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FORMATION OF OIL ASH DEPOSITS ON BOILER SURFACES AND CONTROL BY AN ADDITIVE

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INTRODUCTION

This is the second paper of a series that describes the Defence Research Board of Canada Project No. A18-47-05-01, initiated in 1959, to study the problem of superheater slagging when burning Caribbean source high-vanadium fuel oil in naval boilers. The project was undertaken by the Fuels and Mining Practice Division, Mines Branch, Department of Mines and Technical Surveys on behalf of, and in cooperation with, the Royal Canadian Navy.

The first paper was presented to the 1964 American Power Conference,[1] and it described, (a) a laboratory combustion rig development in which the furnace conditions of a ship's boiler were duplicated in the laboratory, and (b) a fuel-oil additive evaluation and development program in which the chemical composition of an effective fuel-oil additive was established. This

additive contained 40 percent by weight of finely divided oxides of magnesium and aluminum, suspended in a light oil carrier, and the first commercial formulation will be referred to as the "Mark 1" additive.

The present paper describes further fuel-oil additive evaluation tests, and further development work aimed at reducing the viscosity of the Mark 1 additive to improve its handling and blending properties. The latest additive, designated Mark 4, has less than one-thirtieth the viscosity of the Mark 1 additive. This paper also describes the beginning of a study on the mechanism of ash deposition, in which control of ash deposition is being attempted by improving the combustion process. The effect of burner and superheater design on deposit formation is also being investigated.

TEST FUEL OIL

The experiments reported in this and the previous paper were all conducted with a Venezuelan high-vanadium residual fuel oil that meets Canadian Government Specification 3-GP-12C for naval boiler fuel. This specification, together with a range of values for the test fuel, is given in *Table I*.

LABORATORY COMBUSTION RIG TESTS

Additive Evaluation

The side-wall-fired rig, described previously,[1] was used for five 100-hr combustion tests in an extension of the additive evaluation program. Four additional additives were thereby evaluated, including production line samples of both the Mark 1 and Mark 4 additives. *Table II* lists both the elemental composition of each additive and the additive treatment of fuel oil for the
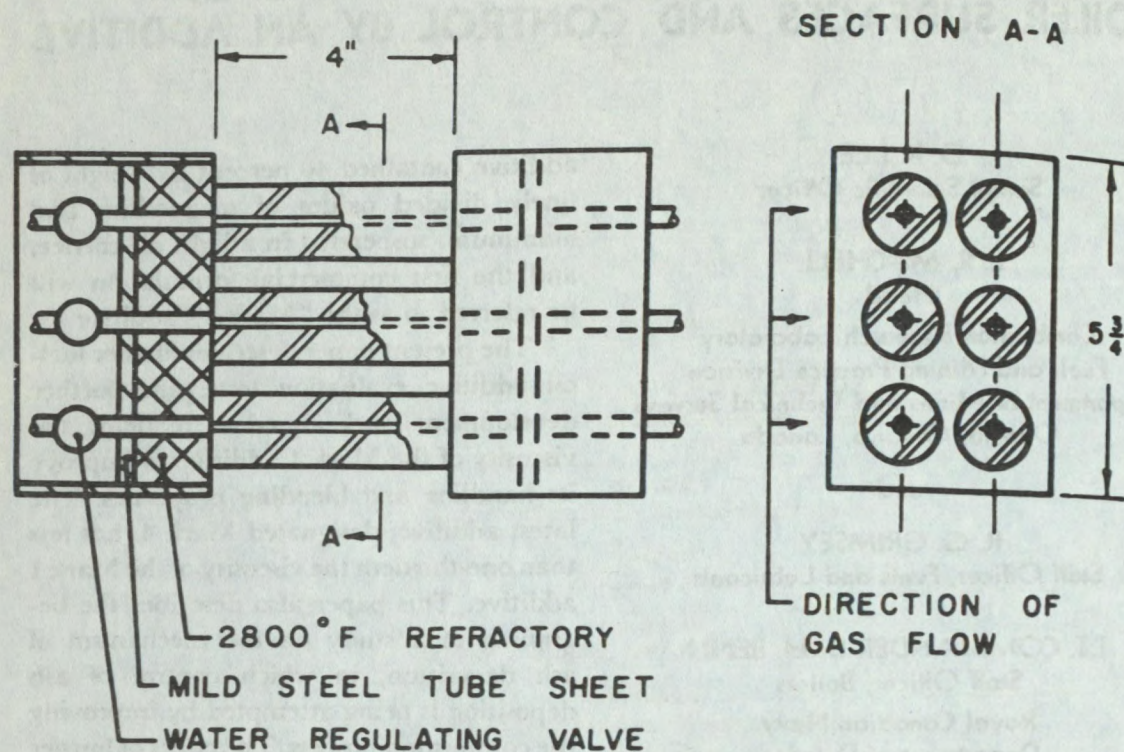
SECTION A-A

Fig. 1—Simulated superheater assembly, consisting of six stainless steel tubes 1¼ in. OD X ¼ in. ID x 4 in. long.

100-hr combustion tests. identified as Tests No. 30. 31. 35. 36 and 47.

For these tests. the same analytical techniques were used as described previously[1] to evaluate the effectiveness of the additives on superheater ash deposit structure. The physical. chemical and mineral characteristics of the deposits are summarized in *Tables III and IV*. and they verify that an additive composition containing magnesium and aluminum oxides has the most beneficial effect on deposit structure. Having done this. further testing of additives was deferred temporarily. in favor of more fundamental studies.

Influence of Physical-Chemical Factors on Deposition

Six physical-chemical factors that might influence the mechanism of ash deposition and deposit buildup were investigated. The six factors are tabulated below, and were evaluated when burning both untreated fuel and fuel treated with the Mark 1 additive:

1. Localized fuel-rich conditions produced by intermittent oil spray on the staggered superheater tube arrangement.

2. An in-line superheater tube arrangement, shown in Fig. 1. to alter the gas flow pattern around the tubes.

3. Reduced gas velocity through the superheater to 103 fps from 190 fps by using a double-width superheater of staggered tube arrangement.

4. Rapid flame quenching by a water-cooled roof.

5. Firing of distillate fuel oil at 50 percent rating for 20 hr at the end of a normal 100-hr run. and

6. Shorter flame. produced by increased turbulence. using burner configurations as shown in Fig. 2.

The experiments that were conducted to study the above factors are tabulated in

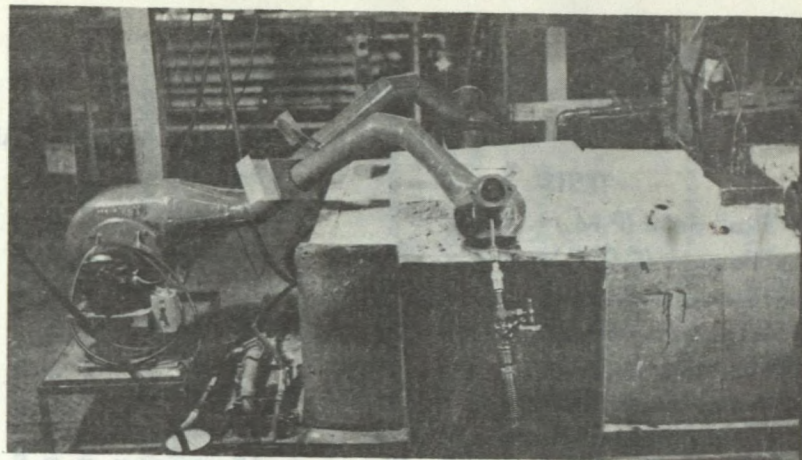Fig. 2.—Laboratory combustion rig with opposed burner configuration.

Table II, each being identified by a number that is used throughout this paper.

In evaluating deposits from treated and untreated oil, the data from Tests No. 30 and 31, respectively, were used as reference levels. The physical characteristics of the deposits produced in the various experiments are given in *Table III*, and their corresponding chemical and X-ray diffraction analyses are given in *Table IV*.

The data from the tests conducted with untreated oil* show that varying the physical-chemical factors that were selected for study does not significantly affect deposition rate, deposit structure, ash-softening temperature or deposit composition. Furthermore, the total weight of deposit from each test was found to depend only on the tube surface area exposed to the gas stream. It may be inferred from these findings that the deposition mechanism for untreated oil, as distinct from deposit buildup, is analogous to convective heat transfer. If such is the case, the predominant oil ash constituents are in the vapor phase, and migration to the tube surface occurs by molecular diffusion. Additional data to support this possible mechanism of deposition are discussed later.

In the tests using oil treated with the Mark 1 additive,** it was found that the

deposit structure, ash-softening temperature and deposit composition were not affected appreciably by varying physical-chemical conditions in the laboratory rig. However, the net weight of deposit was reduced by more than 15 percent when the flame length was reduced and when a distillate fuel oil was burned after a deposit had been formed. Both the in-line superheater arrangement and the reduced gas velocity gave small reductions in the deposition rate, but the total weight of deposit increased because of the larger tube area exposed to the combustion gases. Results of these tests may be summarized as follows:

1. Fuel-rich combustion conditions for short periods of time did not affect the deposit buildup.

2. Neither reducing the gas velocity at the superheater by 46 percent, nor changing to an in-line superheater tube arrangement was effective in reducing the rate of ash deposition. However, an in-line superheater is more readily accessible for cleaning with an air lance.

3. Rapid flame quenching had no measurable effect on the deposit buildup.

4. Existing deposits, if friable and weakly bonded, were partly removed by firing distillate fuel oil at 50 percent rating. This can be explained by a previous observation that deposits

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*Tests No. 31, 32, 34, 37, 39, 41 and 43.
**Tests No. 30, 33, 38, 40, 42, 44 and 45.

TABLE I
TEST FUEL OIL

TESTS		C. G. SPECIFICATION 3-GP-12C	RANGE OF VALUES FOR TEST FUEL OIL
Flash point (P.M.)	°F	150 minimum	198-210
Fire point (C.O.C.)........	°F	200 minimum	270-280
Thermal stability		No. 1 or better	1
Sulphur (bomb)	%	3.5 maximum	1.27-1.41
Explosiveness	%	50 maximum	6-8
Water by distillation	%	0.5 maximum	Trace
Sediment by extraction ...	%	0.12 maximum	0.00-0.01
Pour point	°F	15 maximum	5-10
Ash	%	0.10 maximum	0.04
Viscosity at 122°F	cs	11.8-48.6	26.9-43.2
Specific gravity ......60°/60°F		0.99 maximum	0.94-0.96
.... API		11.5 minimum	15.8-19.0
Compatability		No. 2 or better	1
Vanadium ....(ppm as V)			145-166
Sodium ....(ppm as Na)			28-32

may be loosened by thermal or mechanical shock.

5. By reducing the flame length within the confines of the furnace, the ash deposition rate on the superheater was reduced.

DEPOSIT STRUCTURE

It was clear that the physical-chemical factors described above had less influence on the mechanism of ash deposition than the thermo-physical properties of the fuel ash. Therefore, a thin-section investigation of deposit samples was resumed, to elucidate the processes that may be responsible for both the initiation and growth of deposits on tube surfaces. Detailed examinations were made of all deposits, but only the results of two tests, one involving untreated oil (Test No. 31) and one involving oil treated with the Mark 1 additive (Test No. 30), will be described, because they are typical of the two modes of buildup that are of interest.

Deposit from Untreated Fuel Oil

After untreated oil had been burned, the rig superheater tubes were encircled with a thin, hard, black slag of uniform thickness, as shown in Fig. 3(a). A thin-section examination of this deposit revealed a cream-colored layer of minute granules adjacent to the tube surface, over which a relatively thick layer of interlocked black and amber needle-like crystals had formed. These layers are clearly shown in Fig. 3(b), while the random crystal orientation and the void size distribution in the outer layer are shown in Fig. 3(c).

By X-ray diffraction technique, the inner layer was identified as glassy or poorly crystalline, while the black and amber crystals in the outer layer were identified as sodium vanadyl vanadate type 1:1:5 ($Na_2O \cdot V_2O_4 \cdot 5V_2O_5$), and nickel ortho-vanadate ($3NiO \cdot V_2O_5$), respectively.

Subsequently, chemical analyses revealed that the inner layer contained 47.8 percent water-soluble material, compared

TABLE II
FUEL-OIL ADDITIVES AND TEST VARIABLES SELECTED FOR EVALUATION

DETAILS OF ADDITIVE
ACTIVE CONSTITUENTS

TEST NO.	NAME	FORM	ELEMENTS	LB OF ELEMENT PER 100 LB OF ADDITIVE	GALLONS OF ADDITIVE IN 285 IG OF 3-GP-12C	TEST VARIABLE
30	Mark 1	Solids in suspension	Magnesium Aluminum	10.7 10.7	0.31	Standard reference test
31	Untreated high-vanadium fuel oil			nil	nil	Standard reference test
32	Untreated high-vanadium fuel oil			nil	nil	Intermittent fuel-rich conditions
33	Mark 1	Solids in suspension	Magnesium Aluminum	10.7 10.7	0.31	Intermittent fuel-rich conditions
34	Untreated high-vanadium fuel oil			nil	nil	Flame quenching by water-cooled roof
35	Proprietary	Solids in suspension	Magnesium	28.9	0.19	Additive evaluation
36	Proprietary	Liquid	Manganese Iron	0.05	0.14	Additive evaluation
37	Untreated high-vanadium fuel oil			nil	nil	In-line superheater
38	Mark 1	Solids in suspension	Magnesium Aluminum	10.7 10.7	0.26	In-line superheater
39	Untreated high-vanadium fuel oil			nil	nil	No. 2 fuel-oil-fired continuously for 20 hr at end of standard test
40	Mark 1	Solids in suspension	Magnesium Aluminum	10.7	0.26	No. 2 fuel-oil-fired continuously for 20 hr at end of standard test
41	Untreated high-vanadium fuel oil			nil	nil	Short flame opposed burners
42	Mark 1	Solids in suspension	Magnesium Aluminum	10.7 10.7	0.26	Short flame opposed burners
43	Untreated high-vanadium fuel oil			nil	nil	Reduced gas velocity
44	Mark 1	Solids in suspension	Magnesium Aluminum	10.7 10.7	0.26	Reduced gas velocity
45	Mark 1	Solids in suspension	Magnesium Aluminum	10.7 10.7	0.26	Flame quenching by water-cooled roof
46	Untreated high-vanadium fuel oil			nil	nil	Standard reference test
47	Mark 4	Solids in suspension	Magnesium Aluminum	12.8 12.8	0.18	Additive evaluation

TABLE III
PHYSICAL CHARACTERISTICS OF RIG SUPERHEATER DEPOSITS

TEST NO.	ADDITIVE (AS ELEMENT) TO VANADIUM RATIO LB LB	WEIGHT OF SUPER-HEATER DEPOSIT GM	ABSOLUTE DENSITY GM CC	BULK DENSITY GM CC	ASH SOFTENING TEMPERATURE F*	DEPOSITION RATE MG SQ CM 100 HR	TEST VARIABLE
30	Mg — Al V = 1.75 1	24.2	3.40	1.92	−2800	4.8	Standard reference test
31	nil	10.4	2.78	1.64	1300	2.1	Standard reference test
32	nil	10.6	3.31	1.72	1350	2.1	Intermittent fuel-rich conditions
33	Mg — Al V = 1.75 1	24.4	3.27	2.25	−2800	4.8	Intermittent fuel-rich conditions
34	nil	11.4	3.33	1.64	1350	2.2	Flame quenching by water-cooled roof
35	Mg V = 1.75 1	20.8	3.46	2.15	2730	4.1	Additive evaluation
36	Mn — Fe V = ?	10.6	3.17	1.72	1600	2.1	Additive evaluation
37	nil	13.2	3.47	1.69	1400	2.2	In-line superheater
38	Mg — Al V = 1.75 1	26.7	3.20	2.13	−2800	4.4	In-line superheater
39	nil	10.3	3.24	1.59	1375	2.1	No. 2 fuel oil fired continuously for 20 hr at end of standard test
40	Mg — Al V = 1.75 1	17.7	3.08	2.27	−2800	3.5	No. 2 fuel oil fired continuously for 20 hr at end of standard test
41	nil	11.3	3.25	1.60	1400	2.2	Short flame opposed burners
42	Mg — Al V = 1.75 1	20.1	3.07	2.25	−2800	4.0	Short flame opposed burners
43	nil	21.7	3.33	1.74	1400	2.1	Reduced gas velocity
44	Mg — Al V = 1.75 1	43.8	3.42	1.98	−2800	4.3	Reduced gas velocity
45	Mg — Al V = 1.75 1	24.3	3.33	1.98	−2800	4.8	Flame quenching by water-cooled roof
46	nil	11.4	2.70	1.78	145C	2.2	Standard reference test
47	Mg — Al V = 1.67 1	18.8	3.30	1.92	−2800	3.7	Additive evaluation

*ASTM Standard Method but with 5% oxygen in furnace atmosphere.
NOTE: All tests included salt water injection into the combustion air and soot blowing of superheater tubes.

TABLE IV
ANALYSES OF FUEL-OIL ASH DEPOSITS

TEST NO.	CHEMICAL COMPOSITION (%)							X-RAY DIFFRACTION ANALYSES OF MAJOR CONSTITUENTS	TEST VARIABLE
	V_2O_5	Na_2O	SO_3	Fe_2O_3	NiO	MgO	Al_2O_3		
30	26.9	4.86	22.7	2.86	4.72	14.3	16.6	$MgAl_2O_4 + Na_2O.V_2O_4.5V_2O_5 + MgO$	Standard reference test
31	53.0	7.58	13.7	2.29	2.86			$Na_2O.V_2O_4.5V_2O_5 + NiO.V_2O_4$	Standard reference test
32	54.2	6.78	11 6	3.43	3.40			$Na_2O.V_2O_4.5V_2O_5 + NiO.V_2O_4$	Intermittent fuel-rich conditions
33	29.1	4.20	21.0	1.00	3.38	9.70	15.8	$MgAl_2O_4 + Na_2O.V_2O_4.5V_2O_5 + MgO$	Intermittent fuel-rich conditions
34	44.4	3.30	11.8	1.71	4.32			$Na_2O.V_2O_4.5V_2O_5 + NiO.V_2O_4$	Flame quenching by water-cooled roof
35	28.5	4.20	15.9	3.00	4.34	31.4		$MgO + Spinel + Na_2O.V_2O_4.5V_2O_5$	Additive evaluation
36	56.0	5.09	13.7	3.43	6.92			$Na_2O.V_2O_4.5V_2O_5 + NiO.V_2O_4$	Additive evaluation
37	51.0	6.68	13.3	3.72	7.52			$Na_2O.V_2O_4.5V_2O_5 + NiO.V_2O_4$	In-line superheater
38	28.8	5.24	18.2	2.52	5.02	15.3	13.6	$MgO + MgAl_2O_4 + 5Na_2O.V_2O_4.11V_2O_5$	In-line superheater
39	45.0	6.46	12.7	2.86	6.96			$Na_2O.V_2O_4.5V_2O_5 + NiO.V_2O_4$	No. 2 fuel oil-fired continuously for 20 hr at end of standard test
40	26.8	5.72	22.5	2.72	5.13	13.0	20.6	$MgAl_2O_4 + MgO + Na_2O.V_2O_4.5V_2O_5$	No. 2 fuel oil-fired continuously for 20 hr at end of standard test
41	50.2	8.66	14.9	1.76	7.76			$Na_2O.V_2O_4 5V_2O_5 + NiO.V_2O_4$	Short flame opposed burners
42	26.5	4.63	17.6	4.44	4.60	15.0	18.1	$MgAl_2O_4 + MgO + Na_2O.V_2O_4 5V_2O_5$	Short flame opposed burners
43	52.3	6.62	13.7	1.79	3.70			$Na_2O V_2O_4 5V_2O_5 + NiO V_2O_4$	Reduced gas velocity
44	36.2	4.26	11.8	0.71	1.36	22.0	16.8	$MgAl_2O_4 + MgO + Na_2O V_2O_4 5V_2O_5$	Reduced gas velocity
45	31.0	3.70	13.2	1.46	4.32	25.5	16.8	$MgAl_2O_4 + MgO + Na_2O V_2O_4 5V_2O_5$	Flame quenching by water-cooled roof
46	43.3	11.6	13.4	2.60	4.53			$Na_2O V_2O_4 5V_2O_5 + NiO V_2O_4$	Standard reference test
47	28.0	7.00	20.3	0.77	2.25	17.9	18.3	$MgAl_2O_4 + Na_2O V_2O_4 5V_2O_5 + MgO$	Additive evaluation
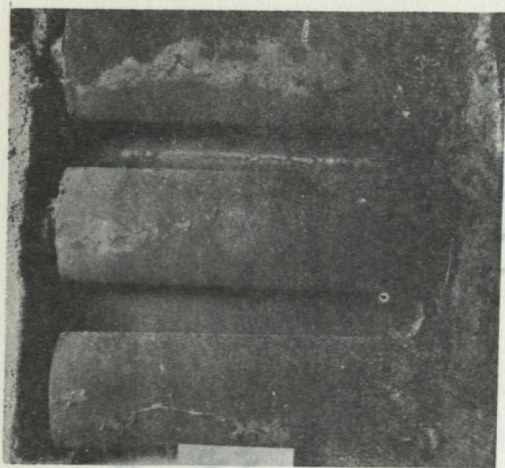
(a) Buildup on upstream surface of superheater.
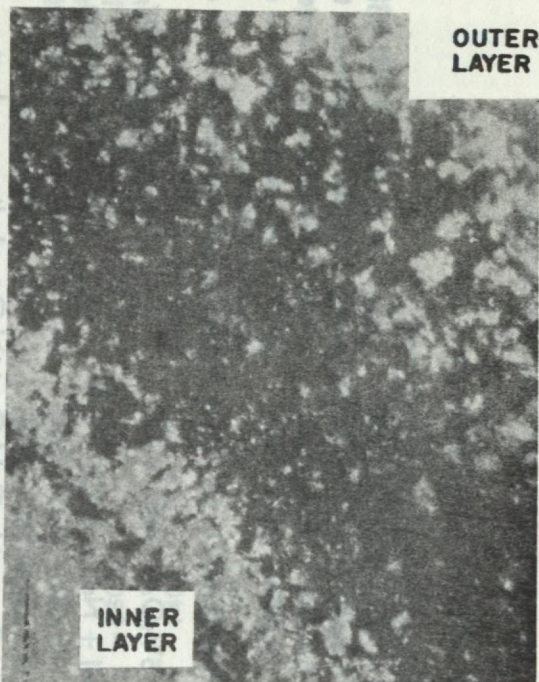
(b) Thin section showing layered structure.
Magnification X 15.
Overall thickness 0.4 to 0.6 mm
Inner layer thickness 0.02 mm
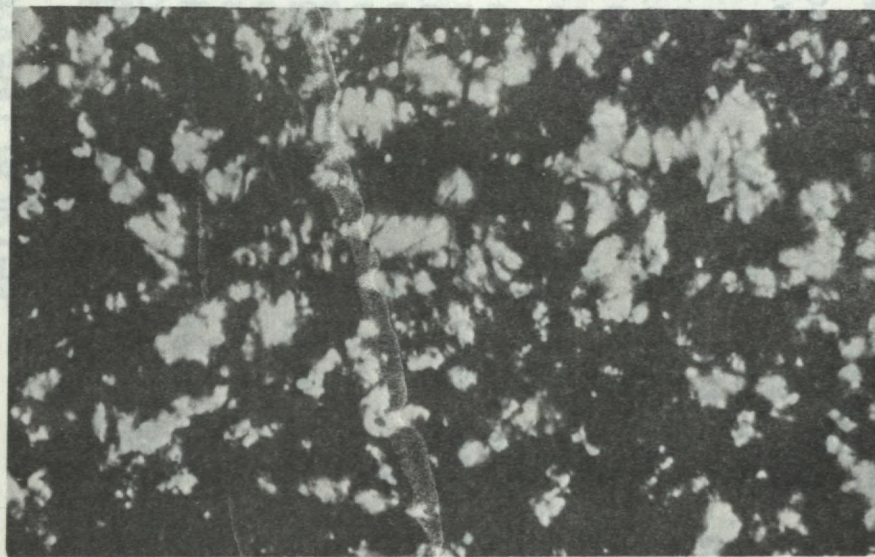
(c) Thin section showing random orientation of needle-like crystals. Magnification X 150.

Fig. 5—Rig superheater deposit after burning untreated fuel oil. Test No. 51.

TABLE V
WATER-SOLUBLE MATERIAL IN RIG SUPERHEATER DEPOSITS

TEST NO.	FUEL OIL	DEPOSIT LAYER	pH	SOLU-BILITY	Na	SO₄ PERCENT	Fe	Mg
31	Untreated	Inner	2.7	47.8	2.4	33.5	3.9	
		Outer	3.4	25.4	2.8	14.6	0.4	
30	Treated	Inner	3.0	49.0	1.3	34.9	4.6	0.15
		Intermediate Upstream	3.1	44.7	4.0	10.1		
		Outer Upstream	7.3	33.9	1.0	2.6		
		Outer Downstream	7.3	36.9	3.0	19.4	0.12	0.11

with 25.4 percent in the outer layer. Both water extracts were acidic, with considerable amounts of sulfate. In addition, the analyses given in *Table V* indicate that $Na_2Fe(SO_4)_2$ may be present in the inner layer. This compound becomes molten and highly corrosive about 1050 F. Consequently, tube surface temperatures should be kept below 1000 F, to prevent corrosion if no corrosion-inhibiting additive is used. Furthermore, when firing with low excess air, there is a possibility of localized chemical reducing conditions in the furnace that may convert the complex sulfate to a sulfide, thereby presenting the danger of intergranular attack on the superheater tubes.

Despite changes in gas velocity, gas flow pattern, and flame turbulence, the thicknesses of both inner and outer layers were uniform, thus supporting the previous postulation that deposition occurs mostly by molecular diffusion. Because the inner layer consists of minute glassy particles, it is probably a sublimate of complex sulfates that forms by rapid supercooling from vapor phase. A low subsequent temperature history would prevent further crystal growth.

In contrast, the well-crystallized outer layer, with a high temperature history, appears to have grown gradually from the vapor phase via condensation on localized crystal nucleation sites. The more compact crystal structure overlying the inner layer may be attributed either to more rapid crystal formation during initial development of the outer layer, or to thermal diffusion of volatile ash constituents through the existing outer layer; subsequent condensation would then occur next to the relatively cool inner layer.

A wide variation in the size distribution of the voids and crystals in an ash deposit from untreated oil is evident from *Table VI*.

Deposit from Oil Treated with the Mark 1 Additive

The deposit formation on the superheater upstream surface, after burning oil treated with the Mark 1 additive, is shown in Fig. 4(a). In section, this deposit contained four layers, as illustrated in Fig. 4(b). A thin-section investigation revealed the following structural features:

1. A dense, thin, inner layer of submicron particles was deposited uniformly over the tube. This layer, which is shown in Fig. 4(c), was loosely adherent and unsintered.

2. A thick, highly porous, wedge-shaped outer layer was deposited on the upstream tube surface and subtended an arc of 90 degrees, centered about the stagnation point. The black striations shown in Fig. 4(d) are a series
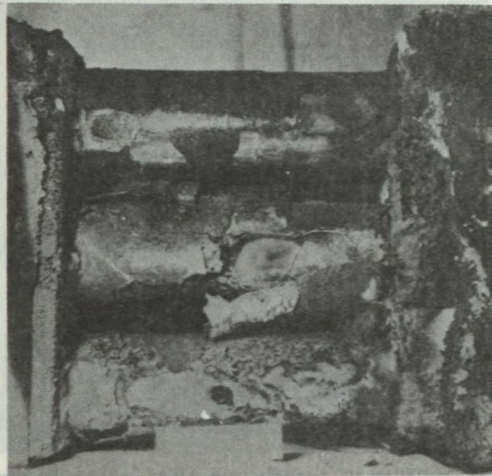
Fig. 4—(a) Buildup on upstream surface of superheater.

of fused surfaces overlying a sintered or partially sintered agglomeration of particles.

3. A moderately porous, friable layer was located on the upstream surface between the inner layer and the wedge-shaped outer layer. This intermediate layer, which also subtended an arc of 90 degrees, centered about

the stagnation point, had a heavily banded structure, as shown in Fig. 4(c).

4. All of the downstream surface, as well as the section of the upstream surface not covered by the wedge-shaped buildup, was coated uniformly with a soft powdery outer layer that was lightly sintered. Although heavily banded, like the intermediate layer on the upstream surface, this layer was characterized by much smaller voids and crystals.

Details of the void and grain sizes in each layer, summarized in *Table VI*, indicate that when the additive was used the inner and the outer downstream layers were deposited by eddy diffusion and thermal diffusion, while the outer and intermediate upstream layers were deposited by inertial impaction, with possibly some buildup due to stream turbulence. In addition, buildup of the wedge-shaped outer layer may be supplemented by particles sticking to the succession of fused upstream surfaces noted previously.

TABLE VI
DETAILS OF DEPOSIT THIN SECTIONS

| TEST NO.	FUEL OIL	DEPOSIT LAYER EXAMINED	CRYSTAL DESCRIPTION TYPE	COLOR	SIZES, μ*	VOID SIZES, μ FIRE-SIDE	TUBE-SIDE
31	Untreated	Outer Upstream	Large needles	Black	10-80	7-36	0-6
			Small needles	Amber	1-20		
		Inner	Glassy mass	Cream	—1		
30	Treated	Outer Upstream	Large grains	Light	2-20	9-120	1-20
		Intermediate Upstream	Large needles	Black	10-70	8-70	
			Small needles	Amber	3-18		
		Outer Downstream	Large needles	Black	10-70	5-50	0-8
			Small needles	Amber	3-18		
		Entire inner layer as well as portions of the other three layers.	Fine grains	Light	—1		

*Needles sizes given are lengths (L:W = 3.6:1).
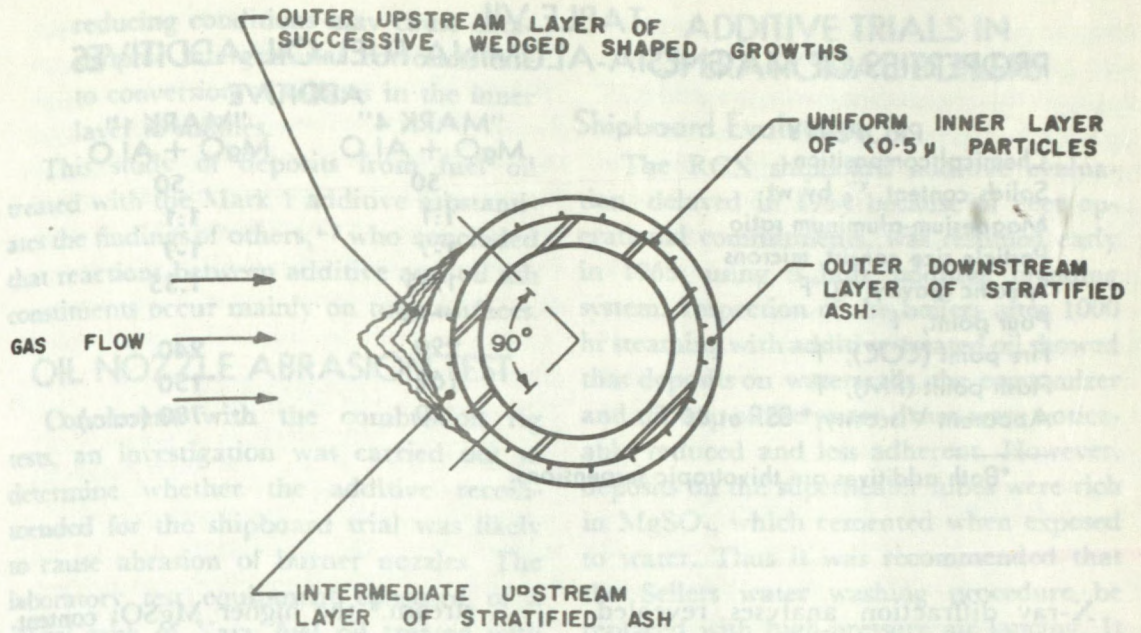
(b) Sectional illustration of deposit buildup.

(c) Thin section of inner and intermediate upstream layers. Magnification X 15.
Overall thickness   1.35 mm
Inner layer thickness   0.07 mm
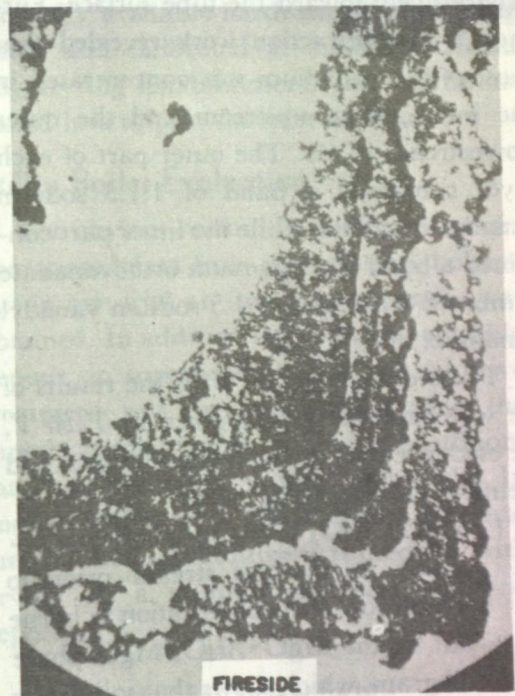
(d) Thin section of outer upstream layer Magnification X 15.
Maximum thickness 4.6 mm

Fig. 4—Rig superheater deposit after burning fuel oil treated with the Mark 1 additive—
Test No. 30.

TABLE VII
PROPERTIES OF MAGNESIA-ALUMINA FUEL-OIL ADDITIVES

PROPERTY	ADDITIVE	
	"MARK 4"	"MARK 1"
Chemical composition	$MgO + Al\,O$	$MgO + Al\,O$
Solids content, % by wt	50	50
Magnesium-aluminum ratio	1:1	1:1
Particle size consist, microns	1-7	1-7
Specific gravity, 70°F	1.45	1.35
Pour point, °F	—10	
Fire point (COC), °F	220	240
Flash point (PM), °F	162	150
Apparent Viscosity,* SSF at 80°F	20	780 (calc.)

*Both additives are thixotropic suspensions.

X-ray diffraction analyses revealed $MgO \cdot Al_2O_3$, $MgSO_4$ and MgO_4 in all four layers. Moreover, $MgO \cdot Al_2O_3$ was uniformly distributed throughout all layers, but the proportion of $MgSO_4$ to MgO increased progressively toward the tube surface. Further X-ray diffraction work revealed that most of the vanadium was concentrated in the intermediate upstream and the outer downstream layers. The outer part of each layer contained a band of 1:1:5 sodium vanadyl vanadate, while the inner part contained a band of magnesium orthovanadate combined with some 1:1:5 sodium vanadyl vanadate.

These data, together with the results of the water-solubility tests given in *Table V*, are evidence that the following physical and chemical processes may occur:

1. $MgO \cdot Al_2O_3$ forms by solid-state reaction in the gas stream prior to deposition. This observation is borne out by the $MgO \cdot Al_2O_3$-MgO phase diagram, which shows that solid-state reactions are unlikely to occur below 2560 F.[2]

2. Due to the instability of $MgSO_4$ above 2050 F, and the fact that SO_3 and MgO do not react in the gas

stream,[3] the higher $MgSO_4$ content of both the inner layer and the intermediate upstream layer may be attributed to an inward but differential diffusion of SO_3 through the deposit pore structure. Apparently, high SO_3 concentrations accumulate in the cooler regions of the deposit, where reaction readily occurs with MgO in situ.

3. The location of the band of 1:1:5 sodium vanadyl vanadate, as shown in Fig. 4(c), suggests that vanadium and sodium diffuse in the vapor state through the deposit voids, and that condensation subsequently occurs.

4. The reason for magnesium orthovanadate forming in a band closer to the tube surface is not clear, but its location and quantity imply a solid-state reaction that progresses at a relatively slow rate.

5. When using the magnesia-alumina additive, metal surfaces can be maintained at 1100 F without being corroded by oil ash constituents, because the Na_2SO_4-$MgSO_4$ eutectic occurs at 1220 F. However, low excess air combustion with localized chemical

reducing conditions may cause catastrophic intergranular corrosion due to conversion of sulfates in the inner layer to sulfides.

This study of deposits from fuel oil treated with the Mark 1 additive substantiates the findings of others,[4,5] who concluded that reactions between additive and oil ash constituents occur mainly on tube surfaces.

OIL NOZZLE ABRASION TEST

Concurrent with the combustion rig tests, an investigation was carried out to determine whether the additive recommended for the shipboard trial was likely to cause abrasion of burner nozzles. The laboratory test equipment consisted of a 50-gal tank of Navy fuel oil treated with 0.14 percent by weight of the "Mark 1" additive (Dosage rate equivalent to: $Mg + Al:V::1.75:1$). a high-pressure pump, an oil preheater. and a mechanical atomizing nozzle with an orifice diameter of 45 microns.

The treated fuel oil, which had been thoroughly blended before the test, was continuously recirculated to the nozzle at 500 psig and 120 F for 10,000 hr. Following this, a microscopic examination of the nozzle showed no measurable changes in orifice shape or diameter. It was then concluded that the larger diameter burner tips used on board ship will not be eroded by the recommended additive.

IMPROVEMENT OF ADDITIVE VISCOSITY

Since June 1965, a second United States chemical manufacturing company has been collaborating in a program to improve the Mark 1 additive blending and handling properties. This has resulted in the production of a new Mark 4 formulation. with the identical chemical composition of the Mark 1 additive, but having less than one-thirtieth its viscosity. The properties of the new Mark 4 additive are given in *Table VII*.

ADDITIVE TRIALS IN OPERATIONAL BOILERS

Shipboard Evaluation

The RCN shipboard additive evaluation, delayed in 1964 because of fleet operational commitments, was resumed early in 1965, using a bulk additive blending system. Inspection of the boilers after 1000 hr steaming with additive-treated oil showed that deposits on waterwalls, the economizer and the top of the water drum were noticeably reduced and less adherent. However, deposits on the superheater tubes were rich in $MgSO_4$, which cemented when exposed to water. Thus it was recommended that the Sellers water washing procedure be replaced with high-pressure air lancing. It was further recommended that additive dosage rate be accurately controlled by a metering pump on the oil burner supply line. Such a metering system, using commercially available hardware, is now being tested and calibrated at the RCN Naval Engineering Establishment, and will be installed in a ship in the near future.

Utility Boiler Evaluation

For obvious reasons, it is difficult to get operational data from power utility boilers. but in one trial an unexpected benefit was obtained. In addition to producing a friable deposit on superheater tubes, the additive treatment was credited with raising the superheat temperature to design conditions that had not been possible previously. In another boiler with 900 F steam temperature the fuel-oil additive was credited with drying up a gummy, corrosive cold-end deposit.

CONCLUSIONS

The dominant mechanism controlling buildup of slag in naval boilers is apparently one of vapor phase diffusion. This being the case, superheater slagging in the present design of naval boilers can be reduced by

using an ashless fuel or a residual fuel treated with an additive, so long as it will positively improve the thermal-physical properties of the oil ash. However, the authors are of the opinion that the slagging problem may be overcome by development of unconventional boiler and burner design concepts. Another solution may lie in the use of low excess combustion air, but this technique seems to be too risky for marine boilers at the present stage of burner development, and emphasizes that new design concepts are needed.

ACKNOWLEDGMENTS

The authors are indebted to several Divisions of the Mines Branch for their generous support of this research project. In particular, credit is due to Dr. J. A. Soles for guidance with the microscopic examination of the deposits; to J. F. Rowland for the X-ray analyses; to the staff of the Analytical Chemistry Subdivision for the chemical analyses; to D. G. Savignac for assistance in petrographic examinations and rig operations; to B. C. Post, R. G. Fouhse, F. D. Friedrich, L. B. Geller and M. A. Rethier, for conducting the combustion rig tests.

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PREPARED DISCUSSIONS

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Many arguments have been presented over the past few years on the chemical aspects of deposits connected with corrosion, compared with the physical ones—of the composition of deposits as related to the conditions that lay them down on jeopardized surfaces. The Authors here have shown clearly, within the limits of their excellent test equipment, that physical factors in their apparatus, involving such parameters as gas velocity, gas flow distribution, and combustion pattern, have little effect on deposit structure or composition. Rather, they con-

sider the problem of deposition as being one of molecular diffusion, where factors such as vapor pressure and gas-phase reactions predominate, rather than physical ones such as particle size and gas velocity. It is a little difficult to reconcile this hypothesis with the Authors' statements, later, regarding tests with their Mark 1 additive, where deposition by inertial impaction definitely caused buildup of deposits. Some further explanation by them, to identify when molecular diffusion is important and when inertial impaction takes over, would be helpful.

This mechanism of deposition is important because it suggests that there is little the furnace designer can do to minimize corrosion and deposits by changes in furnace geometry or in the arrangement of heat-receiving surfaces. Rather, he must be even more considerate than in the past of the quality of the inorganic matter in the fuel he is to burn. Knowledge of such parameters as the amounts of alkalies and their form, of the sulfur level, and of metals such as vanadium and nickel in fuel oil will be even more necessary in the future in selecting fuels.

The sole important factor over which the furnace designer will have control, other than by selection of fuel based on its impurities, is excess air, well proven now in Europe and in the United States, as the most effective single method of all in minimizing deposition problems with residual fuel. The Authors' sole reference to low excess air is that poor mixing of fuel and minimum excess air might lead to localized reducing conditions, with the formation of sulfides, a genuinely catastrophic situation. Such conditions can indeed occur. But here is where the designer's skill and the operator's knowledge come into play. They must assure either that precisely measured proportions of fuel and air enter each burner, or that furnace turbulence is great enough to insure thorough mixing of all fuel and

air, so that near stoichiometric proportions exist throughout the entire furnace cavity. That these goals can be reached is shown by the many oil-fired boiler furnaces now being fired successfully with less than 5 percent excess air, and, in some cases, with less than 1 percent excess air.

Some of the Authors' comments regarding reactions of additives with SO_3 in the furnace should be scrutinized carefully, so that they are not misinterpreted. For example, one of the results of Battelle's research for the Corrosion and Deposits Committee of ASME shows definitely that MgO reacts rapidly with SO_3 to form $MgSO_4$ at 1100 F to 1200 F, whether the MgO is in a fixed bed or deposited on a surface. Although there may be little reaction between MgO and SO_3 at higher temperatures, there is no question but that MgO is an effective scavenger of SO_3 as the temperature drops. Hence, thin layers of MgO accumulating on an exposed superheater tube essentially at tube-metal temperature would be rapidly converted to $MgSO_4$ at the expense of SO_3 in the flue gases. Likewise, MgO suspended in a gas stream would react with SO_3 as the temperature drops. Hence the Authors' statement that "SO_3 and MgO do not react in the gas stream" should be qualified by including "at temperatures well above 1200 F." The important point here is that it is not necessary for high SO_3 concentrations to develop by diffusion through a deposit for ultimate reaction with MgO. The reaction can occur readily with low levels of SO_3, just so the temperature is not appreciably higher than 1200 F.

In regard to the Authors' Mark 1 and Mark 4 additives, it is interesting to speculate why $MgO \cdot Al_2O_3$ should be more effective than MgO alone. It is quite unlikely that Al_2O_3 would react in any way with SO_3, hence its action must be in modifying the physical characteristics of the MgO to which it is added. The phase diagram for the system $MgO\text{-}Al_2O_3$ shows a eutectic at

55 percent Al_2O_3 melting at 3690 F, which, although low compared with the melting point of 5070 F for MgO, is still high compared even with maximum temperatures in boiler furnaces. The spinel $MgO \cdot Al_2O_3$ melts at 3880 F, also too high to be significant. Hence, although the addition of Al_2O_3 lowers the melting point of MgO appreciably, it is doubtful if this has any importance. If a lower melting point were helpful in modifying the physical or chemical characteristics of MgO, then adding SiO_2 rather than Al_2O_3 would be better, for the lowest eutectic in the MgO-SiO_2 system occurs at 2810 F with 65 percent SiO_2. In Europe, a widely used proprietary additive does indeed consist of a mixture of MgO and SiO_2.

It would be interesting to hear the Authors' opinions regarding why Al_2O_3 adds to the effectiveness of MgO as an additive. Are the actions chemical or physical? Is the improvement great enough to warrant the extra cost of preparing a mixture, rather than using a single-component additive? And, finally, how about dirt-cheap dolomite? Does the performance of the Mark 4 additive surpass dolomite sufficiently to justify its costs? These questions are pertinent because, in the long run, economic factors are certain to control the use of additives. The Authors should be in an excellent position to give factual answers.

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This second report describing the continuation of the fuel-oil additive evaluation by the Canadian Department of Mines and Technical Surveys indicates the fine progress being made to combat slagging and corrosion due to the presence of vanadium and sulfur in heavy oil. Also, it apparently holds promise as a possible avenue for the reduction of SO_2 and acid stack emission.

As a supplement to this paper, we would like to provide information on two New England electric utility companies who have placed in use a solid-in-suspension additive formulation, manufactured in collaboration with the Canadian research program, that incorporates a 10 to 1 ratio of magnesium to aluminum oxides. At each location, the boiler involved is capable of 360,000 lb steam per hr at 900 psig and 900 F. One of the units is equipped with a regenerative-type airheater with air recirculation to maintain higher than normal cold end metal temperatures. The other, with a tubular-type airheater, uses steam to raise airheater metal temperatures.

Neither boiler is operated at low excess air, nor does either have ash recirculation systems. One is a peaking-type unit, while the other is base loaded.

Original conditions, as well as results achieved, are practically the same. In each unit, superheater and airheater problems had become a matter of major boiler maintenance and repair costs, due to frequent outages for cleaning, followed by rapidly falling boiler operating efficiencies. Further, in the boiler incorporating the tubular-type airheater, a number of additives had been tried during a four year period, with little success.

The additive referred to herein was originally applied at a ratio of 1000 gal fuel oil per gal additive for a short orientation period. It was then changed to 1500 to 1. The net result at the end of four weeks of operations is as follows:

1. Discontinuance of air recirculation and steam flow in each airheater, with complete absence of usual coating and moisture.

2. Formation of a light powdery, friable

deposit on furnace walls, resulting in continued maintenance of 900 F superheated steam temperatures.

3. Replacement of the hard bonded deposit of slag on the superheater tubes (plus bridging in the convection pass of the generating bank) with a soft friable, powdery deposit, easily removed by sootblowers.

4. Elimination of rising draft loss conditions.

5. Establishment of a clean dry condition at the cold ends of the airheaters.

6. Maintenance of boiler efficiency close to anticipated performance data.

7. Elimination of all special boiler outages for fireside cleaning.

As a result of many studies conducted throughout the world in the past fifteen years, the effectiveness of aluminum and magnesium oxides for control of vanadium and sulfur in residual fuel oil has been well established. However, only since the development of manufacturing techniques which now permit delivery, storage, pumping and proportioning as a solids-in-oil suspension, has the power industry begun to widely test the effectiveness of alumina-magnesia additives.

We can now report a number of consistent aspects of an alumina-magnesia, solid-in-suspension additive for control of vanadium and sulfur in modern high-temperature boilers, as follows:

1. Aluminum oxide, when combined with magnesium oxide, increases friability and fusion temperature of ash.

2. Aluminum oxide raises ash fusion temperatures more than 100 F higher than magnesium oxide alone.

3. Magnesium oxide is reactive with sulfur compounds, with consequent reduction in SO_3 present.

4. Particle sizes of alumina and magnesia should be a maximum of 10 microns, with an average of 2-3, in order to impart maximum friability

to the ash. Submicron sizes should be reduced to a minimum. in order to prevent a high density deposit and high deposition rates (with attendant high stack loss), due to agglomeration of superfine particles.

5. Ratio of magnesium oxide to aluminum oxide should be varied to suit boiler design, operating conditions and fuel oil analysis.

6. Viscosity of additive should be as low as possible to permit satisfactory storage, pumping and proportioning at low winter temperatures.

7. Flash point should be high enough to comply with all local and marine requirements.

Last but not least:

8. The cost should be low enough to justify use of the additive.

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The Authors have presented an interesting and informative account of a careful and thorough investigation. We agree with their conclusion that vapor phase diffusion is apparently the dominant mechanism in slag buildup, and their implied conclusion that additives are of somewhat limited help in controlling deposit formation.

The Authors are of the opinion that low excess air combustion may be a solution to the slagging problem. However, they feel that this technique seems too risky for marine boilers at the present stage of burner development, and that new design concepts are needed.

The interest of steamship operators in

low excess air combustion is apparently very strong, and initial steps are already being taken toward eventual operation at very low excess air rates. As a consequence, we have recently sold a number of marine boilers guaranteed to operate at not over 5 percent excess air. One burner manufacturer has proved, by test, that 3 percent is attainable.

These levels can be attained without modifying present burners. To this end, we are using larger windboxes, individual air ducts and dampers to each burner, greater clearance between burners, fewer burners per boiler and higher windbox pressures. This is currently being done on new installations at only a very insignificant increase in cost.

We believe that it may be possible, eventually, to permit operation at below 2 percent excess air by making relatively minor modifications to boiler and burner design, with particular attention given to windbox and ducting arrangement, burner layout and furnace configuration. However, this will be admittedly difficult to accomplish within the tight space limitations imposed on marine boilers.

AUTHORS' CLOSURE

The authors wish to thank Messrs. Reid, Tallman and Zoschak for their valuable contributions to this paper. These discussions have raised a number of points which the authors wish to clarify.

In reply to Mr. Reid's question on the mechanism of oil-ash deposition, the authors would like to emphasize that deposition of indigenous ash constituents on boiler surfaces occurs primarily by molecular diffusion, regardless of whether untreated oil or oil treated with the Mark 1 additive is burned. The use of the Mark 1 suspended solid additive, in addition to controlling the physical structure of the deposit, modifies the dominant effect of molecular diffusion in the deposition mechanism to the extent of increasing inertial impaction of particles and particle migration.

Whether or not MgO reacts with SO_3 in low temperature gas streams is still controversial. However, recent research in England indicates that MgO and SO_3 do not react in the gas stream even at temperatures below the acid dewpoint. This research, although specific to a particular experimental furnace, showed that treating a residual fuel with 0.14 percent by weight of the Mark 1 additive had no effect on either the SO_3 level or the acid dewpoint of the combustion gases. In contrast, low-temperature corrosion (as measured with a BCURA corrosion probe) was reduced by 35 percent, indicating that neutralization of SO_3 by MgO occurred on the probe surface and not in the gas stream.

The possibility that either MgO alone or a $MgO-SiO_2$ mixture might be equally effective as the Mark 1 additive was investigated during the additive evaluation program. When the fuel was treated with MgO alone, the resulting superheater deposit was fairly cohesive and contained a large amount of $MgSO_4$. The net effect of the $MgSO_4$, which has a melting point of 2050 F, was to decrease both the friability

and the ash fusion temperature of the deposit. Rig tests with MgO-SiO_2 mixtures originally showed considerable promise in alleviating superheater slagging; however, when synthetic sea water was injected into the combustion air to simulate conditions at sea, the MgO-SiO_2 additive formed a dense, hard, fused deposit, having an ash fusion temperature of 2000 F. Petrographic examinations revealed that SiO_2 reacted with sodium in the sea water to form a low melting point compound.

The authors agree with Mr. Reid's suggestion that more economic additive blends can be used, particularly in power utility boilers, where furnace conditions are less severe than on board ship. During the past year, a number of power utilities have successfully used additive formulations with Mg:Al ratios ranging from 10:1 to 3:1. Further details of these trials are given in Mr. Tallman's discussion. To answer Mr. Reid's final question, dolomite was not seriously considered in the additive evaluation program because it was known to cause erosion in oil pumps and burner nozzles.

It was indeed gratifying to learn of Mr. Tallman's success in combating deposition problems in stationary boilers while using additive formulations that were evolved in the authors' research program. His field investigations confirm that additive blends containing Mg:Al ratios of up to 10:1 can be used economically and effectively, to suppress both superheater slagging and low-temperature corrosion in power utility boilers. It should be noted that additive dosage rates are determined by the impurities in the fuel, while Mg:Al ratios are determined by the temperature and velocity conditions at the furnace exit.

It is difficult to answer Mr. Zoschak's remarks without an explanation of the normal boiler operating conditions. The authors' timidity about low excess combustion air is confined to naval boilers, where rapid load swings can be expected. Under these conditions it is difficult to expect conventional hardware to provide a realistic factor of safety. However, it is encouraging to know that modifications to conventional hardware are proving successful in many, less rigorous operations.