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SUMMARY REPORT
OF
THE EFFECTS OF FERROUS PICRATE
ON
SULFURIC ACID CORROSION,
VANADIUM PENTOXIDE,
BOILER EFFICIENCY,
AND
SLUDGE CONTROL

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ABSTRACT

Serious corrosion, fouling, and acid soot problems frequently occur in the flue gases of power generation and process steam boilers when sulfur and vanadium bearing No. 6 fuel oil is burned. With sulfur, this is due to the condensation of sulfuric acid (H_2SO_4) on surfaces of the boiler, flue, economizer, or stack where the temperature is below the acid dewpoint point. Vanadium in the fuel oxidizes to vanadium pentoxide (V_2O_5), a hard deposit that attaches itself to all boiler surfaces and impedes heat transfer.

This report summarizes the results of testing with a ferrous picrate catalyst, (FPCS), formulated to alleviate the corrosion properties of heavy fuel oils. FPCS is a generic designation for the catalyst used during research. The product is now marketed as FPC48.

The spectrum of these tests include studies with individual burners at several commercial boiler sites. Comparisons are also made between the ferrous picrate catalyst and magnesium oxide (MgO) based additives designed to alleviate the same problems.

This report will show conclusively that FPCS was found to be effective in the reduction of problems related to vanadium and sulfur, and that the catalyst also reduces excess air requirements for proper combustion. Therefore, FPCS has the ability to improve boiler efficiency, as well as reduce boiler system maintenance.

Further, findings show FPCS to be 50% more effect in reducing sulfuric acid problems than magnesium oxide-based additives, and at least as effective as magnesium oxide-based additives in reducing vanadium pentoxide fireside deposits.

INTRODUCTION

The main objective in boiler operation is to obtain maximum efficiency with minimum maintenance. With the reduction in overall oil quality, it is becoming more evident that fuel oil additives have a significant role to play in boiler operation in conjunction with the development of state-of-the-art mechanical equipment. And as time goes on, and oil quality deteriorates, problems will increase.

Typically, fuel oil additives can be broken down into subgroups such as:

1) Preburned conditioners that prevent sludge and water formation in storage tanks.

2) Combustion catalysts that act directly on the combustion process to improve combustion efficiency.

3) And slag inhibitors that act upon products of combustion to minimize fireside deposits, corrosion and reduce atmospheric pollution.

While sludge and water formation in storage tanks are a problem, combustion efficiency and fireside deposits are more critical. Fuel additives are mainly used to reduce fireside deposits that decrease the rate of heat transfer, resulting in increased stack temperatures and decreased fuel efficiency. Boiler failure caused by deposits and corrosion result in loss of profit, because of reduced production while making repairs. The magnitude of this loss is often under estimated - loss of production for several days may cost as much as proper fuel treatment for several years.

Fireside fouling and corrosion are principally caused by impurities present in residual fuels. The most commonly found elements are sulfur, vanadium, sodium, nickel and iron; with sulfur, vanadium and sodium being the major contributors. Typically, sulfur is related to low temperature problems, such as acid attack in air heaters, economizers and breeching. Sodium and vanadium cause acid and deposits on boiler tubes at high temperatures.

Included as Appendix 1 is an excerpt from the 39th edition of "STEAM", by Babcock & Wilco. This excerpt explains in some detail the relationship between sulfur, vanadium and sodium reactions in boiler operations. We have entitled this

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The Appendix is entitled "General Information Regarding, Sulfur, Vanadium, Sodium and Boiler Operation". Additional information has been included when further clarification is needed, and is indicated by (*). Such additional data is from a source other than Babcock & Wilcox.

METHODOLOGY

To insure consistent results, all boilers must be operated under identical load conditions, typically base loaded with manual operation, if possible. Once testing starts, no changes are allowed or all test data becomes invalid. Normally, boilers were run base-loaded at low fire, high fire and average load.

Boiler Efficiency

With boilers manually set, the necessary information to determine boiler efficiency was gathered. The following data was recorded:

Steam flow & pressure	Ambient temperature WB/DB
O2	Oil temperature
CO2	Oil pressure
Combustibles	Atomization pressure
Stack temperature	Control settings
Fuel type	Fuel additive used

Acid Corrosion

Again, with boiler operation constant, a Land Model 200 Acid Dewpoint Meter was used to evaluate the effect of the fuel oil additive on acid formation.

An acid film is good conductor of electricity. Therefore, if a nonconducting surface bearing two electrodes is placed in the flue gas, an condensate forming on the surface will be detected by a current flowing between the electrodes.

The Land meter employs a dewpoint detector with a thermo-couple and a pair of electrodes fused into a detecting surface that is air cooled from the rear. This detector is mounted on the end of a stainless steel probe. The probe is inserted into the gas stream and the detector is gradually cooled by the flow of cooling air which is controlled manually at the control unit.

A thin film of acid begins to condense on the detector surface when the detector surface is sufficiently cooled. This

creates a current flow across the electrodes which is monitored at the control unit. The air flow to the detector is then manually adjusted to maintain a constant electrode current. At this constant current, the rate of condensation and evaporation of acid are equal. The temperature at which this takes place is the acid dewpoint temperature, (ADT). This temperature is measured by the thermocouple fused to the surface of the detector.

The corrosion potential of the flue gas can also be assessed by measuring the rate of acid buildup (RBU) at temperatures below the ADT. By plotting a graph of RBU vs. temperature, the peak rate of acid condensation can be equated to a particular temperature. Any metal surfaces at this temperature that are exposed to the flue gases will experience acid condensation, and therefore, corrosion.

By utilizing the RBU data, the direct effect of a fuel catalyst can be evaluated. Fuel oil which is untreated will have a particular RBU profile over a temperature range. If this is compared to the identical boiler operation with treated fuel, the RBU graph will show any effect of the fuel treatment with respect to sulfur and vanadium-related emissions.

Test Instrumentation

Land Model 200 Acid Dewpoint Meter
Bacharach Continuous O2 Analyzer; Model CA-1
Bacharach O2-CO2 Analyzer; Model 10-5020
IMC Instruments Model 6100 Digital Thermometer
Fisher Scientific Sling (Psychrometer)
Combustion Instruments Continuous CO-O2 Analyzer
Thermco Instruments Continuous CO2 Analyzer.

RESULTS

FPCS fuel oil combustion catalyst has shown the following results in preburner system, combustion catalyst, and slag inhibitor studies.

1. As a preburner conditioner, no sludge has been found in test site 'I', (see Table 1), which has been treating for more than one year. Only the normal dirt and sand trash have been trapped by existing strainers, and strainers remained clear of water and sludge buildup.

2. As combustion catalyst, the primary desired effect is to reduce excess oxygen (O2), and thereby improve boiler efficiency. In Table 1, several test sites show reduction in excess oxygen to a point where FPCS was cost-effective when considering only increased boiler efficiency. Other sites showed only marginal results, due primarily to the high quality of fuel being burned, the type of atomization burner, or limited range boiler controls.

3. As a slag inhibitor for fireside deposits, the testing reveals major reductions in the rate of acid buildup, (RBU). Figures 9, 10, 11, and 12 plot results in both water and firetube boilers.

TABLE 1
### Boiler Efficiency Improvements Due to FPC-1

Site	Fuel	Boiler #/Hr Rated	#/Hr Ave	* As Found	+ Baseline	Boiler Efficiency With FPC-1	Gain	Gain
A	No.6	58,000	28,000	75.46	78.39	80.20	1.81	2.30
B	No.5	Hot oil	700hp @ 50%	56.93	73.06	76.31	3.25	4.45
C	No.5	21,000	7,400	83.94	85.04	85.26	.22	.25
D	No.6	25,000	7,500	80.63	80.63	82.63	2.00	2.48
E	No.6	17,500	10,000	80.63	84.80	85.89	1.09	1.29
F	No.6	90,000	72,000	84.40	84.40	85.97	1.57	1.86
	No.6	90,000	9,000	81.63	81.63	87.39	5.76	7.06
G	No.5	3,500	1,400	81.80	83.11	85.09	1.98	2.38
H	No.6	40,000	30,000	78.38	78.38	79.25	.87	1.11
I	No.5	20,700	7,000	81.20	82.90	85.20	2.30	2.77

* As Found - Operation before adjustments or additives.
+ Baseline - Operation with adjustment with no additive.

OBSERVATIONS

1. The use of FPCS reduces the rate of H2SO4 generation and potential acid corrosion.

2. If H2SO4 generation was reduced with all other parameters held constant, such as O2, CO2, CO, stack temperatures and ambient weather conditions, then FPCS reduced the formation of SO2 to SO3.

3. Recalling that SO2 oxidizes to SO3 through the catalyzation of vanadium pentoxide and iron oxide:

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$$SO_2 + 1/2O_2 \xrightarrow[Fe_2O_3]{V_2O_5} SO_3$$
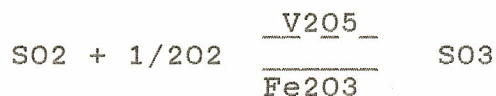
it can further be concluded that the vanadium pentoxide formation has been greatly reduced or even eliminated. At all test sites, using FPC-1 to reduce vanadium pentoxide deposits, the normal six months cleaning is now once a year. The boiler is opened for insurance inspection at this yearly inspection. With FPCS as an oxidizing catalyst, which uses the free O_2 for more complete combustion, it follows that V_2O_3 and V_2O_4 cannot oxidize to V_2O_5.

From the above equation, it is noted that iron oxide (Fe_2O_3) also is a catalyst, and therefore the iron in FPCS could react to help form SO_3. However, the iron in the ferrous picrate of FPCS has a chemical valence of +2 compared with the valence of +3 for Fe_2O_3. Therefore, the iron compounds of FPC-1 do not promote SO_3 formation.

The rate of acid buildup (RBU), related to H_2SO_4, SO_3, and V_2O_5 formation, will varying depending upon the boiler size, flame temperature and type. From previous discussions on atomic oxygen in large high-temperature boilers, it would be expected to have high RBU and increased SO_3 formation, as shown in Table 6. Note also that various additives are already being used, and the RBU is still high.

TABLE 2
Dewpoint-Meter Test Results From Oil-Fired Unit
(ASME Paper 63-WA-108)

Air preheater	Percent sulfur	Cold-end average	Dewpoint	Peak-rate temp	Peak rate, $\mu a/min$	Remarks Corrosion location	Miscellaneous
1	3.97	200–215°F	249°F	213°F	96	Middle of cold layer	Mg(OH)$_2$ (old unit)
2	3.97	200–215°F	256	220	130	Middle of cold layer	Mg(OH)$_2$ (old unit)
3	3.97	200–215°F	256	232	200	Middle of cold layer	Mg(OH)$_2$ (old unit)
4	3.97	200–215°F	257	232	154	Middle of cold layer	Mg(OH)$_2$ (old unit)
5	3.97	200–212	280	255	390	Middle of cold layer	Dolomite
6	3.97	210–215	280	257	366	Middle of cold layer	
7	1.40	223	245	202	202	None in heater	Lime slurry
8	1.40	208	236	193	30		Lime slurry, gas
9	1.40	204	228	193	228		Lime slurry, gas
10	1.40	214	248	207	322		Lime slurry, gas
11	1.79	225	265	222	210	Ductwork after gas out	Lime slurry, gas
12	2.94	195	244–247	222	142	No problem	Gas fired continuously
13	2.57–3.29	204	274	233	695	Movable	Operation with cold end out
14	2.57–3.29	219	249–274	207	574	Cold end of cold int.	Changeable
15	2.57–3.29	191	253	207	1020	Cold end of cold int.	Elements temp swing could account for it
16	1.82	207	258	219	210	Cold end of int. layer	
17	1.82	207	258	219	134		Mg(OH)$_2$, int. layer out
18	1.70–1.73	198–205	235	200	46	Cold end of cold layer	Combo. firing, lime slurry
19	170–1.73	198–205	258	216	315	General in cold layer (CI also)	Higher excess air than #18

DISCUSSION

Test results showing the effect of FPCS on RBU in oil-fired package boilers are given in Figure 9, which shows a typical water tube package boiler, and Figure 8, a smaller fire tube unit. In both figures, FPCS substantially reduced the RBU at all temperatures, as compared to fuel without any treatment.

The oil fired was typical No.6 East Coast oil, with 2.1% sulfur and 200-300 ppm vanadium.

Observations from Figure 9 and 10 relate to the RBU and firing rate response time in treating with FPCS, and corrosive tendencies. As expected, with the increase in firing rate, there will be an increase in the mass flow rate of H_2SO_4, since more fuel is being burned and more sulfur moved through the boiler firebox.

Note: On Figure 10, 7/10/81, 6800 #/hr and 6.0% O2; even with FPCS, there is a saturation point of high excess O2 which nullifies the use of an oxidizing catalyst. The actual saturation point will vary from boiler to boiler, depending upon the firing rate and burners.

Next, it has been observed that the addition of FPCS to a system requires a response or conditioning time. Immediately upon introducing FPCS, improvements in O2 and the flame can be detected, but the full effect may take one month to develop. Thus far, no correlation has been established between final results, as it differs from boiler to boiler, regardless of size, load, existing deposits or burner assembly.
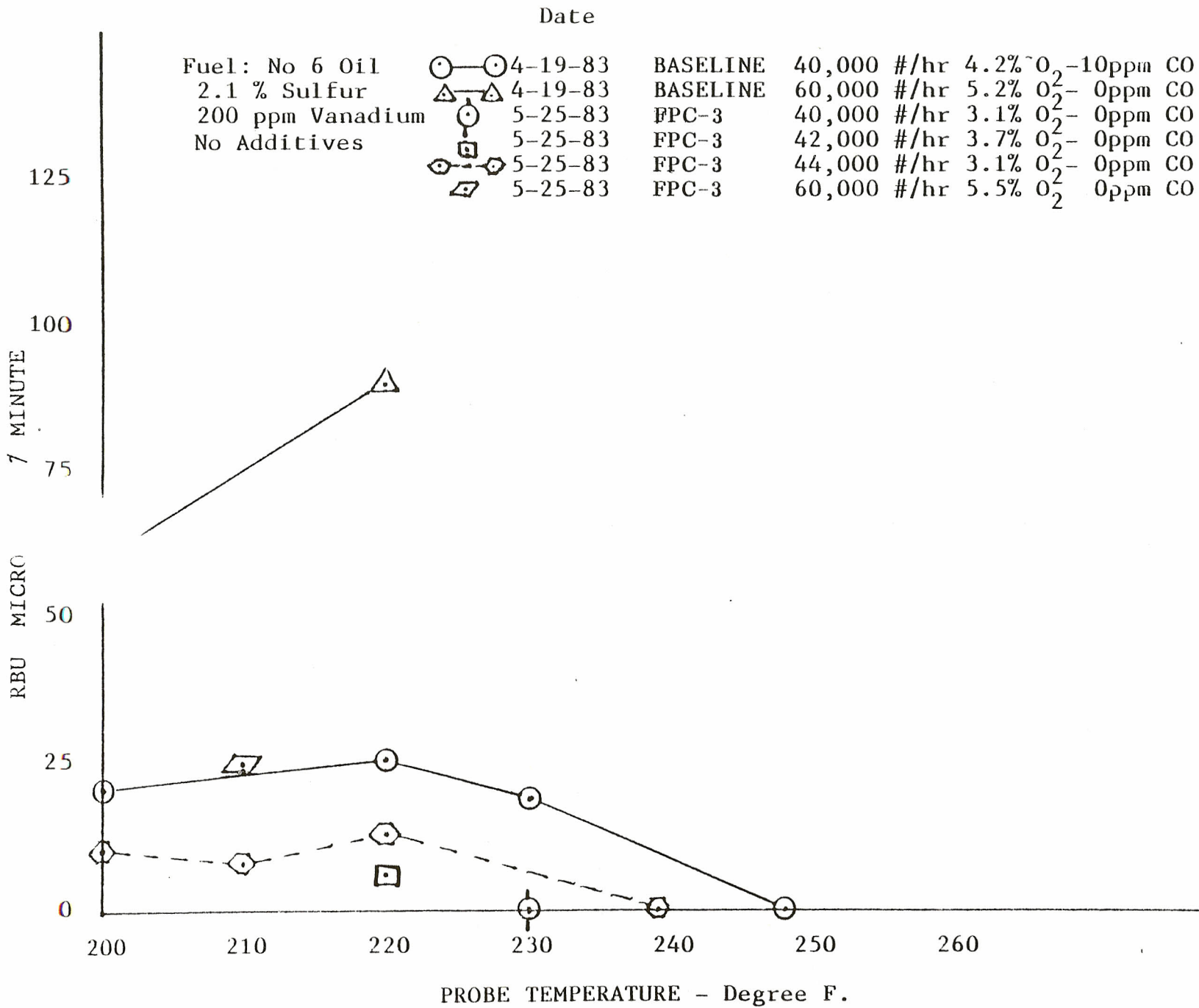
Finally, in testing performed by Clark and Childs in Reference No.1, experience indicates that appreciable corrosive tendencies do not become apparent until RBU goes over 100 microamps per minute. Enough information is still not available to be conclusive regarding 100 microamps as being the absolute breaking point. Figure 10 indicates that fire tubes have no "appreciable" problems, but this is not the case. However, for larger water tube and utility boilers, the 100 microamp RBU tends to agree with past performance and maintenance records.

In comparing FPCS with MgO additives, findings show FPCS to be 50% more effective in reducing sulfuric acid problems, and equal to MgO in reducing vanadium pentoxide fireside deposits. This is based on using both FPCS and MgO at the factory-prescribed mixing ratios. Figures 11 and 12 show that the RBU is

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lower using FPCS, and therefore, acid problems (or cold-end corrosion) have been reduced or eliminated. The vanadium pentoxide problem was controlled well by both FPCS and the MgO additives, as long as proper mixing ratios were maintained.

Another fact regarding Figures 11 and 12, is the RBU and the type of boiler. All watertubes tested to date show a 50% reduction in RBU from untreated fuel to that of fuel with a MgO additive. However, in reviewing the firetube boiler perform- ance, (Figure 12), the RBU with MgO is actually higher than the untreated fuel; while with FPCS, the RBU is essentially "0". FPCS works better in the firetube boiler due to the higher firebox pressure and the elongated flame pattern, which allows for more resonance time for FPCS to react with the fuel.

APPENDIX 1

Date

Fuel: No 6 Oil   ⊙———⊙ 4-19-83   BASELINE   40,000 #/hr 4.2% O_2 -10ppm CO
2.1 % Sulfur   △——△ 4-19-83   BASELINE   60,000 #/hr 5.2% O_2 - 0ppm CO
200 ppm Vanadium   ⊙ 5-25-83   FPC-3   40,000 #/hr 3.1% O_2 - 0ppm CO
No Additives   ▫ 5-25-83   FPC-3   42,000 #/hr 3.7% O_2 - 0ppm CO
                        ⬠⬠ 5-25-83   FPC-3   44,000 #/hr 3.1% O_2 - 0ppm CO
                        ▱ 5-25-83   FPC-3   60,000 #/hr 5.5% O_2 0ppm CO

RBU MICRO / MINUTE

125

100

75

50

25

0

200   210   220   230   240   250   260

PROBE TEMPERATURE - Degree F.

Corrosioin Potential -vs- Temperature

100,000 #/hr Water Tube
Site A

FIGURE 1

Fuel: No 6 Oil
2.1% Sulfur
200 - 350 ppm Va
MgO Baseline
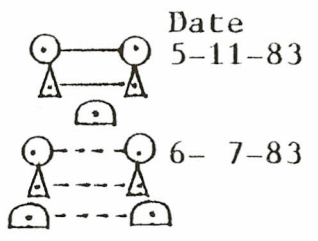
Date
⊙—⊙ 5-11-83   BASELINE   30% Load 3.1% O_2 - 86ppm CO
△—△   BASELINE   50% Load 4.6% O_2 7ppm CO
⌓   BASELINE   60% Load 3.1% O_2 8ppm CO
⊙--⊙ 6- 7-83 FPC-3   30% Load 2.8% O_2 - 5ppm CO
△--△   FPC-3   50% Load 3.4% O_2 0ppm CO
⌓--⌓   FPC-3   60% Load 5.7% O_2 0ppm CO

RBU MICRO-AMPS / MINUTE

125

100

75

50

25

0

200   210   220   230   240   250   260   270   280

PROBE TEMPERATURE - Degree F.
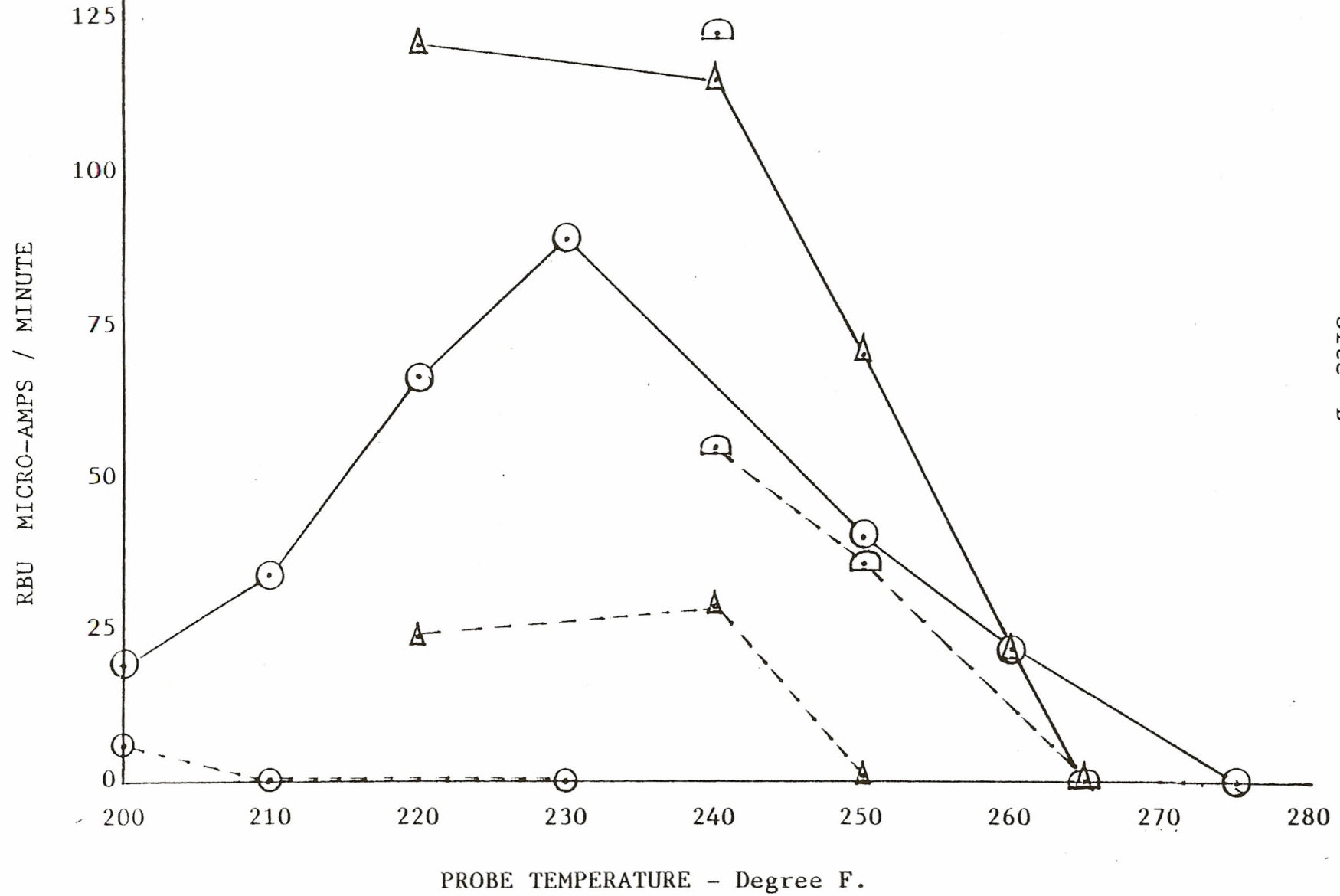
FIGURE 2

Corrosion Potential - vs - Temperature
40,000 #/hr Water tube
Site 'B'

FIGURE 3

Corrosion Potential -vs- Temperature
13,800 #/hr Firetube
Site 'C'

FIGURE 4

Corrosion Potential -vs- Temperature

10,350 #/hr Firetube
Site 'D'

Legend:

Fuel: No 6 Oil ⊙——⊙ 5-12-83 BASELINE 3200 #/hr 5.5% O_2- 0ppm CO
2.1% Sulfur ⊙—·—⊙ 6-30-83 FPC-3 3200 #/hr 4.8% O_2- 0ppm CO
150 - 250 ppm Va ⊙——⊙ 8-11-83 FPC-3 3200 #/hr 4.6% O_2- 0ppm CO
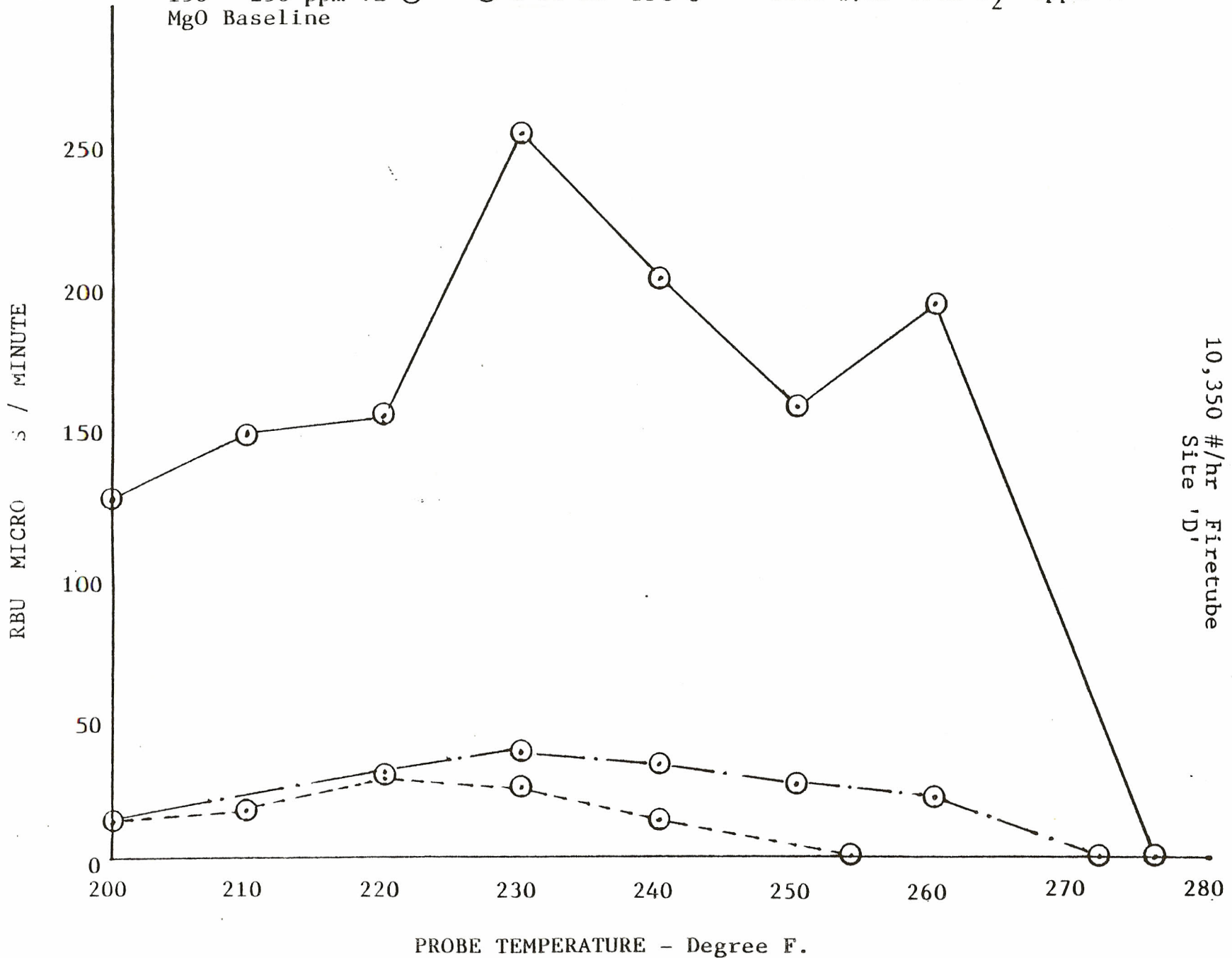MgO Baseline

Date

Y-axis: RBU MICRO s / MINUTE

X-axis: PROBE TEMPERATURE - Degree F.

GENERAL INFORMATION

Regarding Sulfur, Vanadium, Sodium and Boiler Operation

Fuel-oil Ash - 3.1

The ash content of residual fuel oil seldom exceeds 0.2%, an exceedingly small amount compared to that in coal. Nevertheless, even this small quantity of ash is capable of causing severe problems of external deposits and corrosion in boilers. Of the many elements that may appear in oil-ash deposites, the most important are vanadium, sodium and sulfur. Compounds of these elements are found in almost every deposit in boilers fired by residual fuel oil and often constitute the major portion of these deposits.

Origin of Ash - 3.1.1

As with coal, some of the ash-forming constituents in the crude oil had their origin in animal and vegetable matter from which the oil was derived. The remainder is extraneous material resulting from contact of the crude oil with rock structures and salt brines, or picked up during refining processes, storage and transportation.

In general, the ash content increases with increasing asphaltic constituents in which the sulfur acts largely as a bridge between aromatic rings. Elemental sulfur and hydrogen sulfide have been identified in crude oil, and simpler sulfur compounds are found in the distillates of crude oil including thio-esters, disulfides, thiophenes and mercaptans.

Vanadium, iron, sodium, nickel and calcium in fuel oil were probably derived from the rock strata, but some elements such as vanadium, nickel, zinc and copper probably came from organic matter from which the petroleum was derived. Vanadium and nickel especially, are known to be present in organo-metallic compounds known as porphyrins which are characteristic of certain forms of animal life. Table 1 indicates the amounts of vanadium, nickel and sodium present in residual fuel oils from various crudes.

TABLE #1
Vanadium, nickel and sodium content
of residual fuel oils
(parts per million by weight)

Source of Crude Oil	Vanadium	Nickel	Sodium
Africa			
1	5.5	5	22
2	1	5	--
Middle East			
3	7	--	1
4	173	51	--
5	47	10	8
United States			
6	13	--	350
7	6	2.5	120
8	11	--	84

(Continued...)

TABLE #1

Source of Crude Oil	Vanadium	Nickel	Sodium
Venezuela			
9	--	6	480
10	57	13	72
11	380	60	70
12	113	21	49
13	93	--	38

Crude oil as such is not normally used as a fuel, but is further processed to yield a wide range of more valuable products. For example, in a modern U.S. refinery, the average product yield, as a percentage of total throughput, is:

Gasoline	44.4
Lube oil fraction	16.4
Jet fuel	6.2
Kerosine	2.9
Distillates	22.5
Residual fuel	7.6

Virtually all metallic compounds and a large part of the sulfur compounds are concentrated in the distillation residue, as illustrated for sulfur in Table 2. Where low-sulfur residual fuel oils are required, they are obtained by blending with suitable stocks, including both heavy distillates and distillation from low-sulfur crudes. This procedure is also used occasionally if a residual fuel oil must meet specifications such as vanadium, or ash content.

TABLE #2
Sulfur content in fractions of Kuwait crude oil

Fraction	Distillation Range, F	Total Sulfur % by Weight
Crude oil	---	2.55
Gasoline	124-253	0.05
Light naphtha	257-300	0.05
Heavy naphtha	307-387	0.11
Kerosine	405-460	0.45
Light gas oil	477-516	0.85
Heavy gas oil	538-583	1.15
Residual oil	588-928	3.70

Source, Article by F.E. Hixon, Shell Refining and Marketing Co., Ltd.,"Chemistry and Industry",March 26, 1955;page 333.

Release of Ash During Combustion - 3.1.2

Residual fuel oil is preheated and atomized to provide enough reactive surface so that it will burn completely within the boiler furnace. The atomized fuel oil burns in two stages. In the first stage, the volatile portion burns and leaves a porous coke residue; and in the second stage, the coke residue burns. In general, the rate of combustion of the coke residue is inversely proportional to the square of its diameter, which in turn is related to the droplet diameter; refer to Figure #1. Thus, small fuel droplets give rise to coke residues that burn very rapidly and the ash-forming constituents are exposed to the highest temperatures in the flame envelope. The ash-forming constituents in the larger coke residues from the larger fuel droplets are heated more slowly, partly in association with carbon. Release of the ash from these residues is determined by the rate of oxidation of the carbon.

Figure #1   DROP OR PARTICLE DIAMETER, MICRONS

COMBUSTION TIME AS FUNCTION OF PARTICLE SIZE
AND TYPE OF FUEL
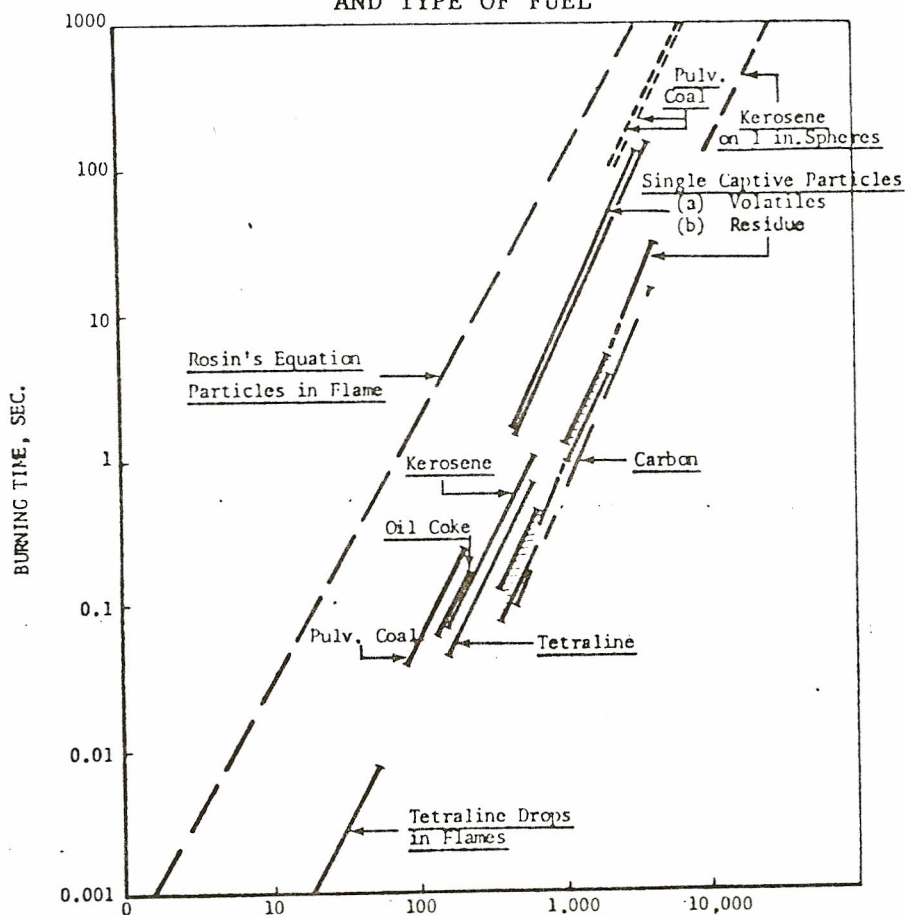
Source, Report by D.J. Burnett, BSc; Babcock&Wilcox Canada Ltd., "Development & Design of Low Excess Air Oil Burners", April 2, 1970

During combustion, the organic vanadium compounds in the residual
fuel oil thermally decompose and oxidize in the gas stream to
V_2O_3, V_2O_4 and finally V_2O_5. Although complete oxidation may not
occur and there may be some dissociation, a large part of the
vanadium originally present in the oil exists as vapor phase V_2O_5
in the flue gas. The sodium, usually present as chloride in the
oil, vaporizes and reacts with sulfur oxides either in the gas
stream or after deposition on tube surfaces. Subsequently, re-
actions take place between the vanadium and sodium compounds with
the formation of complex vanadates having melting points lower
than those of the parent compounds; for example:

$$(4) \qquad Na_2SO_4 + V_2O_5 \longrightarrow 2NaVO_3 + SO_3 \uparrow$$

Melting Points 1625F   1275F   1165F
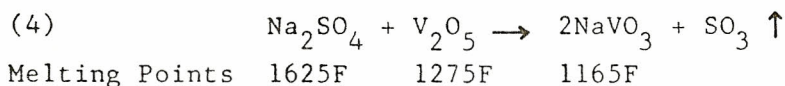
Excess vanadium or sodium in the ash deposit, above that necessary
for the formation of the sodium vanadates (or vanadyl vanadates),
may be present as V_2O_5 and Na_2SO_4, respectively.

The sulfur in residual fuel is progressively released during com-
bustion and is promptly oxidized to sulfur dioxide (SO_2). A small
amount of sulfur dioxide is further oxidized to SO_3 by a small
amount of atomic oxygen present in the hottest part of the flame.
Also, catalytic oxidation of SO_2 to SO_3 may occur as the flue
gases pass over vanadium-rich ash deposits on high-temperature
superheater tubes and refractories.

*Vanadium Pentoxide Formation – 3.1.2.1

Vanadium, which is present in fuel oil as soluble organic complexes,
decomposes during combustion. The initial product of vanadium
combustion is vanadium trioxide, V_2O_3, with a melting point of
3578^OF. If this form of vanadium remains, it will pass through
the boiler as a dry dust causing no slagging or corrosion problems.
If further oxidation occurs, then:

$$2V_2O_3 + O_2 \longrightarrow 2V_2O_4 \quad \text{(Vanadium Tetroxide-melt. pt. 3578F)}$$
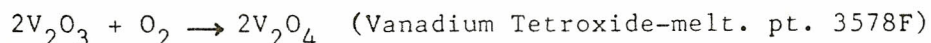
Vanadium tetroxide is also a dust and easily carried out of the
boiler. However, further oxidation accelerated by high levels
of excess air, will result in the formation of vanadium pentoxide:

$$2V_2O_4 + O_2 \longrightarrow 2V_2O_5 \quad \text{Vanadium Pentoxide-melt. pt. 1247F)}$$
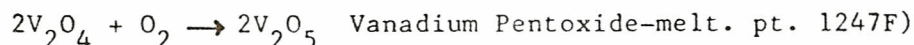
The vanadium pentoxide may also combine with sodium, nickel and iron
to form other low-melting point vanadate compounds. Low-melting
vanadate deposits are most severe on the boiler surfaces first con-
tacted by molten vanadium compounds, supports and hangers, the fur-
nace and the first rows of convection tubes are usually severely
affected by vanadium deposits. The immediate result is increased
draft loss and increased stack temperatures. The inevitable result
is the tremendous maintenance burden when attempting to remove the
hard vanadium slag.

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In addition to the deposits, vanadium compounds also create corrosion problems. Corrosion occurs when the metal oxide coating which normally protects metal surfaces is dissolved by the vanadates. Oxidation of the metal follows from the oxygen available in the combustion gases and then the cycle repeats until the metal surface fails.

The refractory burner throats can also be attacked by vanadium if burners are not properly set. The vanadium can diffuse back into the porous refractory and can be absorbed; and since the slag deposits and refractory expand and contract at different rates, the throat can crack or spall.

Therefore, vanadium is responsible for most hot-section slag deposits and corrosion problems in the boiler fireside.

*Sulfuric Acid Formation – 3.1.2.2

Fuel oil normally contains sulfur; either in the elemental form, or as hydrogen sulfide, nercaptan sulfides, disulfides, thiophenes, or polysulfides. This sulfur reacts with oxygen during fuel oil combustion to form sulfur dioxide:

$$S + O_2 \longrightarrow SO_2$$
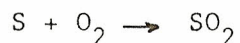
About one (1) to five (5) percent of the sulfur dioxide then reacts with available oxygen to form sulfur trioxide:

$$SO_2 + \tfrac{1}{2}O_2 \underset{Fe_2O_3}{\overset{V_2O_5}{\rightleftharpoons}} SO_3$$
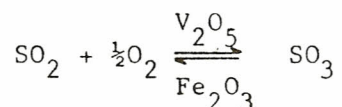
The amount of SO_3 formed is therefore a function of the level of excess air present. Furthermore, the formation of SO_3 is catalyzed by vanadium pentoxide and iron oxide, as shown by the above equation. Finally, the SO_3 combines with moisture present in the flue gas to form sulfuric acid when the combustion gases are cooled below the acid dewpoint:

$$SO_3 + H_2O \rightleftharpoons H_2SO_4$$
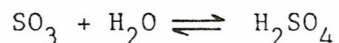
There are two details that now require more explaination with respect to SO_3 formation, depending upon the size of the boiler. Typically, in a large utility boiler the flame temperatures are higher than a small package boiler. As a result, a phenomenon occurs where oxygen (O_2) is broken to "O", or atomic oxygen, which will adhere to any free atoms and therefore form SO_3 in the hottest part of the flame. This temperature is estimated at $3400^{\circ}F-3800^{\circ}F$. However, in the smaller package boilers, the flame temperatures are normally $2400^{\circ}F-3200^{\circ}F$, and SO_3 formation will be the direct result of excess O_2 combined with vanadium or iron catalyzation.

Oil-slag Formation and Deposits - 3.2

The deposition of oil-ash constituents on the furnace walls and superheater surfaces has been a serious problem in recent years. This deposition, coupled with corrosion of superheater and reheater tubes by deposits, was largely responsible for the break in the trend towards higher steam temperatures that occurred in the early 1960's.

Practically all boiler installations are now designed for steam temperatures in the $1000-1015^{\circ}F$ range to minimize those problems and to avoid the higher capital costs of the more expensive alloys required in tubes, steam piping and turbine for $1050-1100^{\circ}F$ steam conditions.

There are many factors affecting oil-ash deposition on boiler heat absorbing surfaces. These factors may be grouped into the following interrelated categories:

1. Characteristics of the fuel oil
2. Design of the boiler
3. Operation of the boiler

Characteristics of Fuel-oil Ash - 3.2.1

Sodium and vanadium are the most significant elements in the fuel oil because they can form complex compounds having low melting temperatures, $480-1250^{\circ}F$, as shown in Table 3. Such temperatures fall within the range of tube-metal temperatures generally encountered in furnace and superheater tube banks of many oil-fired boilers. However, because of its complex chemical composition, fuel-oil ash seldom has a single sharp melting point, but rather softens and melts over a wide temperature range.

An ash particle that is in a sticky, semi-molten state at the tube-surface temperature may adhere to the tube if it is brought into contact by the gas flow over the tube. Even a dry ash particle may adhere due to mutual attraction or surface roughness. Such an initial deposit layer will be at a higher temperature than that of the tube surface because of its relatively low thermal conductivity. This increased temperature promotes the formation of adherent deposits. Thus, fouling will continue until the deposit-surface temperature reaches a level at which all of the ash in the gas stream is in a molten state so that the surface is merely washed by the liquid without freezing and continued buildup.

TABLE #3

Melting points of some oil-ash constituents

Compound	Melting Point, F
Aluminum oxide, Al_2O_3	3720
Aluminum sulfate, $Al_2(SO_4)_3$	1420*
Calcium oxide, CaO	4662
Calcium sulfate, $CaSO_4$	2640
Ferric oxide, Fe_2O_3	2850
Ferric sulfate, $Fe_2(SO_4)_3$	895*
Nickel oxide, NiO	3795
Nickel sulfate, $NiSO_4$	1545*
Silicon dioxide, SiO_2	3130
Sodium sulfate, Na_2SO_4	1625
Sodium bisulfate, $NaHSO_4$	480*
Sodium pyrosulfate, $Na_2S_2O_7$	750*
Sodium ferric sulfate, $Na_3Fe(SO_4)_3$	1000
Vanadium trioxide, V_2O_3	3580
Vanadium tetroxide, V_2O_4	3580
Vanadium pentoxide, V_2O_5	1275
Sodium metavanadate, $Na_2O \cdot V_2O_5 (NaVO_3)$	1165
Sodium pyrovanadate, $2Na_2O \cdot V_2O_5$	1185
Sodium orthovanadate, $3Na_2O \cdot V_2O_5$	1560
Sodium vanadylvanadates	
$\quad Na_2O \cdot V_2O_4 \cdot V_2O_5$	1160
$\quad 5Na_2O \cdot V_2O_4 \cdot 11V_2O_5$	995

*Decomposes at a temperature around the melting point

In experimental furnaces, it has been found that the initial
rate of ash buildup was greatest when the sodium-vanadium ratio
in the fuel oil was 1 to 6, but an equilibrium thickness of de-
posit (1/8 to 1/4 in. thick) was reached in approximately 100
hours of operation. When the fuel oil contained more refractory
constituents such as silica, alumina, and iron oxide in addition
to sodium and vanadium, an equilibrium condition was not reached
and the tube banks ultimately plugged with ash deposits. However,
these ash deposits were less dense; ie, more friable than the
glassy slags encountered with a 1 to 6 sodium-vanadium fuel oil.
Both the rate of ash buildup and the ultimate thickness of the
deposits are also influenced by physical factors such as the
velocity and temperature of the flue gases and particularly the
tube-metal temperature.

In predicting the behavior of a residual oil insofar as slagging
and tube-bank fouling are concerned, several fuel variables are
considered including, (1) ash content, (2) ash analysis, parti-
cularly the sodium and vanadium levels and the concentration of
major constituents, (3) melting and freezing temperatures of the
ash, and (4) the total sulfur content of the oil. Applying this
information in boiler design is largely a matter of experience.

Boiler Design - 3.2.2

Generally speaking, progressive fouling of furnaces and super-heaters should not occur if the tube-metal temperatures do not exceed $1000^{\circ}F$. If such trouble is encountered, the solution can usually be found in improving combustion conditions in the furnace and/or modifying the sootblowing procedures.

Studies on both laboratory and field installations have shown that the rate of ash deposition is approximately proportional to the velocity and temperature of the flue gases, and the concentration of oil-ash constituents in the flue gases. The geometry of the furnace and the spacing of tubes in the convection banks are selected in the design of a boiler to minimize the rate of deposition. It is common practice to use in-line tube arrangements with progressively wider lateral spacings for tubes located in higher gas-temperature zones. This makes bridging of ash deposits between tubes less likely and facilitates cleaning of tube banks by the sootblowers.

Boiler Operation - 3.2.3

Poor atomization of the fuel oil results in longer flames and frequently increases the rate of slag buildup on furnace walls which, in turn, makes it more difficult to keep the convection sections of the boiler clean. Completing combustion before the gases pass over the first row to tubes is especially important. Relatively large carbonaceous particles have a far greater tendancy to impinge on the tubes than do the smaller ash particles. If these larger particles are in a sticky state, they will adhere to the tubes where oxidation will proceed at a slow rate with consequent formation of ash. Fouling from this cause is difficult to detect by inspection during boiler outages because the carbonaceous material has usually disappeared completely. It can generally be detected during operation since flames are usually long and smoky and sparklers may be carried along in the flue gases.

Regular and thorough sootblowing can have a decisive effect on superheater and reheater fouling. To be fully effective, however, sootblowing cycles should be frequent enough so that ash deposits cannot build up to a thickness where their surfaces become semi-molten. If this point is reached, complete removal of the ash deposit can be very difficult because the sootblowers now have a dual task to perform: (1) to cool the surface of the deposit below its freezing temperature and (2) to shatter the now solid mass of slag and break its bond to the tube surface. In instances of extreme slagging, it is sometimes necessary to relocate soot-blowers, install additional sootblowers to control deposition in a critical zone, or to use additives.

The boiler load cycle can also have a significant effect on the severity of slagging and superheater fouling. A unit that is base-loaded for long periods is more apt to have fouling problems on a borderline fuel oil than a unit that takes daily swings in load. In the latter instance, the furnace generally remains cleaner due to periodic shedding of slag, with the result that the gas temperatures through the superheaters are appreciably lower. This eases the burden on the sootblowers and goes a long way towards controlling ash-deposit formation in the superheater-reheater tube banks. Overloading the boiler, even for an hour or two a day, should be avoided, especially if excess air has to be lowered to the point where some of the burners are starved of air. The furnace is apt to become slagged and ash deposition creeps into the superheater and reheater tube banks.
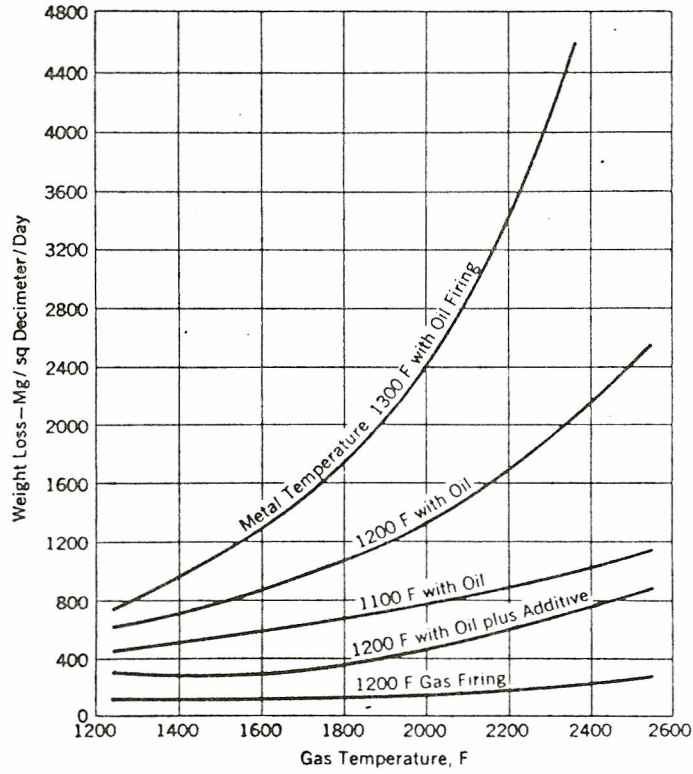
Oil-Ash Corrosion - 3.3

High-temperature corrosion - 3.3.1

The sodium-vanadium complexes, usually found in oil-ash deposits, are corrosive when molten. The corrosion mechanism is probably one of accelerated oxidation of metal brought about by oxygen transfer to its surface by the constituents in the molten ash, accompanied by the removal by the ash of the normal protective oxide coating on the metal surface.

Corrosion can also be caused by sulfate attack, particularly when sodium (or some other) chloride is also present in the fuel oil, and this may occur at metal temperatures as low as 1000°F. This type of corrosion is more apt to be encountered on boilers burning a low-vanadium fuel oil, but containing several hundred ppm of sodium chloride. Even when the chloride content of the fuel oil is negligible, sulfate corrosion may still be severe when reducing or alternating oxidizing-reducing conditions prevail around the tubes.

A measurable corrosion rate can be observed over a wide range of metal and gas temperatures, depending on the amount and composition of the oil-ash deposit. Fig. 2 shows the combined gas and metal temperature effects on corrosion for a specific fuel oil composition of 150 ppm vanadium, 70 ppm sodium and 2.5% sulfur. As the vanadium concentration of the fuel oil varies, the amount of corrosion, compared to a 150-ppm vanadium fuel, will increase or decrease according to the curve shown in Fig. 3.

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Figure #2

Effect of gas and metal temperatures on corrosion
of 304, 316 and 321 alloys in a unit fired with
oil containing 150ppm vanadium, 70ppm sodium and
2.5% sulfur. Test duration 100 hours.

Figure #3
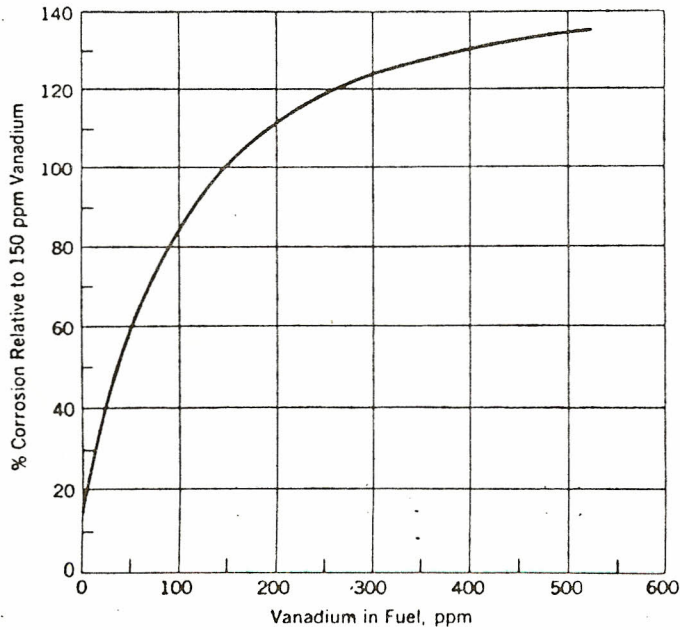
Effect of vanadium concentration on oil–ash corrosion.

The effect of the sodium level in the fuel oil is not quite so clear-cut because combustion conditions and the chloride content of the fuel oil may be controlling. The sodium content does, however, definitely effect the minimum metal temperature at which corrosion will be significant.

At the present time, there does not appear to be any alloy that is immune to oil-ash corrosion. In general, the higher the chromium content of the alloy, the more resistant it is to attack. This is the main reason for the use of 18Cr-8Ni alloys for high temperature superheater tubes. High chromium contents, greater than 30%, give added corrosion resistance, but at the expense of physical properties; 25Cr-20Ni has been used as a tube cladding, but even this alloy has not provided complete protection. The presence of nickel in high-temperature alloys is needed for strength. High nickel alloys may be fairly resistant to oil-ash attack under oxidizing conditions, but they are liable to sulfide attack brought about by local reducing conditions or by the presence of chloride in the ash deposit. Since it is difficult to avoid such conditions entirely, high-nickel content of alloys may be of limited value. In any event, the higher material cost must be justified by longer life, which is not always predictable.

Low-temperature corrosion — 3.3.2

In oil-fired boilers, the problem of low-temperature corrosion resulting from the formation and condensation of sulfuric acid from the flue gases is similar to that previously described for coal firing.

Oil-fired boilers are more susceptible to low-temperature corrosion than are most coal-fired units for two reasons: (1) the vanadium in the oil-ash deposits is a good catalyst for the conversion of SO_2 to SO_3 and (2) there is a smaller quantity of ash in the flue gases. Ash particles in the flue gas reduce the amount of SO_3 vapor in the gas. Since oil has considerably less ash than coal, significant differences would be expected. Furthermore, coal ash is more basic than oil ash and tends to neutralize any acid deposited; oil ash generally lacks this capability.

Under certain conditions, oil-fired boilers may emit acidic
particulates from their stacks that stain or etch painted
surfaces in the neighborhood of the plant. The acidic deposits
or smuts are generally caused by metallic surfaces (air
heaters, flues and stacks) operating well below the acid dew
point of the flue gases or by soot which has absorbed sulfuric
acid vapor in its passage through the boiler. Methods that can
be used to prevent acid-smut emission include:

1. Minimize SO_3 formation in the flue gases,
2. Neutralize SO_3 in flue gases,
3. Maintain all surfaces in contact with the flue
   gases above about $250^{\circ}F$ and,
4. Completely burn fuel oil to eliminate soot particles

Low-Temperature Corrosion and Percent Sulfur - 3.3.2.1

In order to reduce low-temperature corrosion, it is necessary to
use fuel with a sulfur content below 0.3%, or prevent the forma-
tion of SO_3. Cold-end corrosion can exist even with only 1% sulfur
oil, since the rate of conversion of SO_2 to SO_3 increases as sulfur
content decreases; as shown in Figures 4 and 5.

Methods of control - 3.3.3

The methods on control that have been used or proposed to
control fouling and corrosion in oil-fired boilers are sum-
marized in Table 3, but in every instance economics governs
their applicability. There is no doubt that reducing the
amount of ash and sulfur entering the furnace is the surest
means of control, and that minimizing the effects of the ash
constituents, once they have deposited on the tubes, is the
least reliable. Since the severity of fouling and corrosion
depends not only on the fuel-oil characteristics, but also
on boiler design and operating variables, a generalized
solution to these problems cannot be prescribed.

TABLE #4
Classification of methods for controlling fouling
and corrosion in oil-fired boilers

	Fuel Oil Supply
Reduce amount of	Selection
fuel ash constituents	Blending
to the furnace	Purification

	Design
Minimize amounts of fuel	Furnace geometry
ash constituents reaching	Tube bank arrangement
heat transfer surfaces	Metal temperature
	Gas temperature
	Sootblower arrangement

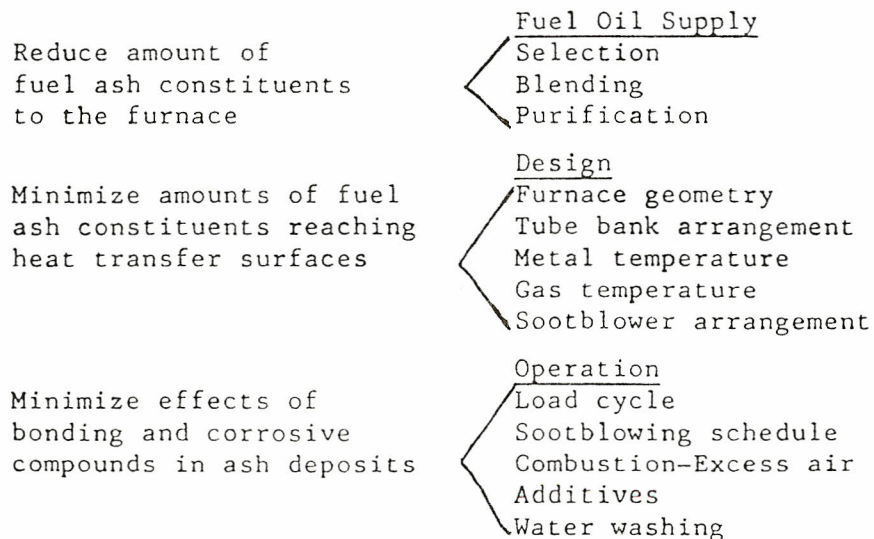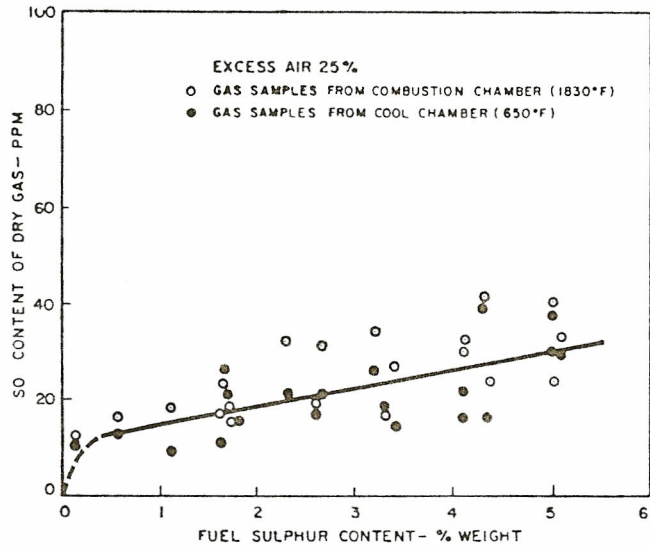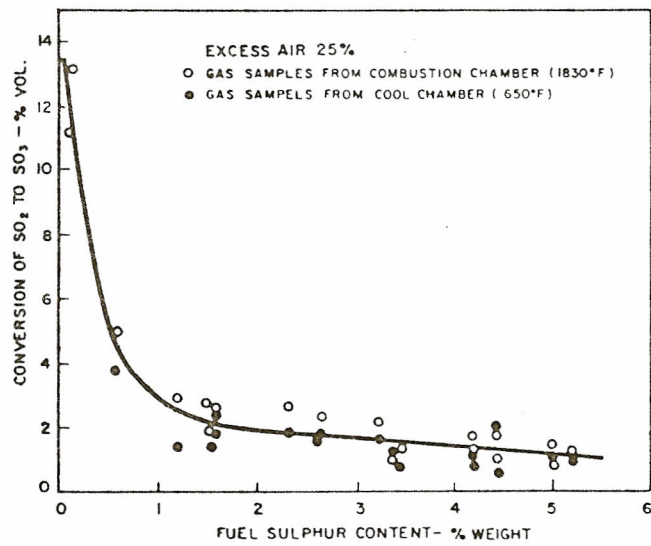|	Operation
Minimize effects of	Load cycle
bonding and corrosive	Sootblowing schedule
compounds in ash deposits	Combustion-Excess air
	Additives
	Water washing

Figure #4

Experimental furnace - variation of SO₂ content of flue gas
with sulfur content of fuel. Combustion, Aug. 1959.

Figure #5

variations of flue gas to sulfur content, same
paper, Combustion, Aug. 1959.   Rendle, Wilsden and Whittingham

Fuel oil supply – 3.3.4

Although fuel selection and blending are practiced to some extent in this country, it is done to provide safe and reliable handling and storage at the user's plant rather than to avoid fouling difficulties. Since the threshold limits of sodium, sulfur and vanadium are not accurately defined for either fouling or corrosion, utilization of these means of control cannot be fully exploited.

Processes are available for both the desulfurization and de-ashing of fuel oils. Water washing of residual fuel oil has been successfully applied to a few marine-type boilers, but it is doubtful that it will be widely used because only sodium and sediment, mainly rust and sand are removed by the process. Use of low-sulfur crudes and desulfurized fuel oil is expected to increase.
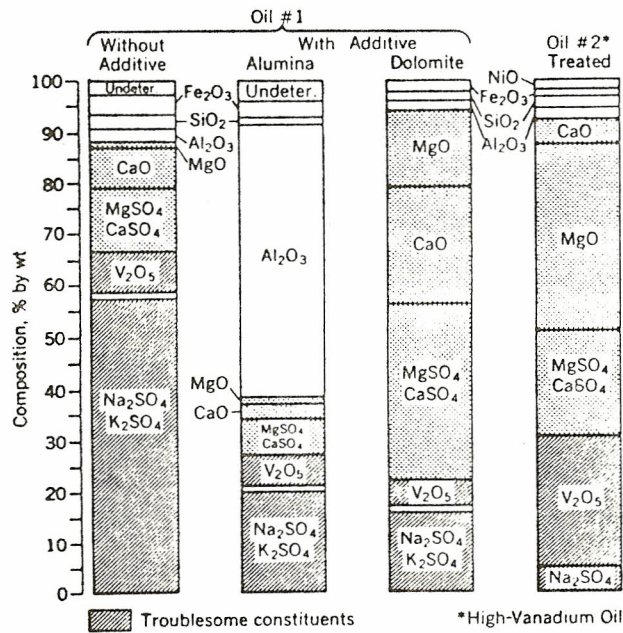
Fuel oil additives – 3.3.5

The practice of water washing out of service and, to a limited extent, in service has been beneficial in overcoming some of the troubles experienced with present oil fuels. In addition, continued study of the problem has revealed another approach that is effective where the fuel-oil ash is most troublesome. In brief, the method involves adding to the fuel or furnace small amounts of materials that change the character of the ash sufficiently to permit its removal by steam or air sootblowers or air lances.

Additives are effective in reducing the troubles associated with superheater fouling, high-temperature ash corrosion, and low-temperature sulfuric acid corrosion. Most effective are alumina, dolomite and magnesia. Kaolin is also a source of alumina. Analyses of typical superheater deposits from a troublesome fuel oil, before and after treating it with alumina or dolomite, are shown in three bar graphs at the left in Fig. 6. The results for a different oil treated with magnesia are shown in the bar graph at the right.

The reduction of fouling and high-temperature corrosion is accomplished basically by producing a high melting-point ash deposit that is powdery or friable and easily removed by sootblowers or lances. When the ash is dry, corrosion is considerably reduced.

Low-temperature sulfuric acid corrosion is reduced by the formation of refractory sulfates by reaction with the SO_3 gas in the flue gas stream. By thus removing the SO_3 gas, the dew point of the flue gases is sufficiently reduced to protect the metal surfaces. The sulfate compounds formed are relatively dry and easily removed by the normal cleaning equipment.

Figure #6

Effect of fuel oil additives on composition of oil ash deposit

In general, the amount of additive used should be about equal to the ash content of the fuel oil. In some instances, slightly different proportions may be required for best results, especially for high-temperature corrosion reduction, in which it is generally accepted that the additive should be used in weight ratios of 2 or 3 to 1, based on the vanadium content of the oil.

Several methods have been successfully used to introduce the additive materials into the furnace. The one in general use consists of metering a controlled amount of an additive oil slurry into the burner supply line. The additive material should be pulverized to 100% through a 325-mesh screen (44 microns) for good dispersion and minimum atomizer wear.

For a boiler fired by a high-pressure return-flow oil system, it has been found advantageous to introduce the additive powders by blowing them into the furnace at the desired locations. The powder has to be 100% through a 325-mesh screen for good dispersion.

A third, and more recent method, is to introduce the additive as a water slurry through specially adapted sootblowers or lances. This method offers the advantage of applying the additive in exactly the location desired, with a possible reduction in the quantity required. Some caution should be observed with this system to prevent possible thermal shock (quench-cracking) damage to the hot tubes. The presence of chlorides in the water slurry, from either the water or the additive material, could possibly produce stress-corrosion cracking of austenitic tubing and should be considered.

The choice of the particular additive material depends on its availability and cost to the individual plant and the method of application chosen. For example, alumina causes greater sprayer-plate wear than the other materials when used in an oil slurry.

The quantity of deposit formed is, of course, an important consideration for each individual unit from the aspect of cleaning. A comparison of the amounts of deposit formed with different additives shows that dolomite produces the greatest quantity because of its sulfating ability; alumina and kaolin form the least, and magnesia is intermediate. However, when adequate cleaning facilities are available, the deposits are easily removed, and the quantities formed should not be a problem.

Excess air control – 3.3.6

As mentioned previously, the problems encountered in the combustion of residual fuels – high-temperature deposits (fouling), high-temperature corrosion, and low-temperature sulfuric acid corrosion-all arise from the presence of vanadium and sulfur in their highest states of oxidation. By reducing the excess air from 7% to 1 or 2%, it is possible to avoid the formation of fully oxidized vanadium and sulfur compounds and, thereby, reduce boiler fouling and corrosion problems.

In a series of tests on an experimental boiler, it was found that the maximum corrosion rate of type 304 stainless steel super-heater alloy held at $1250^{o}F$ in $2100^{o}F$ flue gas was reduced more than 75% (see Fig. 7) when the excess air was reduced from an average of 7% to a level of 1-2%. Moreover, the ash deposits that formed on the superheater bank were soft and powdery, in contrast to hard, dense deposits that adhered tenaciously to the tubes when the excess air was around 7%. Also, the rate of ash buildup was only half as great. Operation at the 1-2% excess air level practically eliminated low-temperature corrosion of carbon steel at all metal temperatures above the water dew point of the flue gases (Fig. 8). However, much of the beneficial effects of low excess air combustion are lost if the excess air at the burner fluctuates even for short periods of time to a level of about 5%. Carbon loss values for low excess air were approximately 0.5%, which is generally acceptable for electric utility and industrial practice.

Figure #7
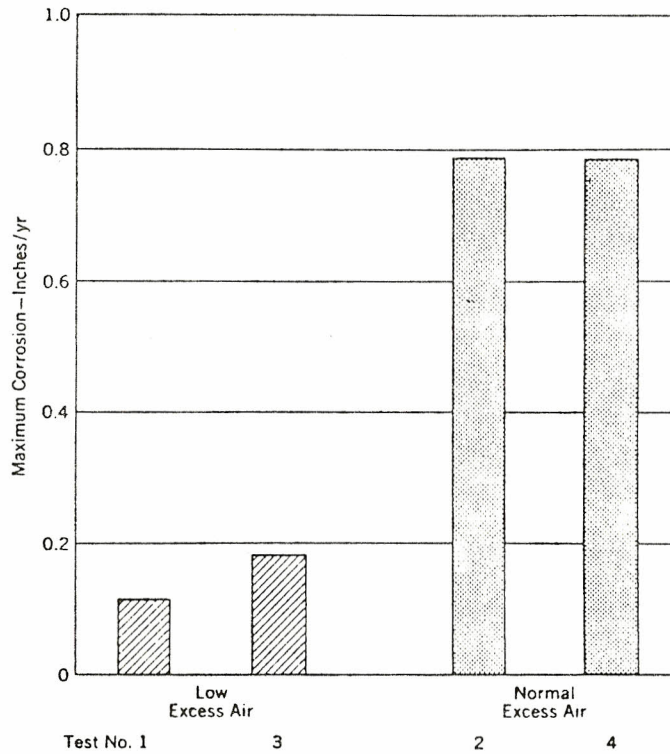
Effect of low excess air combustion on high-temperature oil ash corrosion

Figure #8
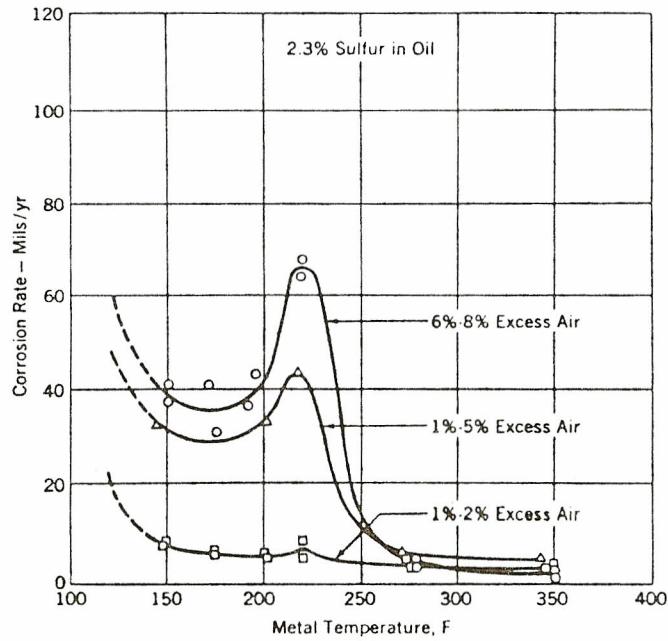
Effect of excess air on low-temperature corrosion of carbon steel

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A number of large industrial boilers, both in this country and in Europe, have been operating with low excess air for several years. As a result, the benefits of reducing low-temperature corrosion are well established. However, the benefits on high-temperature slagging and corrosion are not wholly conclusive. In any event, great care must be exercised to distribute the air and fuel oil equally to the burners, and combustion conditions must be continuously monitored to assure that combustion of the fuel is complete before the combustion gases enter the convection tube banks.