



DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA

*CONTROL OF OIL ASH DEPOSITS
AND POLLUTION ABATEMENT
BY AN ADDITIVE*

G. K. LEE

FUELS RESEARCH CENTRE

Reprinted from the Fuel Society Journal, Volume 20, 1969.

© Crown Copyrights reserved

Available by mail from the Queen's Printer, Ottawa
and at the following Canadian Government bookshops

HALIFAX
1735 Barrington Street

MONTREAL
Æterna-Vie Building, 1182 St. Catherine St. West

OTTAWA
Daly Building, Corner Mackenzie and Rideau

TORONTO
221 Yonge Street

WINNIPEG
Mall Center Bldg., 499 Portage Avenue

VANCOUVER
657 Granville Street

or through your bookseller

Price 50 cents Catalogue No. M38-8/92

Price subject to change without notice

Queen's Printer for Canada
Ottawa, 1970

Control of Oil Ash Deposits and Pollution Abatement by an Additive

by G. K. LEE, B.Sc., M.Sc., P.Eng.†

ABSTRACT

The formulation and principal properties of a fuel-oil additive developed by the Canadian Combustion Research Laboratory are described. The effectiveness of the additive in controlling problems that are universal to boilers burning high-vanadium, high-sulphur residual oil is discussed together with a detailed explanation of the additive's physico-chemical interactions with oil ash and combustion products. Results of additive trials in both operating boilers and combustion research rigs are presented.

1. INTRODUCTION

Problems associated with the burning of residual oil have been actively investigated in a broad research programme at the Canadian Combustion Research Laboratory (CCRL) since 1958. In the initial stages of this programme, fundamental studies of slag build-up in a combustion research rig provided data which inferred that the mechanism of oil-ash deposition was primarily one of vapour-phase diffusion¹. This postulation agrees with research conducted at Sheffield² and implies that slagging of boiler tubes cannot be overcome by simple boiler design modifications. Nonetheless, theoretical and experimental information available at³ that time indicated that slagging and corrosion in high-temperature regions of the boiler could be alleviated if a chemical additive for fuel oil could be found that would deposit simultaneously with the oil ash during combustion to modify the slag structure. This led to an evaluation of many proprietary and experimental materials of which the most effective proved to be a formulation of partially dehydrated hydroxides of magnesium and aluminium having a particle-size range of 1-7 microns. This, in turn, led to the development of a series of additives based on this formulation to suit a range of combustion conditions. They are now commercially available in North America with elemental magnesium to aluminum ratios ranging from 1 : 1 to 10 : 1.

Being satisfied that the slagging problem could be controlled as well as the high-temperature corrosion associated with it, research was then concentrated on the low-temperature corrosion problem. In the beginning it was obvious that the magnesium component of the additive would be ideally suited to chemically neutralizing sulphuric acid. This was verified both in laboratory studies and in field trials where cold-end corrosion was overcome and air pollution was reduced.

This paper first describes the additive and then explains how it (a) alleviates high-temperature deposits and corrosion, (b) controls low-temperature deposits and corrosion, (c) reduces SO₃ and NO_x in flue gases, and (d) abates acid smut emission.

† Research Scientist, Canadian Combustion Research Laboratory, Fuels Research Centre, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

2. ADDITIVE FORMULATION

The fuel-oil additive contains finely divided, non-abrasive particles of partially dehydrated hydroxides of magnesium and aluminum suspended and dispersed in a hydrocarbon carrier with a suitable surfactant. Chemically, the magnesium and aluminum active ingredients can be denoted by $\text{MgO} \cdot x\text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3 \cdot y\text{H}_2\text{O}$ respectively where $x < 1$ and $y < 3$.

The optimum size range of the partially dehydrated hydroxide particles was found to be 1 to 7 microns. This size range provides the optimum physical conditions for control of deposition rate and deposit structure. Furthermore, the specified active ingredients have high specific surface to maximize chemical reaction with combustion residues in gas, vapour and liquid state and their pore diameters range from 17 to 20 Angstroms to achieve optimum physical adsorption of gas-phase pollutants.

The surfactant, which is used to keep the partially dehydrated hydroxide particles in suspension is compatible with both the active ingredients and the hydrocarbon carrier. It transforms the highly viscous, two-phase mixture into a free-flowing, pumpable suspension that blends readily with fuel oil. By using surfactant concentrations ranging from 0.7 to 3.5% by weight, it has been possible to manufacture stable additive suspensions having (a) an elemental magnesium to aluminum ratio ranging from 1:1 to 10:1, (b) a solids content of 40–60% by weight, (c) a Saybolt viscosity of less than 115 universal seconds at 45°C, and (d) a pour point of -24°C.

3. ADDITIVE EVALUATION

3.1 ALLEVIATION OF HIGH-TEMPERATURE DEPOSITS AND CORROSION

3.1.1 *Laboratory Combustion Rig Experiments*

In closely controlled laboratory combustion rig experiments³, an additive formulation, containing an elemental magnesium to aluminum ratio of 1 to 1, was particularly effective in changing normally dense, rock-like superheater slag, Fig. 1(a), into a friable, powdery deposit that was easily removed by routine

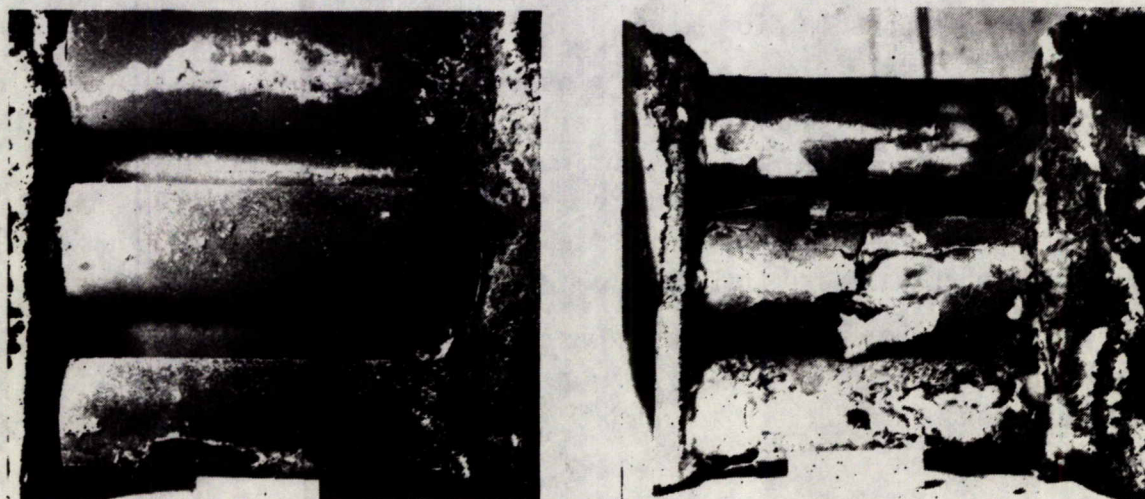


Fig. 1. Deposits on rig superheater upstream surface
(a) Untreated oil. (b) Additive-treated oil (dosage rate 1/1000 with $\text{Mg}/\text{Al} = 1/1$).

soot-blowing. The deposit build-up after using the additive was loosely bonded to the tubes and weakly agglomerated as shown in Fig. 1(b).

To clarify the role of additive properties, such as mineral composition and physical state in preventing slag formation, the deposits from both untreated and additive-treated oil were evaluated by chemical, X-ray diffraction and petrographic techniques. This evaluation^{1,3} revealed that (a) indigenous oil-ash deposits consisted mostly of interlocked needle-like crystals of 1 : 1 : 5 sodium vanadyl vanadate which melted at 625°C and that (b) the ash from additive treated oil was a highly porous, unconsolidated powder containing large amounts of magnesium oxide, magnesium sulphate and magnesia-alumina spinel together with smaller amounts of 1 : 1 : 5 sodium vanadyl vanadate and magnesium orthovanadate. Photomicrographs of typical thin sections of superheater deposits from a research rig after burning untreated and additive-treated oil are shown in Figs. 2(a) and 2(b) respectively.

By examining the mineral distribution in thin sections of deposits from additive-treated oil it was determined that the magnesium and aluminum active ingredients play independent but synergistic roles in modifying slag structure. The magnesium component transforms the normally molten slag deposits into a dry, friable ash by chemically inhibiting and physically diluting low-melting vanadium complexes. The latter effect minimizes high-temperature corrosion by preventing any molten slag constituents from coming in contact with metal surfaces.

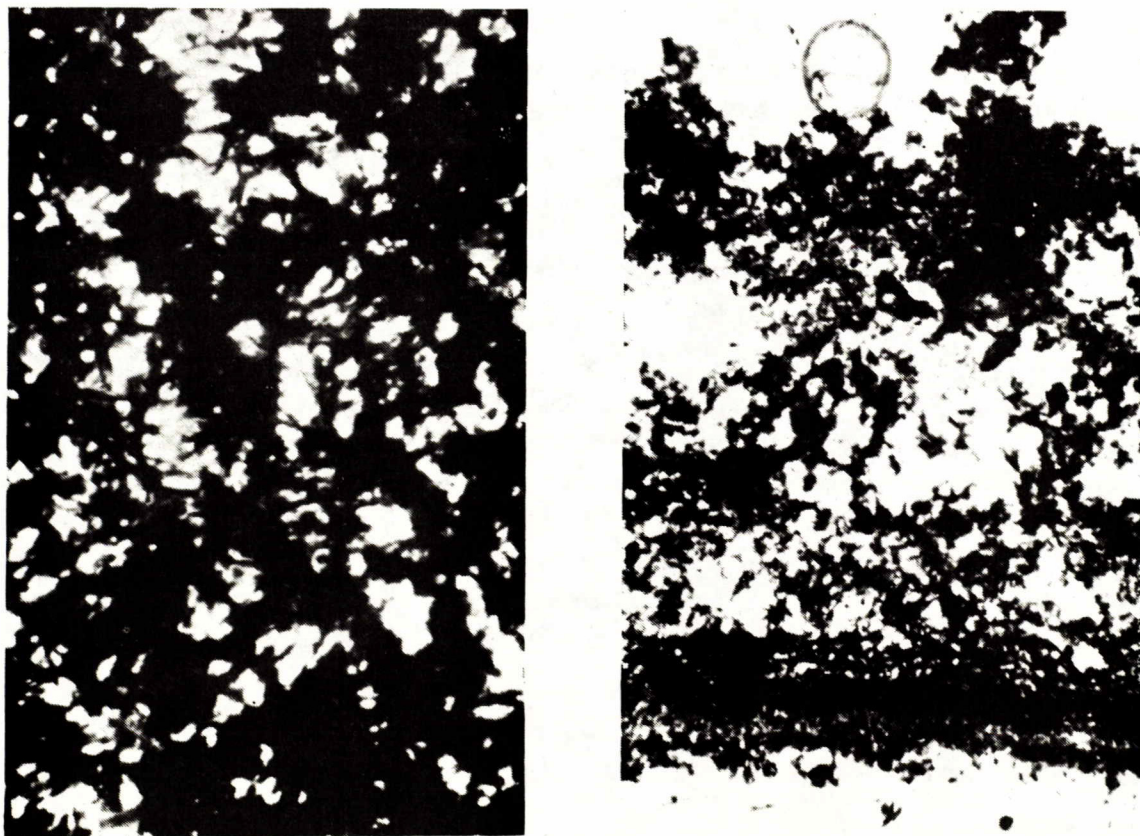


Fig. 2. Thin sections of rig superheater deposits

(a) Dense deposit of interlocked needle-like crystals from untreated oil. Magnification X150.

(b) Highly porous deposit having low cohesive strength from additive-treated oil (dosage rate 1/1000 with Mg/Al = 1/1). Magnification X15.

The aluminum component combines selectively with an equivalent weight of magnesia in a flame to form spinel which plays two important roles in modifying slag structure. The first role is to reduce the magnesium available for subsequent sulphation on tube surfaces. Obviously, the formation of magnesium sulphate, which is molten and sticky at 1172°C, should be minimized when gas temperatures at the furnace exit exceed 1200°C. Therefore, the additive is formulated with a ratio of elemental magnesium to aluminium of 3 to 1 or less. The second role of the spinel is to increase the friability and decrease the cohesive strength of a slag deposit by virtue of its cubic symmetry and octahedral shape.

Porosity measurements on deposit samples revealed that high porosity and large voids were specific to partially dehydrated hydroxides of magnesium and aluminum having a particle-size range of 1 to 7 microns. Control of particle size range is important because theoretical studies indicate that particles larger than 10 microns tend to form undesirable, densely impacted deposits. On the other hand, particles less than 0.5 microns tend to form undesirable cohesive deposits having small voids.

To summarize, the additive prevents both slagging and oil-ash corrosion of tube surfaces operating at temperatures up to 650°C by producing a dry, friable deposit having an ash fusion temperature of over 1600°C. However, when the additive is used in combination with low excess air there is a danger of converting complex sulphates in the inner deposit layer to sulphides which might be the source of catastrophic intergranular corrosion.

3.1.2 *Utility Boiler Evaluation*

To supplement the laboratory research, two power utility companies conducted additive trials in operating boilers. In both cases the boilers, which were rated at 360,000 lb/hr of steam at 900 psig and 900°F, were plagued with expensive maintenance and repair costs due to slagging and blocking of superheater elements every 4 to 6 weeks. Several proprietary anti-slugging additives had been tried during a four-year period but all were expensive and ineffective.

The COTL additive chosen for the trial contained an elemental magnesium to aluminum ratio of 10 to 1 and a dosage rate of 1 gallon of additive per 1500 gallons of fuel oil was used. It was of grave concern to the utility that nothing seemed to happen in a few days but, after four weeks it was found that (a) the hard, bonded slag build-up was replaced with a soft, friable powder that was easily removed by soot blowing, (b) bridging in the convection pass of the generating bank was eliminated, and (c) a light coating of additive oxides on the surface walls helped to raise superheat temperatures to design conditions for the first time¹. By continued use of the additive it is now possible to operate these boilers for at least 6 to 12 months without outages for boiler cleaning.

3.2 CONTROL OF LOW-TEMPERATURE DEPOSITS AND CORROSION

3.2.1 *Laboratory Research*

Combustion rig experiments using an elemental magnesium to aluminum ratio of 2 to 1, demonstrated that the additive reduced sulphuric acid corrosion on low-temperature boiler surfaces by 35 to 66% depending on the additive

dosage rate⁴. Laboratory studies have also shown that a thin, uniform layer of active ingredients builds up by a process of agglomeration on cold-end surfaces. The magnesium component of the deposit chemically neutralizes any condensed acid while the aluminum component increases the effectiveness of the magnesium component by providing a highly porous, or extended, surface that accelerates acid-neutralization reactions. The additive + acid reaction product forms a dry, powdery, loosely bonded deposit that is continually entrained by the gas stream and is replaced by unreacted additive. The net result is that cold-end surfaces are self-cleaning and are at the same time protected from sulphuric acid corrosion.

3.2.2. *Field Trials in Utility Boilers*

During the past two years, many field trials with an additive formulation containing an elemental magnesium to aluminum ratio of 10 to 1 have been conducted on a number of power utility boilers that experienced serious cold-end fouling and corrosion. In all trials, the additive was initially applied at the rate of 1 gallon per 1500 gallons of oil, after which the dosage rate was reduced to 1 in 1800.

At the end of eight weeks of operation with additive-treated oil, the draft loss across the airheater of each boiler remained constant, clearly indicating that plugging of the tubular airheaters had been overcome. Inspection of the airheaters later revealed that the additive had completely dried up the original gummy, corrosive cold-end deposits and replaced it with a thin coating of additive material that was loose and powdery.

The boilers, which are now operating regularly on additive-treated oil, no longer require soot-blowing in the airheater zone and regular bi-monthly boiler outages for cleaning and replacement of airheater elements have been eliminated. The extremely low rate of increase in draft loss across the airheaters of these boilers indicates that cleaning of fireside surfaces can be programmed to coincide with annual boiler maintenance.

3.2.3. *Field Trials in a Heating Boiler*

In Canada, typical heating boilers for office and apartment buildings operate with metal temperatures that are continuously or intermittently below acid dew-point. Traditionally this class of equipment with steel tubes suffers from accelerated corrosion due to heavy condensation of sulphuric acid even on surfaces that may be within sight of flame. In severe cases, corrosion rates of up to 50 mils per year are common, with the result that tubes and sometimes tube sheets must be replaced after one or two years of service.

Low-temperature corrosion under these conditions was suppressed completely in a typical heating plant by using an additive containing an elemental magnesium to aluminum ratio of 10 to 1. In this field demonstration it was necessary to develop an additive injection system to suit the boiler "on-off" cycle as well as low oil burning rate that requires an additive dosage rate of only 0.01 gallon per hour. This system employs a Moyno-type pump to recirculate continuously a 25% by volume blend of additive in fuel oil and a solenoid valve to meter the additive blend into the oil burner supply line on demand.

TABLE 1. Emission of NO_x and SO₃ from CCRL Research Boiler^{1/}

Fuel Oil	Firing Rate	Furnace Heat Release Rate Btu/cu ft/hr	Nitrogen Oxides (NO _x)		Sulphur Trioxide (SO ₃)	
			Measured, ppm v/v	Neutralized by additive %	Measured, ppm v/v	Neutralized by additive
Untreated	Normal	49,700	258	0	10.4	0
	High	66,250	260	0	16.1	0
Additive-treated Dosage Rate 1/1500) (Mg : Al = 10 : 1)	Normal	49,700	181	30	3.0	71
	High	66,250	227	13	3.2	80

^{1/}Data shown are for a boiler steam pressure of 15 psig and flue gases containing 5%O₂.

After 4 months of additive treatment the boiler surfaces were inspected and found to be coated with a thin, powdery deposit that contained mostly magnesium sulphate with smaller amounts of magnesium oxide; no corrosion products or acidic residues were detected. Corrosion rates are now well below the economic limit of 5 mils per year and routine cleaning of heavily fouled boiler tubes has been eliminated. It is expected that use of the additive will extend the life of this boiler by 10 years or more.

3.3 REDUCTION OF SO_3 AND NITROGEN OXIDES IN FLUE GASES

Laboratory research, presently in progress, has shown that the additive effectively neutralizes 13 to 30% of NO_x and 71 to 80% of SO_3 in boiler flue gases. Typical data taken from the CCRL research boiler when burning a 2.5% sulphur residual oil are shown in Table 1. The same trend in SO_3 reduction was found in one field trial where an additive formulation and dosage rate identical to that used in the laboratory experiments resulted in a 90% reduction of SO_3 in the stack gases. During this trial, SO_3 levels were reduced from 30 to 3 ppm and the white acid plume from the stack was eliminated.

3.4 ABATEMENT OF ACID SMUT EMISSION

Another benefit from using the additive has been the abatement of acid smut emission. When the additive is not used, soot soaked with sulphuric acid normally builds up on the cold-end surfaces and on the stack lining to some equilibrium thickness, and then periodically breaks free. When emitted to atmosphere these corrosive, sticky flakes of acid smut fall on people and property creating a serious nuisance problem and in some cases considerable damage to fabrics, crops and automobile finishes.

The formation and control of acid smut in low-temperature heating boilers have been investigated in the laboratory and the experimental results will be published early in 1969⁵. In this investigation, the additive converted the normally sticky, corrosive acid smut into a dry, inert, free-flowing powder having a high electrical resistivity. Fig. 3 shows the sulphuric acid and the neutralized sulphate content of soot emitted to atmosphere from the combustion of both untreated and additive-treated oil. These data confirm that (a) the free-acid content of soot from additive-treated oil is much lower than for untreated oil, (b) the soot from additive-treated oil has higher acid-sorption and acid-neutralization capacities than soot from untreated oil, and (c) at O_2 levels below 3.5% the soot from untreated oil still contains free acid. The effect of additive treatment on soot structure is clearly illustrated in Fig. 4.

In large oil-fired boilers temperatures in economizer and air-heater elements often fall below the acid dewpoint. When this occurs, and the additive is not used, electrostatic precipitators should be by-passed because of the potential fire hazard from the wet, combustible acid smut that is usually present. In such cases, smut emission is particularly bad and atmospheric-pollution ordinances are likely to be violated.

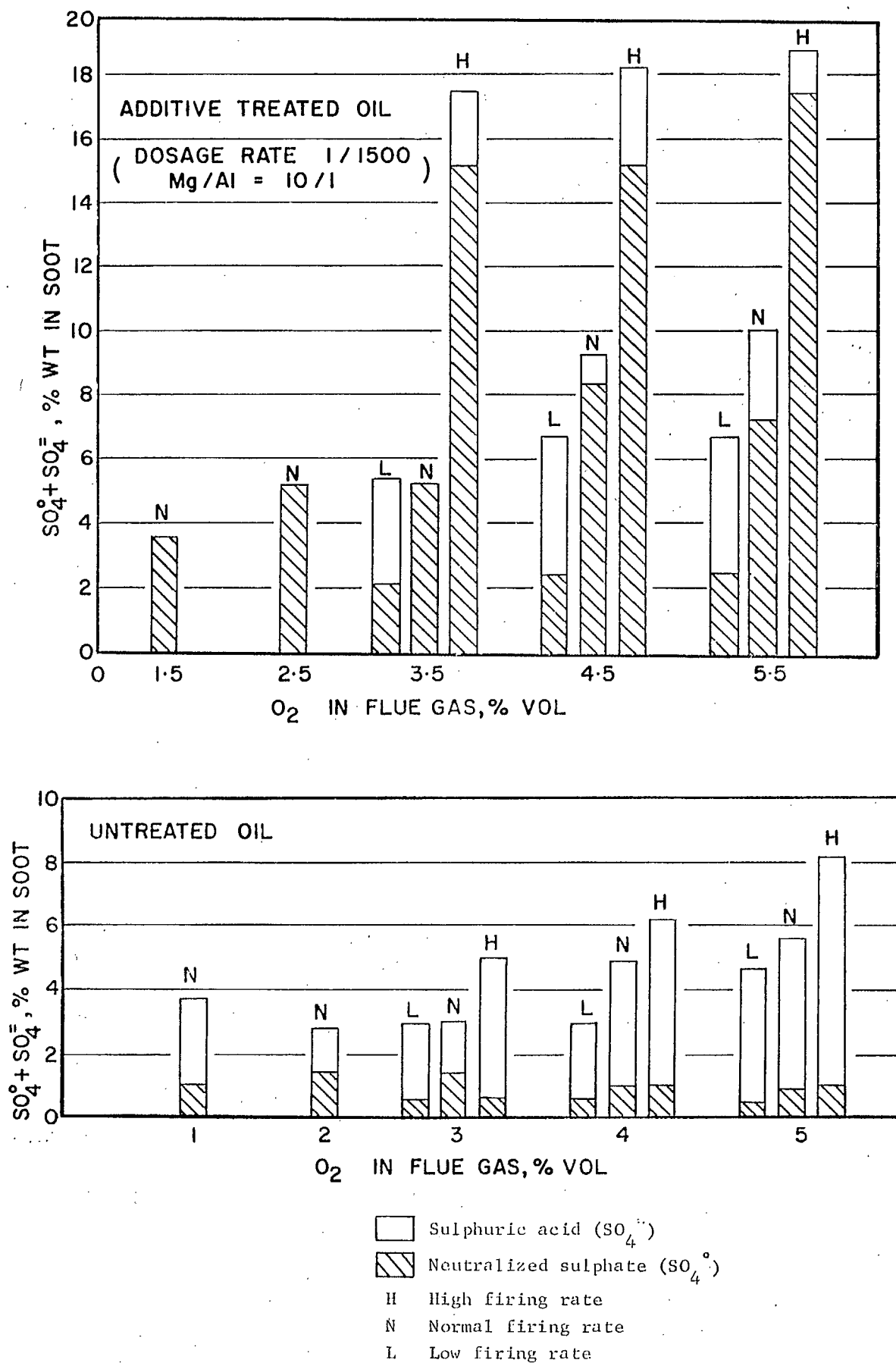


Fig. 3. Sulphate content of soot from untreated and additive-treated oils.



Fig. 4. Photomicrograph of soot particles. Magnification X160.

(a) Corrosive, sticky smut from untreated oil.

(b) Dry, powdery residue from additive-treated oil (dosage rate 1/1500 with Mg/Al = 10/1).

This problem was eliminated entirely in power utility boilers by applying an additive formulation containing an elemental magnesium to aluminum ratio of 10 to 1 at the rate of 1 gallon of additive per 1500 gallons of fuel oil. Furthermore, the electrical resistivity of the solid residues leaving the boiler was improved to the extent that particulate matter can now be collected by the electrostatic precipitators. This solid residue, being dry and powdery is also easily removed from boiler and dust-collector hoppers.

4. CONCLUDING REMARKS

The CCRL additive is a specific, quality-controlled formulation that inhibits oil ash and combustion products by well-defined physico-chemical interactions and provides an effective means of controlling or eliminating some boiler problems. Economic benefits arise from increased boiler availability and efficiency, reduced maintenance and fuel costs, and in some cases a financial credit on the sale of vanadium-rich ash. Another, but less tangible benefit is the favourable public image created by minimizing the emission of some noxious atmospheric pollutants.

The additive, which is normally metered continuously and automatically into the oil supply to each burner, can be formulated to the particular requirements of a particular boiler. Additive dosage rates are determined by sulphur and vanadium in the fuel while the ratios of magnesium to aluminum are determined by the combustion conditions at the furnace exit.

5. ACKNOWLEDGEMENTS

This work forms part of a continuing research program at the Canadian Combustion Research Laboratory where flame research and combustion source pollution are considered inseparable. Permission to publish this paper by the Director, Mines Branch, Department of Energy, Mines and Resources is appreciated.

6. 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. Amer. Power Conf., Vol. XXVIII (1966), pp. 613-630.
2. HEDLEY, A. B., BROWN, T. D. and SHUTTLEWORTH, A. Vanadium Pentoxide Deposition for Combustion Gases. ASME Paper 65-WA/CD-2.
3. LEE, G. K., MITCHELL, E. R., GRIMSEY, R. G. and HOPKINS, S. E. An Investigation of Fuel-Oil Additives to Prevent Slagging in Naval Boilers. Proc. Amer. Power Conf., Vol. XXVI (1964), pp. 531-552.
4. Private Communication, BP Canada Limited.
5. LEE, G. K., MITCHELL, E. R. and FRIEDRICH, F. D. Control of SO₂ in Low-pressure Heating Boilers by an Additive. J. Inst. Fuel (to be published 1969).

