2 021	1 695	
1/1 000 treated	Normal	5.5		45		23	262	185	130	110	1 218-1 441	1 270	
		0.5		12		4	< 150	0			1 267-1 674	1 695	
Untreated	Single-burner system												
	Low	3.0		5		2	< 150	0			1 007-1 316	1 480	
Untreated	Normal	5.0		8		1	< 150	0			1 089-1 312	1 315	
		1.0		22		4	2	< 150	0	115	25	1 128-1 446	1 650
Untreated	High	5.0		41		6	6	252	55	140	72	921-1 037	1 315
		3.0		45			10	260	95			1 052-1 226	1 480
1/2 000 treated	Normal	5.0		34			18	265	180			932-1 172	1 315
		1.5				2	2	< 150	0	60	37	1 297-1 400	1 605
1/1 500 treated	Low	5.5				24	13	262	190	130	125	900-1 095	1 270
		3.5				3	1	< 150	0			1 015-1 204	1 435
1/1 500 treated	Normal	5.5				12	1	< 150	0			972-1 098	1 270
		1.5				1	1	< 150	0	90	20	1 169-3 576	1 605
1/1 500 treated	High	5.5				13	13	265	145	126	100	719-3 316	1 270
		3.5				50	22	275	200			996-1 246	1 435
1/1 000 treated	Normal	5.5				70	25	260	325			901-1 087	1 270
		1.5				2	2	< 150	0	60	30	1 525-2 688	1 605
1/1 000 treated	Normal	5.5				16	10	260	90	115	90	3 151-3 211	1 270

## 6. Gas phase test results

### 6.1. SO<sub>3</sub>, acid dewpoint and R.B.U. measurements

Typical measurements of SO<sub>3</sub>, acid dewpoint and R.B.U., shown in Table 4, show a dependence on O<sub>2</sub> in the flue gas, firing rate, additive dosage rate and burner system. As would be expected both SO<sub>3</sub> and R.B.U. increase sharply with O<sub>2</sub>, although the acid dewpoint changes little. In general, SO<sub>3</sub> measurements decreased progressively between Stations 1 and 4 in all tests.

With the two-burner system both SO<sub>3</sub> and R.B.U. measurements were higher with untreated oil than with additive-treated oil. On the other hand, the single-burner system yielded higher SO<sub>3</sub> and R.B.U. measurements with additive-treated oil than with untreated oil. This anomaly is apparently due to the greater adsorption of SO<sub>3</sub> 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.

### 6.2. Nitrogen oxide measurements

Measurements of NO<sub>2</sub> and total nitrogen oxides (NO<sub>x</sub>) were taken at the transition section and at the breeching, but there was found to be no significant difference due to location. Table 4 shows average NO<sub>x</sub> and NO<sub>2</sub> concentrations v. O<sub>2</sub> in the flue gas for both the two-burner and the single-burner systems, burning untreated and additive-treated oil.

There is a fairly clear-cut reduction in NO<sub>x</sub> with increasing additive dosage, but the NO<sub>2</sub> concentration, while decreasing with additive dosage, is at a higher level than with untreated oil until the dosage rate reaches 1/1000. This is similar to the trends found in SO<sub>3</sub> and R.B.U. measurements under comparable conditions. It may be noted that with regard to untreated oil, NO<sub>x</sub>

formation increases more rapidly with O<sub>2</sub> 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.

### 6.3. 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, reported as methane, ranged from 5 to 12 ppm by volume for both untreated and additive-treated oil, while no aldehydes were detected by the analytical technique used.

### 6.4. Gas phase carcinogens

During normal load tests with untreated oil at 1% and 3% O<sub>2</sub> in the flue gas, it was found that soot-free flue gas contained no measurable carcinogens. Mukai *et al.*<sup>5</sup> 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.

### 6.5. SO<sub>2</sub> measurements

Table 4 gives some typical results from the SO<sub>3</sub> measurements which, as previously explained, were taken in series with the SO<sub>3</sub> measurements. It can be seen from Table 4 that the measured SO<sub>3</sub> values were sometimes higher and sometimes lower than the theoretical values calculated from the sulphur content of the fuel. A.P.I. Procedure 774-54 for sulphur oxides is apparently susceptible to interferences by organic acids and nitrogen oxides, therefore an adaptation of the U.S.P.H.S. West-Gaeke Method,<sup>6</sup> which is specific for SO<sub>3</sub>, will be used in future experiments.

## 7. Particulate matter test results

### 7.1. Control of acid soot and low-temperature corrosion

As a result of the anomalies noted during the gas phase SO<sub>2</sub> measurements, detailed studies were undertaken to determine the role of soot 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<sub>2</sub> levels in the flue gases ranging from 1 to about 6%.

#### 7.1.1. Mechanism of acid soot formation in low-pressure steam boilers when burning untreated oil

The following postulated mechanism, based on theoretical considerations,<sup>7</sup> and the test results, indicate 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 concentrations high enough to act as heterogeneous nucleation sites for condensation of supersaturated SO<sub>3</sub> (H<sub>2</sub>SO<sub>4</sub>) 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<sub>3</sub>, and acid soot concentrations in the combustion gases leaving the furnace. This explains the low measured values of SO<sub>3</sub> and R.B.U. 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.

#### 7.1.2. Neutralization ratio of soot in flue gas

Soot samples, collected at Stations 3 and 4, were analysed chemically for sulphates in the form of reaction products (SO<sub>4</sub><sup>0</sup>) and free sulphuric acid (SO<sub>4</sub><sup>-</sup>), and the following ratio was used to assess the conversion of SO<sub>4</sub><sup>-</sup> to SO<sub>4</sub><sup>0</sup> under different combustion conditions:

$$\text{Neutralization ratio} = \frac{\text{SO}_4^0}{\text{SO}_4^0 + \text{SO}_4^-}$$

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 Fig. 2, neutralization ratios at the transition section for normal firing rates are lowest for untreated oil and progressively increase with additive dosage rate.

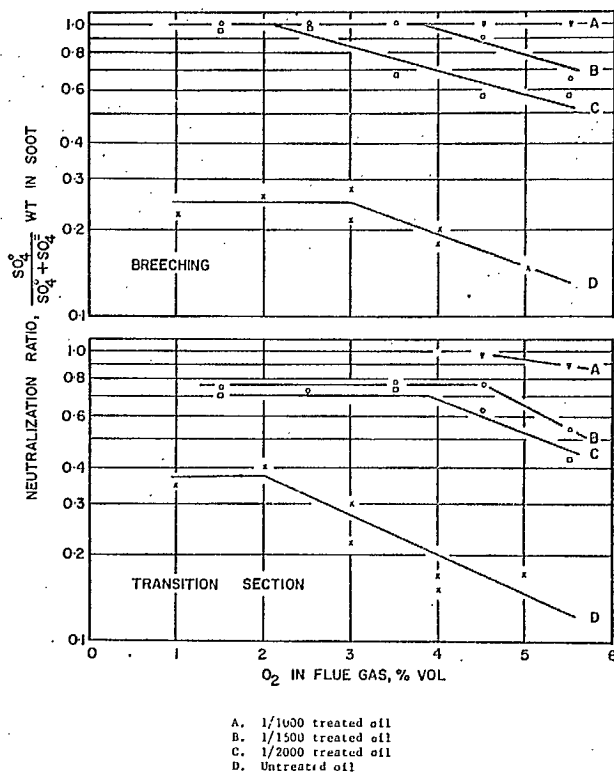


FIG. 2 Neutralization ratio plotted against O<sub>2</sub> in flue gas for untreated and treated oil, single-burner system, normal firing rate.

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<sub>2</sub> 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 Fig. 2 that when operating at O<sub>2</sub> levels down to 1%, the soot from 1/1 500 treated oil contains little or no free acid, while the soot from untreated oil is still relatively acidic. Therefore, in combustion systems where O<sub>2</sub> in flue gas cannot be reduced below 1%, successful control of acid soot can be achieved by using the additive described in Table 2.

In general, neutralization ratios for untreated oil and 1/1 500 treated oil were independent of firing rate with one exception. At low firing rate with additive-treated oil the neutralization ratio decreases appreciably with only about 40% of the sulphate in the soot being neutralized. The neutralization ratios at low firing rate were the same at both the transition section and breeching and this suggests that, if sufficient additive is present at low firing rates, acid soot particles are rendered dry and non-corrosive by physical dilution until chemical neutralization is complete. This method of acid inhibition is evident from Fig. 4 described later.

#### 7.1.3. 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 build-up 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 continual blockage and corrosion problems. In the research boiler, the Mg : V ratio of soot decreased gradually with increases in mean residence time of flue gas when burning additive-treated oil, as shown in Fig. 3. 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.

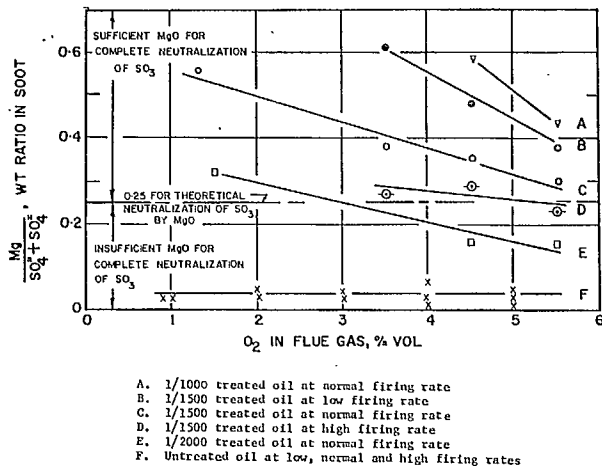


FIG. 4 Effect of additive dosage rate, firing rate and O<sub>2</sub> in flue gas on magnesium/sulphate ratio in soot at the breeching single-burner system.

Levy and Merryman<sup>8</sup> have demonstrated that MgO-coated iron reacts with SO<sub>3</sub> stoichiometrically to produce MgSO<sub>4</sub> which physically retards the contact of flue gas with iron.

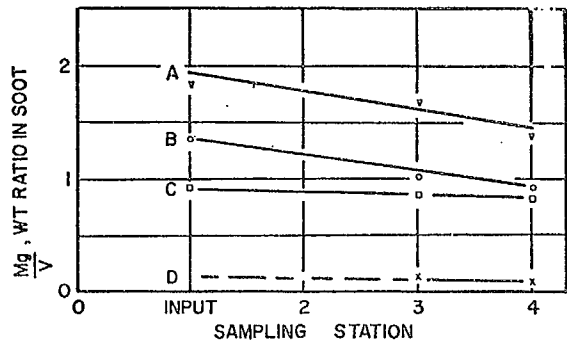
7.1.4. Optimum additive properties and dosage rate

If the aforementioned mechanism of acid soot formation (Section 6.1.1) is valid, an additive to control SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> 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
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<sub>4</sub><sup>o</sup> + SO<sub>4</sub><sup>=</sup>] as a function of O<sub>2</sub> in the flue gas, firing rate and additive dosage rate. The results, shown in Fig. 5, verify that an additive dosage rate of 1/1 500 by volume is sufficient to neutralize acid soot produced under the combustion conditions selected. At O<sub>2</sub> levels below 2% and at low firing rates the additive dosage rate can be reduced by at least 33% to compensate for corresponding reductions in SO<sub>3</sub> formation. These



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

FIG. 3 Variation of Mg/V ratio in soot between sampling stations for untreated and treated oil, single-burner system, normal firing rate.

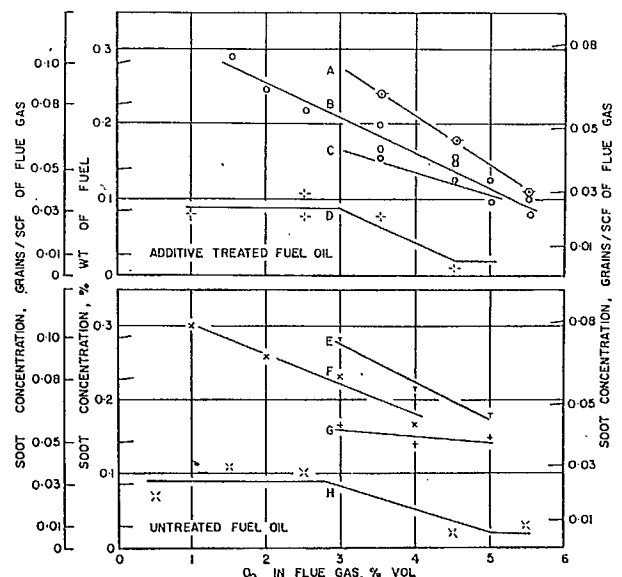
conclusions agree with observations made during additive trials in operational boilers, where additive treatment of oil effectively prevented cold-end corrosion and acid soot emission.

7.2. 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.

7.2.1. Soot concentration

The soot concentration in the flue gas is shown in Fig. 5 as a function of O<sub>2</sub> in flue gas, firing rate and burner



- 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. 5 Effect of additive dosage rate, firing rate and O<sub>2</sub> in flue gas on soot concentration at the breeching.

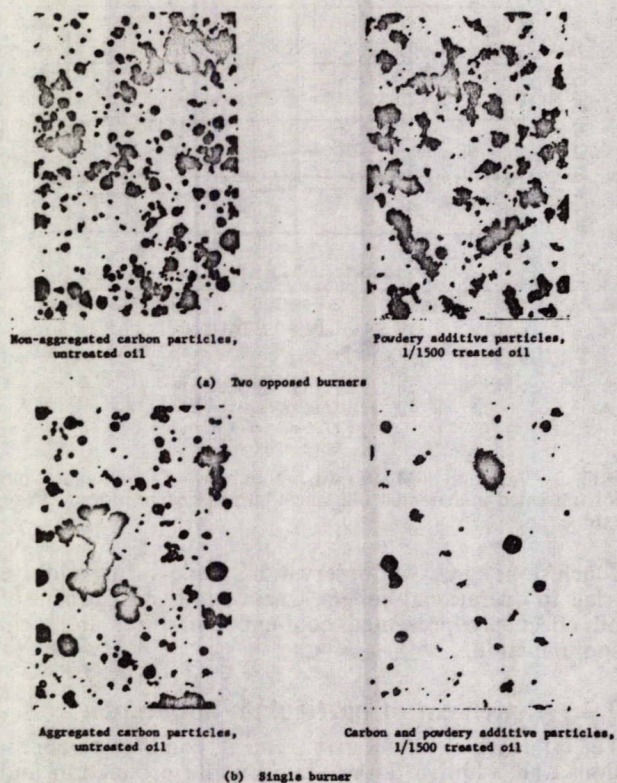


FIG. 6 Photomicrograph of soot particles for untreated and 1/1 500 treated oil, normal firing rate. Magnification  $\times 160$ .

arrangement when burning both untreated and additive-treated oil. Referring to the single-burner tests at normal firing rate, it is evident that soot concentrations increase with decreases in O<sub>2</sub>, 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% weight of fuel which compares favourably with a British Standard of 0.4% weight<sup>9</sup> and North American Standards that range upward from 0.8% weight of fuel.<sup>10,11</sup>

In tests with the two-burner system, soot concentrations were even lower for both untreated oil and 1/1 500 treated oil because of highly turbulent air-fuel mixing that prevailed.

### 7.2.2. Physical characteristics of soot

Microscopic examinations of soot samples from both untreated oil and 1/1 500 treated oil at normal load revealed a variety of particle forms ranging from 30 $\mu$  cenospheres to sub-micron granules. Particulate aggregates ranging from 10 to 70 $\mu$  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 illustrated in Fig. 6, while the physical properties of the soot are summarized in Table 5. 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.

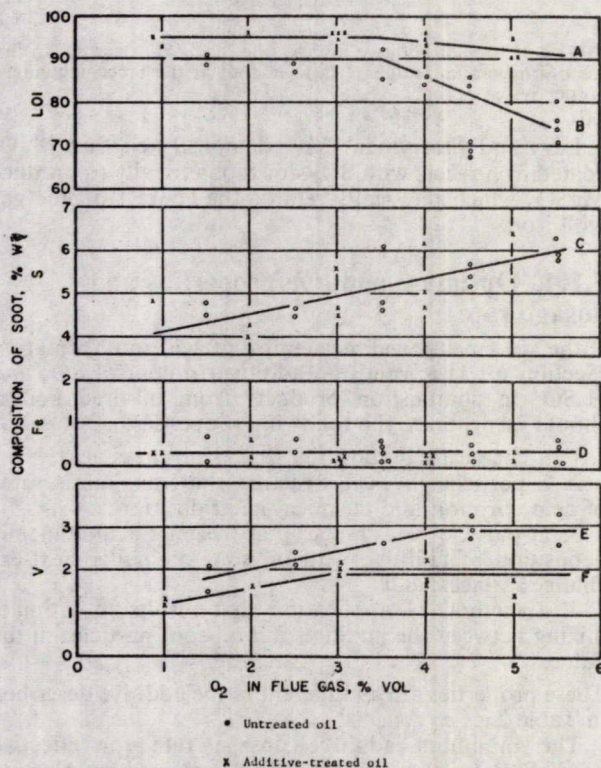
To illustrate the practical advantages of improvements in soot electrical resistivity, reference is made to Fig. 5 which shows maximum soot concentrations at the

TABLE 5 Physical properties of soot

Burner arrangement	Fuel oil	Soot properties		
		Description of particles	LOI %	Electrical resistivity $\Omega/\text{CM-ft}$
Two opposed burners	Untreated	Damp, non-aggregated	75-90	$10^9-10^9$
	1/1 500 treated	Dry, free flowing	65-80	$10^{10}-\infty$
Single burner	Untreated	Wet, sticky aggregates	92-95	$10^9-10^9$
	1/1 500 treated	Dry, free flowing	75-90	$10^{10}-\infty$

breaching of about 0.3% weight of fuel corresponding to 0.10 grains/S.C.F. of flue gas. If an electrostatic precipitator efficiency of only 90% 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% by weight of fuel or 0.01 grains/S.C.F. 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 1/1 500 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.



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. 7 Composition of soot at the breaching, for untreated and treated oil, single-burner system, normal firing rate.



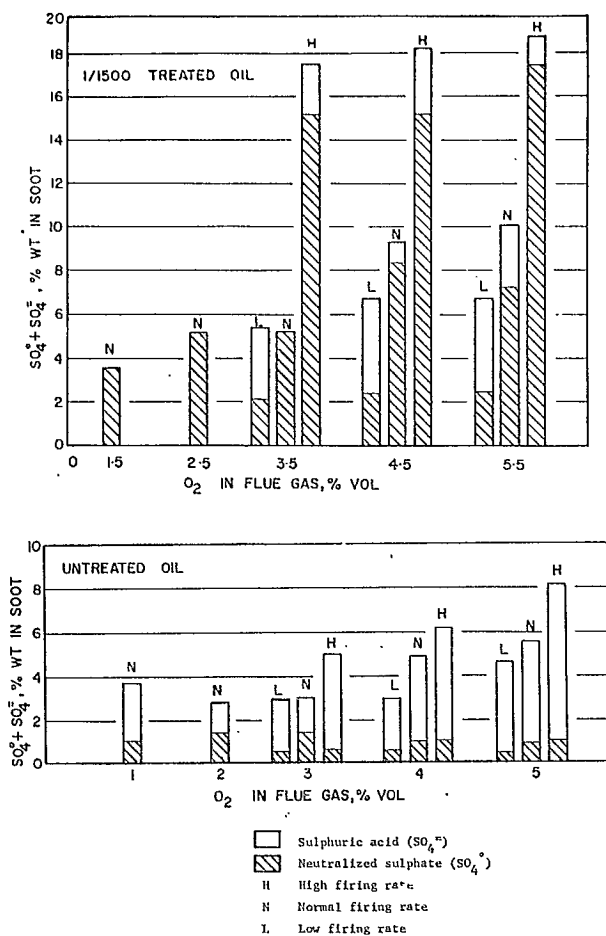


FIG. 8 Sulphate content of soot at the breeching, for untreated and 1/1 500 treated oil, single-burner system, normal firing rate.

### 7.2.3. 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 Fig. 7 for a range of O<sub>2</sub> 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<sub>2</sub> levels. Consequently, additive-treated oil soot looks encouraging as a source of vanadium.

Fig. 8 shows the neutralized sulphate and free acid content of soot at the breeching for both untreated oil and 1/1 500 treated oil at low, normal and high firing rates. These results, in conjunction with the neutralization data discussed in Section 7.1.2 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 1 500 gallons of oil. It can also be seen that (a) the free acid content of soot from 1/1 500 treated oil is much lower than soot from untreated oil, (b) the soot from 1/1 500 treated oil has higher acid sorption and neutralization capacities than soot from untreated oil, and (c) at O<sub>2</sub> levels below 3.5% the soot from 1/1 500 treated oil is completely neutralized while the soot from untreated oil still contains free acid.

The oily matter content in selected samples of soot from untreated and additive-treated oil ranged from 656 to 11 573 µg/g of soot. This oily matter appears to be essentially unburnt fuel oil, and tends to concentrate in the — 2 µ size particles which comprise about 20% 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/1 000 Nm<sup>3</sup> of flue gas, contained less than ambient air levels in Ottawa which range between 0.18 and 3.40 µg/1 000 Nm<sup>3</sup> of air. These findings agree with data reported by Howe<sup>12</sup> who concluded that oil-fired combustion systems are unlikely to emit abnormal levels of carcinogenic irritants.

### 7.2.4. 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 for untreated oil and additive-treated oil respectively at normal firing rates, can be summarized thus:

1. Less than 1% 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<sub>2</sub> levels between 1% and 5% about 65% of the sulphur is present in non-sulphate form, 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<sub>2</sub> levels increase; therefore, the additive should minimize the risk of high-temperature corrosion due to localized sulphidation attack at O<sub>2</sub> levels over 3%.

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

## 8. Conclusions

While the numerical levels of SO<sub>3</sub>, R.B.U., NO<sub>2</sub> and other measurements made on the combustion research boiler may not necessarily be directly extrapolated 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<sub>2</sub>SO<sub>4</sub> content of soot from burning untreated oil decreases gradually with decreasing O<sub>2</sub> levels in the flue gas; however, the soot still contains free acid at an O<sub>2</sub> level of 1%. With additive-treated oil, any H<sub>2</sub>SO<sub>4</sub> in soot is physically and/or chemically inhibited at all O<sub>2</sub> levels up to 5%.

- (b) Additive treatment of the oil removes NO<sub>x</sub> and SO<sub>3</sub> 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<sub>3</sub> and condensed H<sub>2</sub>SO<sub>4</sub> 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 resistivity 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  $\text{SO}_3$  and R.B.U. readings in flue gas farther downstream. Therefore, any assessment of corrosion potential in this type of equipment must be analysed 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,  $\text{SO}_3$  and R.B.U. levels increase sharply with increasing firing rate.

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## Appendix—A method for determining the relative electrical resistivity of soot particles emitted from residual oil flames

The apparatus for measuring the electrical resistivity of soot particles 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 20  $\mu$ . The resistivity equation for the apparatus described is given by

$$\rho = \frac{A}{L} \left( \frac{E}{I} \right)$$

where  $\rho$  = resistivity,  $\Omega$ /CM-ft (ohms/circular mil ft)

$E$  = potential difference, volts

$I$  = current, amperes

$A$  = cross-sectional area of the conductor  
= 62 500 CM

$L$  = length of conductor, ft  
= 0.021 ft

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