



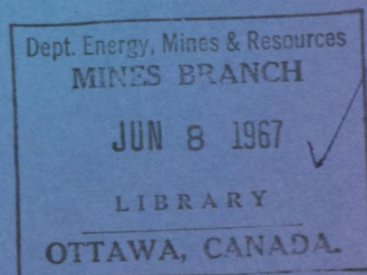
DEPARTMENT OF  
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MINES BRANCH  
OTTAWA

*CONTROL OF OIL-ASH SLAGGING  
BY AN ADDITIVE*

G. K. LEE AND E. R. MITCHELL

FUELS AND MINING PRACTICE DIVISION

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# Control of Oil-Ash Slagging by an Additive

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Conventional cleaning methods were found to be inadequate for removing slag deposits from high-temperature heat-transfer surfaces of oil-fired boilers. The research project described in this paper first established that minute interconnecting voids in slag deposits were sufficiently large to allow penetration by water treated with a suitable surfactant. From this was developed a practical water washing procedure that has been adopted as routine maintenance in certain marine boilers.

Subsequently, fundamental combustion studies established that the mechanism of deposition for indigenous oil-ash constituents is primarily one of molecular diffusion. This finding indicates that new and radical burner and boiler design concepts are needed to overcome operational problems when untreated high-vanadium fuel oils are burned.

Also described is a program of research on fuel oil additives to alleviate the superheater slagging problem. This includes the evaluation of many additive materials in a laboratory combustion rig and the development of a particular magnesia-alumina formulation that has promise as a practical and effective additive.

Several large power utility boilers are now operating regularly on additive formulations developed through this research program, and preliminary reports indicate a high degree of success.

IN THE PAST DECADE, rapid advances in the design and operation of large residual oil-fired boilers have created many new and unresolved technical problems. One of the more serious problems, the loss of boiler availability and efficiency due to slagging of high-temperature boiler heat-transfer surfaces, has been actively studied since 1958 in a continuing research program at the Department of Energy, Mines and Resources in Ottawa.

The severity of the oil-ash deposition problem is evident from Fig. 1, which shows the partially blocked gas passages of a superheater after only a few months operation.

The hard, rock-like deposits were so strongly bonded to the tubes that the inner deposit layer, shown in Fig. 2, could not be completely removed by pneumatic hammers.

Detailed laboratory studies by the authors revealed that the slag deposits contained a network of minute interconnecting pores and that the inner layer was a water-soluble sulphate. In addition, bench scale ex-

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periments established that the deposit pore structure was impervious to water but could be penetrated by water treated with a penetrating-type surfactant.

These findings led to the development of a slag removal process which is now being used successfully to clean marine boilers. Essentially, the process involves soaking the slagged surfaces of the cold boiler for about 48 hr. with water containing 0.1-0.2 per cent by weight of a suitable surfactant. This soaking process dissolves and weakens the adherent inner layer

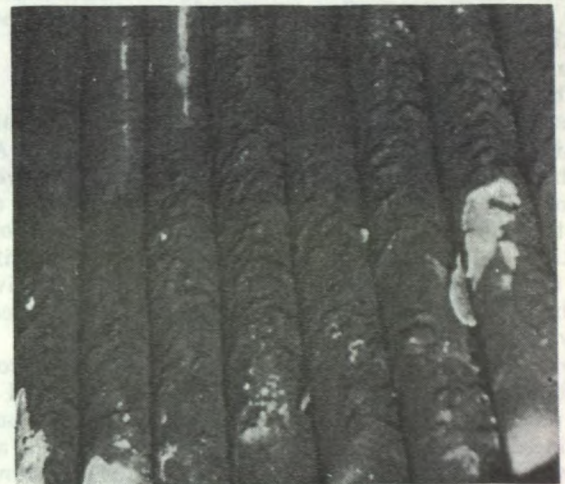


Fig. 1 Superheater of a residual oil-fired boiler before deposit removal.

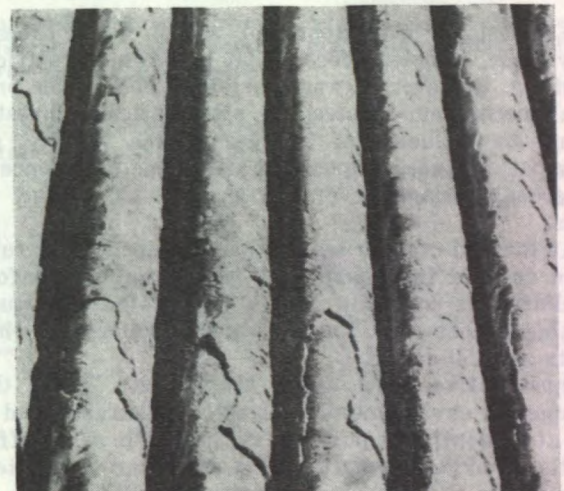


Fig. 2 Superheater of a residual oil-fired boiler after deposit removal by mechanical means.

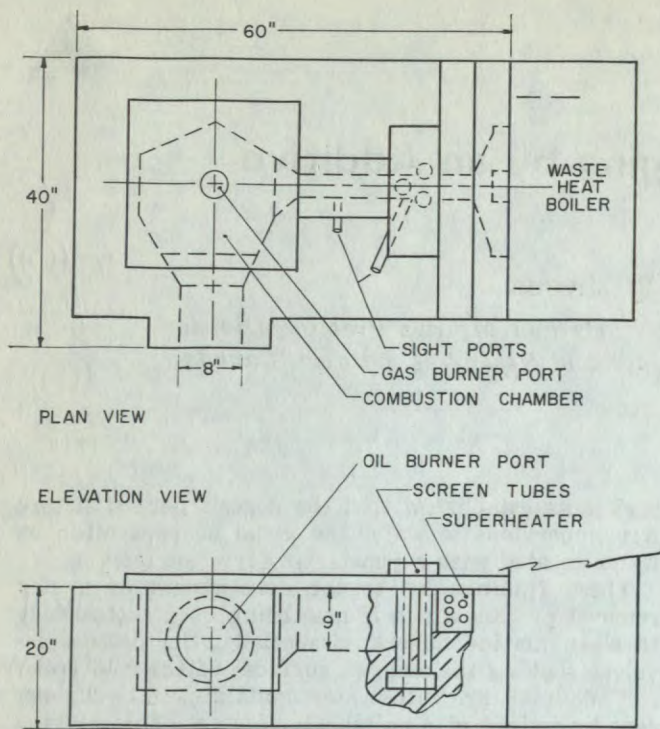


Fig. 3. Laboratory combustion rig.

to the extent that slag deposits can be removed to bare metal by ordinary water lancing.

The slag removal process, although satisfying an urgent need, does not solve the basic problem of maintaining clean boiler surfaces during operation. Accordingly, two phases of the research program were planned to study means of controlling the oil ash deposition mechanism by improvements in both the combustion process and superheater design, and modifying the slag structure by the use of fuel-oil additives so that boiler surfaces may be cleaned by normal soot-blowing.

Both phases were carried out using a laboratory combustion rig that was designed to duplicate all of the physical-chemical conditions known to contribute to slag formation when high-vanadium fuel oils are burned. An illustration of the laboratory rig is shown in Fig. 3.

#### THE MECHANISM OF OIL ASH DEPOSITION

The deposition of untreated oil ash on boiler tubes is a dynamic, complex process that is extremely difficult to study. However, it was possible to deduce the principal mechanism involved by systematically investigating the influence of changes in gas velocity, gas flow pattern, gas composition and flame turbulence on superheater slagging during a series of 100-hr. rig tests.

At the end of each test all of the superheater tubes were encased in a hard, thin, fused slag of uniform thickness, as shown in Fig. 4. The major constituent of this deposit was sodium vanadyl vanadate, which melts at 1250 deg. F.

Quantitative data from these tests show that changes in environmental conditions, characterized by the aforementioned parameters, had little or no effect on the thickness, density, composition or fusion temperature of the resulting deposits. In addition, the deposition rate for each test remained relatively constant regardless of the tube surface area exposed to the gas

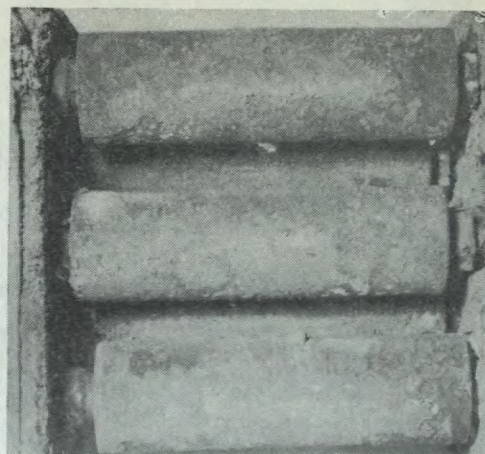


Fig. 4. Deposit on upstream surface of rig superheater after burning untreated fuel oil.

stream.

These observations indicate that most of the indigenous oil ash constituents migrate to the tube surfaces by molecular diffusion and that subsequent deposit build-up is controlled mainly by condensation or sublimation of compounds in the vapour state.

By petrographic examinations, these deposits were all found to consist of two distinct layers, as shown in Fig. 5.

The inner layer, shown at the lower left of Fig. 5, was composed of minute, glassy, cream-coloured granules that appear to have sublimated by rapid super-cooling from vapour phase. Being non-crystalline, these granules did not yield X-ray diffraction patterns, but chemical analysis indicated that sodium ferric sulphate may be present. This compound becomes liquid and highly corrosive at 1050 deg. F. Consequently, if tube surface temperatures exceed 1000 deg. F. a corrosion inhibiting additive must be used to prevent excessive tube wastage.

The outer layer consisted of a relatively thick layer of interlocked black and amber needle-like crystals, which were identified as sodium vanadyl vanadate and nickel orthovanadate, respectively. These needle-like crystals, shown in Fig. 6, appear to have grown gradually from vapour phase via condensation on localized crystal nucleation sites.

Despite changes in the aerodynamic and combustion conditions in the combustion rig, the structure

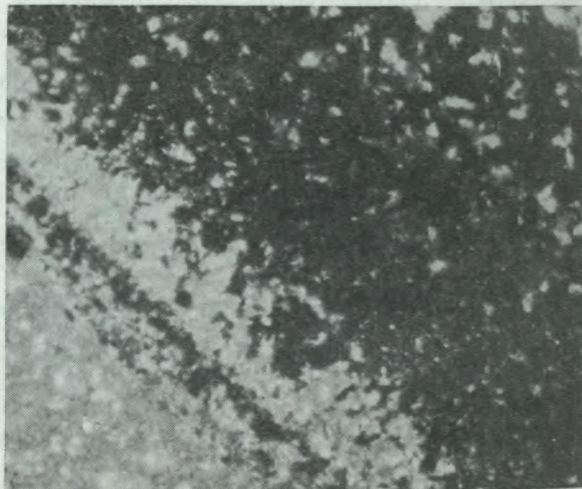


Fig. 5. Thin section showing layered structure of deposit from untreated fuel oil. Magnification,  $\times 15$ .

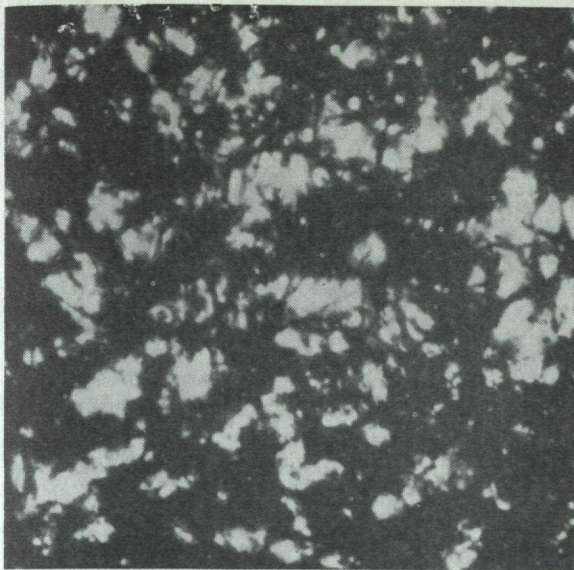


Fig. 6. Thin section showing random orientation of needle-like crystals in deposit from untreated fuel oil. Magnification,  $\times 150$ .

and the weight of both inner and outer deposit layers were relatively uniform. These findings are further confirmation that molecular diffusion is the dominant mechanism controlling deposition of oil ash on boiler tubes. It follows that slagging of heat transfer surfaces in operational boilers cannot be overcome by simple design modifications.

#### FUEL-OIL ADDITIVE EVALUATION

In order to assess the effectiveness of various fuel-oil additive compositions, 24 proprietary and experimental materials were used in a series of 100-hr. combustion rig tests. At the end of each test deposits from the rig superheater were evaluated by

- a. Chemical and X-ray diffraction analyses
- b. Ash fusion, absolute density and specific density determinations
- c. Petrographic examinations

These data, which are reported in detail elsewhere [1, 2], permitted an accurate quantitative assessment of any changes in deposit structure due to additive treatment of the fuel oil.

In general, most of the proprietary additives tested, produced deposits similar to those from untreated oil and were ineffective in changing the thermal-physical properties of the oil ash. For this reason, several experimental additives containing known compositions were blended in the laboratory from materials that were specially synthesized for miscibility with fuel oil. One of these, a suspension of magnesia and alumina particles in a light oil carrier, was particularly effective in producing a porous, friable, powdery deposit that can easily be removed by normal soot-blowing. As shown in Fig. 7, the deposit from the magnesia-alumina additive was loosely bonded to the tubes and weakly agglomerated.

#### THE ROLE OF MAGNESIA AND ALUMINA IN PREVENTING SLAG FORMATION

The deposits from the magnesia-alumina additive were subjected to an intensive thin-section investigation to clarify the role of additive properties, such as mineral composition and physical state, in preventing slag for-

mation. Microscopic examinations of deposit thin sections showed a thin, dense, unsintered layer of sub-micron particles next to the tube surface. Subsequent deposits, illustrated in Fig. 8, formed an intermediate upstream layer of friable, moderately porous material, an outer upstream layer having a thick, porous, wedge-shaped structure and an outer downstream layer of powdery, moderately porous, lightly sintered crystals.

By optical and X-ray diffraction methods, it was determined that a magnesia-alumina reaction product, known as spinel, was uniformly distributed throughout all four layers and that the proportion of magnesium sulphate to magnesium oxide increased progressively toward the tube surface. The work also revealed that most of the vanadium was concentrated in the intermediate upstream and the outer downstream layers as bands of sodium vanadyl vanadate and magnesium orthovanadate. The magnesia, therefore, prevents slagging of low-melting sodium and vanadium compounds by both mechanical dilution and chemical reaction.

On the other hand, alumina, which does not react chemically with any ash constituent, plays two important roles in modifying the slag structure. First, alumina, by reacting selectively with magnesia in the flame to form spinel, reduces the magnesia available for later reaction with sulphur oxides on the tube surface. The formation of magnesium sulphate, which is molten and sticky at 2,050 deg. F. should be minimized, particularly when gas temperatures at the fur-

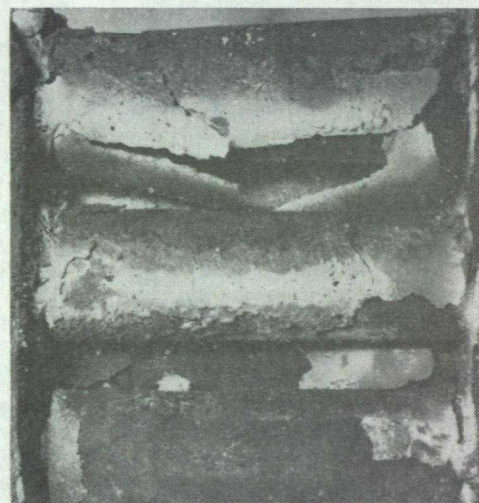


Fig. 7. Build-up on upstream surface of rig superheater after using suspended-solid magnesia-alumina additive developed in the laboratory.

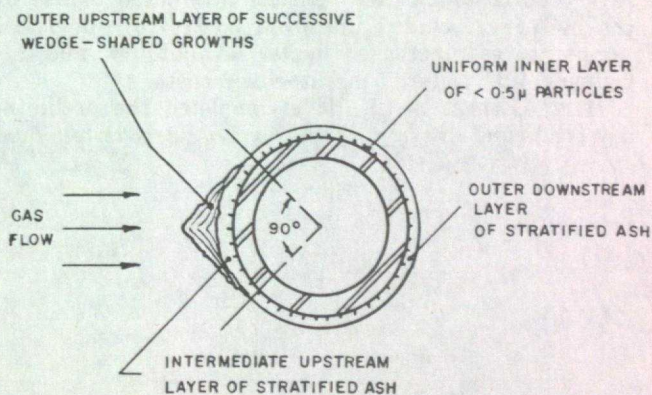


Fig. 8. Sectional illustration of deposit build-up after using suspended-solid magnesia-alumina additive.

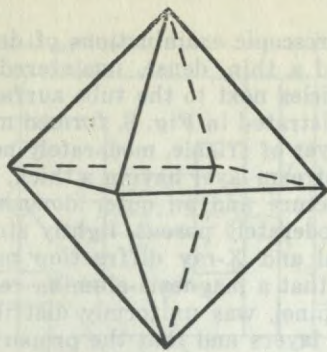


Fig. 9. Spinel crystal of octahedral shape having a cubic structure.

nance exit are above 2,100 deg. F. Secondly, the magnesia-alumina reaction product reduces the tendency of unreacted but superfine magnesia particles to agglomerate. This control over agglomeration is probably due to the presence of uniformly distributed spinel particles that form cubic crystals similar to that illustrated in Fig. 9.

Porosity measurements on deposit samples also revealed that high porosity and large voids (Fig. 10) were specific to magnesia-alumina additives having particle sizes ranging from 1 to 7  $\mu\text{m}$ . Control of particle size consist is important because theoretical studies indicate that particles larger than 10  $\mu\text{m}$  tend to form densely impacted deposits, whereas particles less than 0.5  $\mu\text{m}$  tend to form cohesive deposits having small voids.

To summarize, a magnesia-alumina fuel-oil additive, having the properties shown in Table I, is eminently suitable for controlling slag deposits on boiler surfaces.

This additive produces a porous, friable, flaky deposit that is characterized by a predominantly cubic crystal structure and an ash-fusion temperature of over 2,800 deg. F. When using the magnesia-alumina additive, tube surface temperatures can be maintained at 1,100 deg. F. without being corroded by oil ash constituents. However, during operation with low excess combustion air, complex sulphates in the deposit may cause catastrophic intergranular corrosion.

#### ADDITIVE TRIALS IN OPERATIONAL BOILERS

During the past year field trials with a magnesia-alumina fuel-oil additive have been conducted in a number of power utility boilers in the United States. In all trials, the additive, which was initially applied at the rate of 1 gal. per 1000 gal. of fuel oil, effectively suppressed both superheater slagging and low-temperature corrosion. Other benefits attributed to use of the additive included improved control of superheat temperatures, increased boiler availability and efficiency, and reduced maintenance costs.

Most of these plants have completed the preliminary trials and are now operating regularly on residual

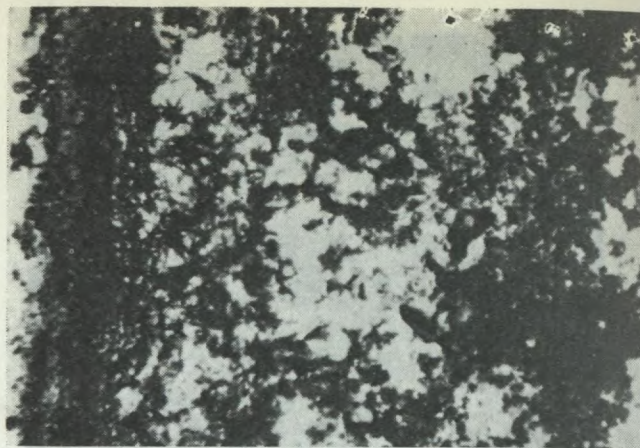


Fig. 10. Thin section showing porous deposit structure produced by using suspended-solid magnesia-alumina additive. Magnification,  $\times 15$ .

TABLE I Properties of Magnesia-Alumina Fuel-oil Additive.

Property	Specifications
Chemical composition.....	MgO + Al <sub>2</sub> O <sub>3</sub>
Solids content, % by weight.....	50
Magnesium-aluminum ratio.....	1:1 to 10:1
Particle size consist, $\mu\text{m}$ .....	1-7
Specific gravity at 70 deg. F.....	1.45
Pour point, deg. F.....	- 10
Fire point (COC), deg. F.....	220
Flash point (PM), deg. F.....	162
Apparent viscosity*, SSF at 80 deg. F.....	20

\*Additive suspension is thixotropic.

oil treated with 1 gal. of alumina-magnesia additive per 1,500 gal. of oil. No problems have been experienced in metering the additive and burner tips have shown no sign of erosion after six months operation.

#### ACKNOWLEDGMENTS

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