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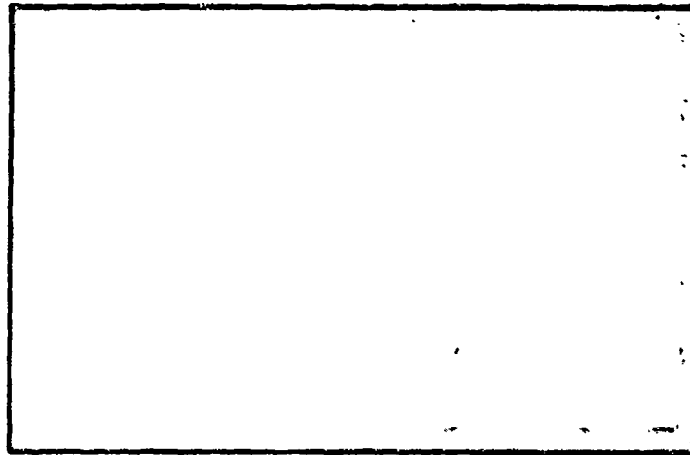
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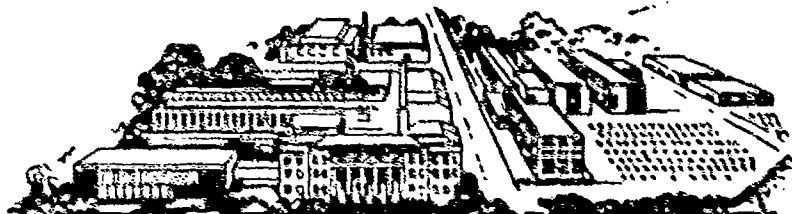
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⑥ STATE-OF-THE-ART REPORT

on

CONTROL OF CORROSION AND DEPOSITS
IN STATIONARY BOILERS
BURNING RESIDUAL FUEL OIL,

to

BUREAU OF YARDS AND DOCKS
NAVY DEPARTMENT

⑪ May 1, 1963,

by

P. D. Miller, C. J. Slunder,
H. H. Krause, and F. W. Fink •

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CONTROL OF CORROSION AND DEPOSITS IN STATIONARY BOILERS BURNING RESIDUAL FUEL OIL

INTRODUCTION

Fire-side corrosion and deposits are found in boilers fired with either residual fuel oil or coal. This state-of-the-art report is primarily concerned with plants using residual fuel oils, or No. 6 fuel oil, as the source of energy.

The Bureau of Yards and Docks regularly receives reports on stationary boilers under Navy control. For many of the boilers, the reports indicate that the steam-raising plant contains modern and well-equipped boilers and that they are operating with a minimum of difficulty. Operators of other plants, because of such factors as sudden changes in the steam demand, contamination of the fuel supply, boiler design or installation features, or lack of facilities for measurements, inspection, or chemical analyses, are not in a good position to provide BuDocks with complete information.

BuDocks is interested in developing information leading to improved performance and to economies in their steel water-tube stationary boilers which use residual fuel oil as the main energy source. BuDock's interest and concern arises partly from the fact that in recent years the quality of residual fuel oil has deteriorated and is continuing to deteriorate. This, and the gradual broadening of the temperature range of such boilers, have tended to intensify problems caused by corrosion and deposits.

BuDocks, through various commercial interests, is being offered a wide variety of corrective treatments for residual fuel oil. The Navy Department does not intend to become bound to a single source of treatment for residual fuel oil. An impartial investigation by an unbiased agency is desired to establish the best procedures for minimizing corrosion and deposits in boilers operated by BuDocks.

The type of boiler selected for a shore station in the Navy will vary according to the service required. Some power plants provide steam for special purposes, such as electricity generation (steam turbines) or for a testing facility (e.g., a catapult rig). Most of the boiler plants provide mainly steam for hot-water heating, hospitals, cafeterias, shops, and other buildings, and for supply when needed to ships in dock. The load will vary with the time of day, with change in seasons, and with the special activities at the particular base. In the selection of an oil-fired boiler, attention must also be given to the Navy's alternative fuel requirements in some areas; e.g., pulverized coal or natural gas may serve as alternative fuels.

An estimate of the range of boilers under BuDock's administration, resulting from discussions held in Washington, D. C., is as follows:

<u>Description</u>	<u>Percentage of Interest</u>
15 to 125-psi saturated steam	70
125 to 400-psi superheated steam	20 to 25
Small utility-type boilers	5 to 10

A useful discussion on the manifold types of boilers available and their characteristics is given in a recent book by Shields^{(185)*}. Because boilers vary greatly in shape, size, and arrangement, any attempt to classify particularly troublesome areas should be based on general patterns rather than on specific designs. Jacklin, Anderson, and Thompson⁽⁹¹⁾ indicated that temperature is the most important single factor affecting fire-side deposits.

Five principal temperature zones may exist in boilers. The gas and tube or metal temperatures in each are as follows:

	<u>Gas Temperature, F</u>	<u>Tube Temperature, F</u>
Radiant section	3000-2000	650-450
Superheater	2000-1000	1200-600
Convection	1500-500	650-450
Economizer	800-300	600-200
Air preheater	600-300	500-200

In individual boilers, one or more of these areas may be absent. Also, for each area, the temperature found in a large boiler may be near the upper limit of the range shown, while for a smaller boiler it may be near the lower limit of the temperature range. Figure 1 is a schematic drawing showing some of the components often found in a steam boiler.

Low-temperature corrosion and deposits occur in the cold end of the boiler. These are usually caused by the condensation of an acid liquid film on the metal surfaces when the metal temperature drops below the acid dewpoint of the flue gases. This situation may exist in the economizer, air preheater, and stack areas. The deposits are usually wet and sticky. Many materials are subject to corrosion by aqueous acid solutions.

Similarly, high-temperature problems occur in the hot zones of the boiler. Deposits on superheaters may be hard and adherent, and corrosion may be caused by high-temperature oxidation or sulfidation, sometimes accelerated by the presence of molten ash deposits.

During the past 15 years, the problems associated with the burning of residual fuel oils have been greatly intensified. Difficulties associated with corrosion and deposits from residual fuel oil coincided approximately with the period of increasing interest in boilers producing steam at 1000 F or higher and also in the development of oil-burning gas turbines. In both of these applications, metal temperatures at certain points would be expected to exceed about 1100 F. Heavy fuel oils had been used for many years at lower temperatures without serious slagging or corrosion difficulties according to Schab⁽¹⁷⁸⁾. Therefore, it seemed apparent that part of the difficulties were related to the higher operating temperatures. Numerous studies and investigations have been conducted to gain additional information about the problem.

The large volume of published literature indicates that the interest is world wide. Within the past few years, reviews and bibliographies on this subject have appeared in several countries, covering both low- and high-temperature aspects of the problem. Reference to these reviews are given at this point merely to provide a background on the activities in the field, but the pertinent information they contain which relates to

*Literature references start on page 119.

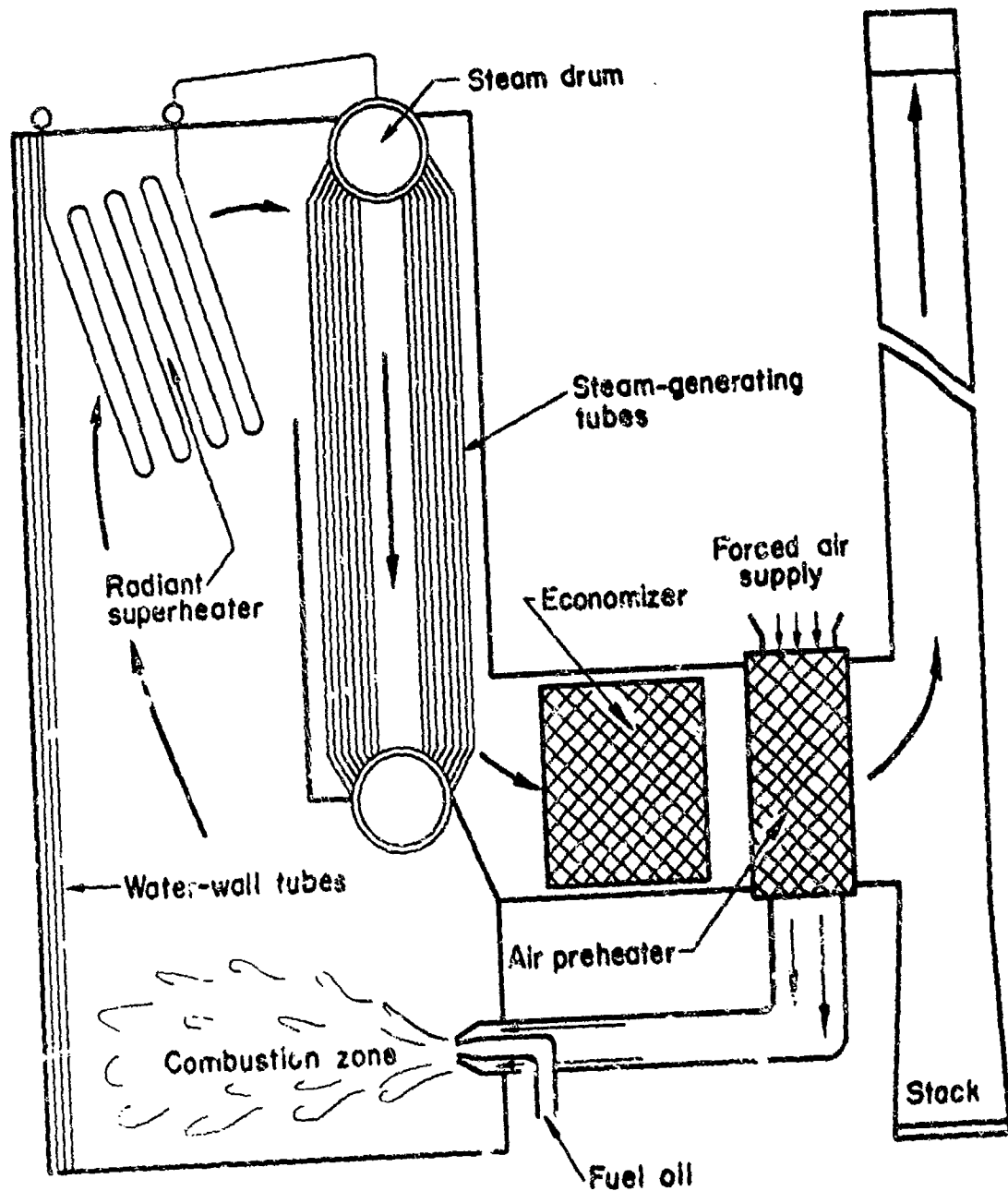


FIGURE 1. SCHEMATIC DRAWING OF PRINCIPAL COMPONENTS OF AN OIL-FIRED STEAM-GENERATING BOILER

either low- or high-temperature problems will be discussed in the subsequent chapters of this report.

BIBLIOGRAPHIES AND REVIEWS

In 1959, a comprehensive review of the available information on corrosion and deposits in coal-fired and oil-fired boilers and in gas turbines was published by the American Society of Mechanical Engineers⁽³⁾. A 10-year bibliography by Schab already has been cited⁽¹⁷⁸⁾. A bibliography, including short abstracts of the references listed, on corrosion by vanadium pentoxide was prepared by the Mond Nickel Company, Ltd.⁽¹¹⁾. As indicated by the title, most of the references deal specifically with the corrosion problem. Residual oil-ash corrosion was also discussed in a review by Slunder⁽¹⁹¹⁾, and a bibliography on the subject (listing articles prior to 1948 and for each subsequent year through 1958) was prepared by NACE Task Group T-5L-3⁽¹⁰⁾. In Germany, Gurnz published a review covering the effects of fuel composition, combustion conditions, and metal temperature on corrosion by flue gases.⁽⁷⁷⁾ Gurnz also published a bibliography including abstracts of the most recent and important articles on corrosion by flue gases.⁽⁷⁶⁾ Another comprehensive review, specifically relating to the high-temperature corrosion caused by vanadium pentoxide, was published in England by K. Sachs.⁽¹⁷⁵⁾ A review of the literature, also on the vanadium pentoxide problem, was prepared by Fairman.⁽⁵⁵⁾ Two reviews of gas-turbine fuels^(47,61) included discussion of the corrosion and deposition problems associated with residual oil. A very recent survey compiled by Edwards⁽⁵¹⁾, on behalf of the Admiralty Fuels and Lubricants Committee, includes a comprehensive discussion of fire-side corrosion and deposits in oil-fired naval and land-based boilers and in gas turbines, and a bibliography of over 200 references. Several chapters in a recent Russian book⁽¹⁹⁵⁾ are concerned with the behavior of heat-resistant alloys under vanadium corrosion conditions, and with preventive measures such as coatings for metals, and additives in the oil. An abstract of an article by Panetti⁽¹⁴³⁾ indicates it is a review of the subject published in Italy. Several useful reviews of low-temperature corrosion also have been presented. Two very useful ones are those by Kear⁽⁹⁸⁾ and by Moskovitz⁽¹³⁵⁾.

Most recently an international conference was held in England by the Central Electricity Generating Board in May 1963, to review again the vast amount of information available today on external corrosion and deposits. In all, 46 papers were presented to the 150 corrosion technologists present. Publication is planned of the proceedings of this conference, but the material is available at the time of writing only as reprints.

While these bibliographies may show some duplication in references, the topics emphasized in each of the various reviews varied according to the objectives of the reviewers.

CHAPTER I. FLUE-GAS CONDENSATE CORROSION IN THE LOW-TEMPERATURE ZONES OF THE BOILER

CORROSION IN LOW-TEMPERATURE ZONES

Susceptible Boiler Components

The economizers, air preheaters, and stacks of oil-burning water-tube boilers are particularly susceptible to corrosive attack, as are fire tubes in some shell-type boilers, because conditions are often favorable at these sections for the formation of corrosive liquid films by condensation of gaseous combustion products.⁽²¹²⁾ It is well established that these boiler components are attacked by flue-gas condensate films at higher reaction rates than is the case when these items are maintained in the dry state at temperatures slightly above the dewpoint.

Flue-Gas Compositional Factors

Sulfur Compounds

The major factor in corrosion observed at the low-temperature end of the boiler is the acidic sulfur compounds present in the combustion gases. Under some special conditions, hydrochloric or nitric acids also may form, and their presence in the flue gas would tend to increase the rate of attack.

Deposits in the low-temperature zones of the boiler are composed largely of iron sulfates, sulfuric acid, carbon, and ash. Since less ash is formed in oil firing than in coal firing, the problems associated with ash deposits usually are less severe in oil-fired boilers.

Sulfuric Acid

The major portion of the sulfur in the fuel is burned and appears as sulfur dioxide in the flue gas. A small portion of the SO_2 may be further oxidized to SO_3 . The dewpoint is markedly affected by the total SO_3 present. Films of sulfuric acid are formed on metal surfaces at relatively high temperatures, such as 350 F, as a result of the condensation of sulfuric acid vapor formed by the combination of SO_3 and water vapor in the flue gas. Temperatures of 350 F and lower often arise as the flue gas approaches the exit end of the boiler. In most boilers, the much lower metal temperatures of 100 to 105 F required for the deposition of sulfurous acid and hydrochloric acid are not reached.

The dewpoint of the flue gas is markedly increased by small increases in the sulfur content of the fuel oil, up to about 0.5% sulfur. At higher sulfur contents in the

fuel, the increase in SO_3 in the flue gas is much more gradual and follows the relationship illustrated in Figure 2, taken from data published by Rendle and Wilsdon⁽¹⁶⁶⁾. These authors also summarized results from other investigations^(40, 58, 204).

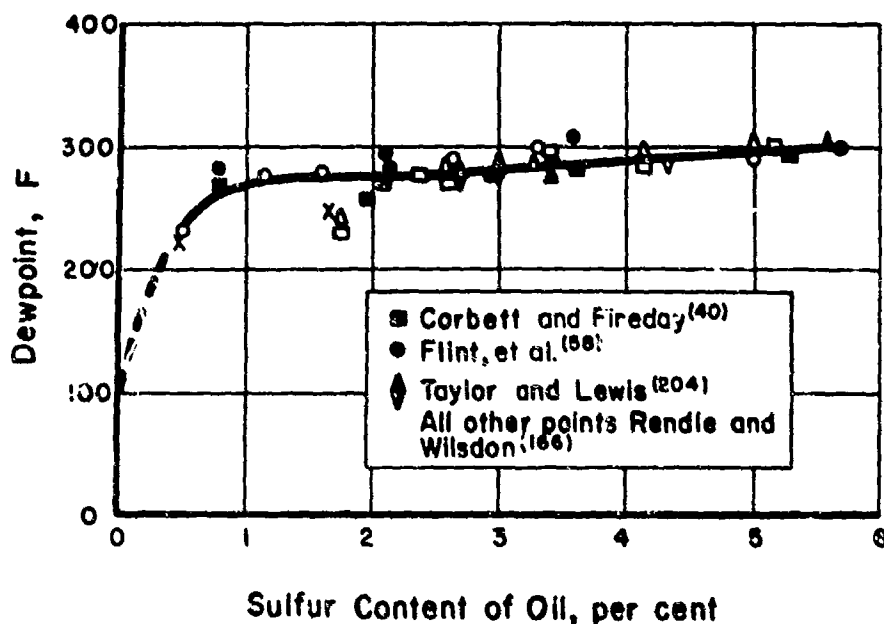


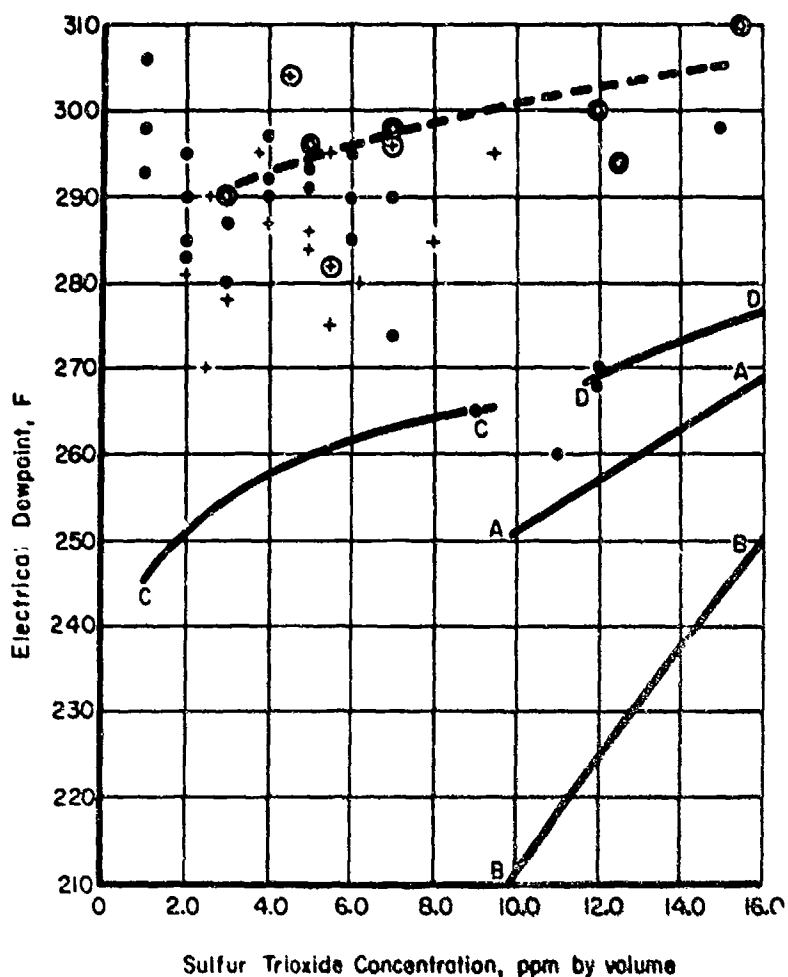
FIGURE 2. RELATIONSHIP OF DEWPOINT TO SULFUR CONTENT OF OIL⁽¹⁶⁶⁾

Data refer to 25% excess air for combustion.

It can be seen that in order to lower the dewpoint below about 250 F, it would be necessary to reduce the sulfur content of the oil well below 0.5%. The control of low-temperature acid corrosion by removal of the sulfur in the fuel oil is not economically feasible, according to presently available information.

It is of interest to note that at very low excess air, when the oxygen in the flue gas is less than about 0.5 per cent, there is a marked decrease in the SO_3 level, irrespective of the sulfur content of the fuel.

Dewpoint Determinations. Recently, the dewpoint in boilers was measured by different methods by Alexander and her associates.⁽²⁾ They concluded that, at least at low SO_3 contents, there is no simple relationship between the dewpoint and the amount of SO_3 in the flue gas. Their results, reproduced in Figure 3, show that even at low SO_3 concentration (such as 2 to 10 ppm), the dewpoint can be as high as 300 F. Figure 3 also includes references to other studies made with an operating boiler and with clean gas in the laboratory. The curve obtained by Alexander lies well above those presented by other workers. It is suggested that such differences are related to the effect of dust on the condensation phenomenon.



- No. 2 boiler, Bromborough, air heater inlet, no additive
- No. 7 boiler, Bromborough, air heater outlet, no additive
- ⊕ No. 2 boiler, Bromborough, air heater outlet, no additive
- AA P.F. Corbett, flue gases from an oil-fired boiler (21)

- BB A.A. Taylor, clean gases in the laboratory (202)
- CC W.E. Francis, clean gases in the laboratory (63)
- DD Rylands & Jenkinson, clean gases in the laboratory (173)
- Chemical dewpoint

FIGURE 3. EFFECT OF SULFUR TRIOXIDE CONCENTRATION ON DEWPOINT(2)

Corrosion Variables. Although the dewpoint temperature is a critical corrosion variable, in that corrosion rates at temperatures above the dewpoint are negligible, other factors are important in controlling the corrosion rate under conditions of condensation. Studies to date show that the more important variables controlling rates of corrosion are these:

- (1) Rate of acid condensation
- (2) Concentration of condensed acid.

As would be expected, the rate of acid condensation is directly related to the SO_3 content of the flue gas. Thus, the greater the partial pressure of SO_3 in the flue gas, the more rapidly will the metal structure be corroded.

The second corrosivity variable (concentration of condensed acid) is not dependent(135,212) on the amount of SO_3 present but is more directly related to metal-surface temperature and to the percentage of water vapor in the combustion gases.

Thus, the over-all corrosion rate is dependent on a complex combination of variables.

Acid Strength Versus Condensation Temperature. Figure 4 shows data obtained experimentally by Taylor(203) on the relation of the strength of the initially condensed acid to the temperature at which it condenses. The gases used contained acid corresponding to a dewpoint at 395 F and about 8% of moisture. The curve shows that the acid (which condenses out at temperatures slightly below the dewpoint) will be highly concentrated. In the range of 200 to 250 F, the acid will have a strength of 70 to 80%. As the temperature decreases, the strength of the acid condensed also will decrease. Thus, it is apparent that combustion gases from an oil-burning boiler can deposit sulfuric acid films, over a wide range of concentrations, onto metal and other surfaces.

Research has shown that the rate of corrosion of steel by sulfuric acid decreases to rates low enough to be tolerable only in the regions of extremely low and high acid concentrations. Room-temperature data presented by Fontana(60) are summarized in Table 1. It can be seen that at this temperature a corrosion rate of almost 2500 mils per year could be anticipated in 10% acid, and a rate of only about 10 mils per year at 90% concentration. It should be pointed out that, since these rates are for room temperature, the rates at the temperatures indicated in Figure 4 would be much greater. In addition, dilute acids would not be deposited at the surface temperatures encountered in many air preheaters and economizers during the operating cycle. However, during damp periods, the concentrated sulfuric acid on boilers not then in operation would be expected to be diluted by moisture absorbed from the air.

Designers usually provide that the normal temperatures of boiler heat-exchanger surfaces usually are maintained above the regions where the highly corrosive acid strengths of less than 60 per cent are formed.

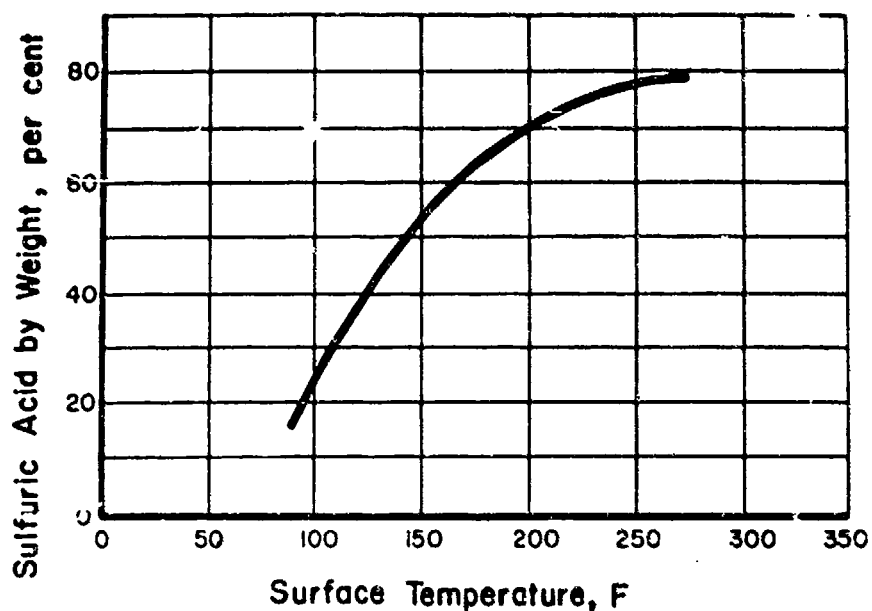


FIGURE 4. RELATIONSHIP OF CONCENTRATION OF CONDENSED SULFURIC ACID TO TEMPERATURE OF CONDENSING SURFACE(203)

TABLE 1. CORROSION OF STEEL BY SULFURIC ACID(60)

Concentration, per cent	Corrosion Rate, mils per year at 75 F	Concentration, per cent	Corrosion Rate, mils per year at 75 F
0.005	8	50.0(a)	1600
0.05	15	60	50
0.5	120	70	15
1.0	200	80	20
3.0	875	90	10
5.0	1200	100	5
10.0(a)	2300		

(a) Between 10 and 30% acid, the corrosion rates for steel are extremely high.

The ASME⁽³⁾ publication on corrosion and deposits reviewed the corrosion of steel as well as other metals from information published up to 1958. Since that time, Haneef⁽⁸⁰⁾ has measured corrosion rates of different materials in flue gases from an oil-fired water-cooled furnace. He confirmed the conclusion, reached earlier by Kear and others, that the maximum corrosion occurs in the region about 50 F below the dewpoint.

When a metal reacts with an acid, one of the products is gaseous hydrogen. A novel method for estimating the corrosion by flue-gas condensate is based on measuring the amount of hydrogen in the flue gas and correlating this information with the rate of metal consumed by the acid. According to Alexander⁽¹⁾, the method is being used in Belgium.

Sulfurous Acid

Laboratory and plant experiences have shown that the relationship between metal-surface temperature and corrosion rate is in the form of a curve with two maxima, as illustrated in Figure 5 adapted from Whittingham⁽²¹²⁾. As was mentioned in the previous section, the increase in corrosion occurring about 50 F below the acid dewpoint is caused by sulfuric acid. The other sharp increase in corrosion, which occurs just below the water dewpoint, is caused by sulfurous acid attack resulting from the combination of SO₂ and water. The temperature range where this occurs is near 100 F.

It should be mentioned that Rylands and Jenkinson⁽¹⁷⁴⁾ have shown that both cast iron and steel were attacked 25 times faster by H₂SO₃ than by H₂SO₄, both in 5% strength, in tests lasting 24 hours at 60 F. Thus, it can be seen that the potential for corrosion would be very great if boilers were operated so that exit-gas temperatures reach the water dewpoint. Since there always is much more SO₂ than SO₃ present in the flue gas, the flue-gas condensate forming at the water dewpoint is bound to be corrosive to iron.

Shanks and his associates⁽¹⁸³⁾ recently studied low-temperature corrosion in oil-fired cast-iron sectional boilers and found an acid dewpoint near 250 F. The maximum corrosive attack occurred at 160 F. They recommend operation of the boiler at a water temperature sufficiently high to stay beyond the accelerated-corrosion range. It is interesting that they reported an overnight cyclic shutdown of the burner had a negligible effect on the corrosion rate, whereas many investigators feel that shutdown periods can be very detrimental.

Hydrochloric Acid

Residual fuel oils normally do not contain chlorides, but when contamination with sea water or other saline water has occurred, appreciable quantities may be present. Since hydrogen chloride can be formed when such contaminated oils are burned, some consideration must be given to the corrosion effects. First, it should be mentioned that hydrochloric acid is an extremely corrosive material, in many respects much more so than sulfuric acid. It is fortunate that liquid films containing hydrochloric acid usually are not present in boiler plants unless the exit-gas temperature has reached the water dewpoint; otherwise, even more-severe corrosion could be anticipated than is presently found. The corrosivity of flue gases containing hydrochloric

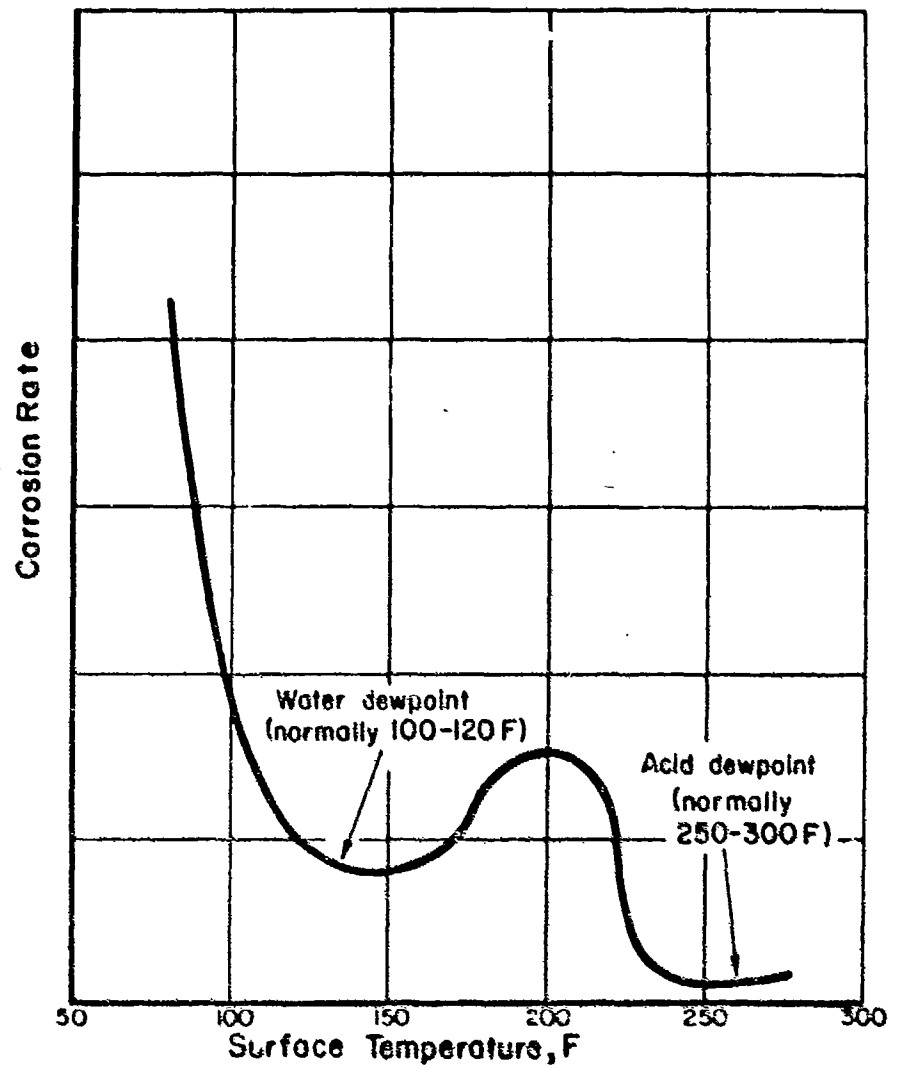


FIGURE 5. RELATIONSHIP BETWEEN METAL SURFACE TEMPERATURE AND CORROSION⁽²¹²⁾

acid has been demonstrated in the laboratory by several investigators. For example, Kear(100) showed that at 115 F the corrosion of a mild-steel probe was about 40% greater with the addition of 0.015% HCl along with 0.1% SO₂ than with the same amount of SO₂ alone. Other work by Rylands and Jenkinson(173) showed that the concentration of HCl in the condensate rose rapidly at temperatures below the water dewpoint when HCl was added to combustion gases. Studies by Piper and VanVliet(151) in a power station burning coal containing 0.66% Cl showed that HCl was deposited when the gases reached 140 F. It is quite significant that it was found that below 100 F the amount of HCl deposited was greater than that of H₂SO₄. Thus, the necessity for maintaining the exit-gas temperature above the water dewpoint is well documented.

In addition, the importance of removing sea water from fuel oil is emphasized since it is possible that in some cases corrosion ordinarily attributed to sulfuric acid may be partially caused by HCl, even at temperatures above the water dewpoint.

Flue-gas composition, as reported in the literature, usually does not include the HCl content. It would be interesting to establish for a boiler, using a residual fuel oil containing a known amount of sea water, the relationship between the chloride content and HCl in the resultant flue gas.

Another factor not generally recognized is the quantity of salt in the air near the seacoast, particularly during and after stormy weather. In view of the large volume of air going to the boiler this can provide an appreciable source of chlorine to induce corrosion, even though the fuel may be free of salt water contamination.

CONTROL OF CORROSION

In England, the Central Electricity Generating Board has encountered a wide variety of corrosion problems in converting certain of its boiler plants to oil firing. Dadswell and Thompson(46) reviewed the procedures taken to minimize corrosion of air preheaters. The procedures reviewed were:

- (1) Design of the air preheater so that the metal temperature at the cold end is never below the acid dewpoint
- (2) Use of the most-corrosion-resistant metals or protective coatings, to prevent attack
- (3) Reduction of the SO₃ content of the flue gas by operating the burner with minimum excess air
- (4) The use of additives to neutralize the SO₃ or to inhibit the pickling action of the H₂SO₄.

Design Considerations

The CEGB has considered the following modifications in air-preheater design:

- (1) Hot-air recirculation and air bypassing. The plants are operated with an air-preheater exit-gas temperature of around 350 F when bypassing is used. With hot-air recirculation, the air-inlet temperature is 150 to 200 F.

- (2) Rearrangement from counterflow to parallel flow.
- (3) Introduction of oil burners in cold-air inlets.
- (4) Use of a closed hot-water heat exchanger to warm the air.
- (5) Use of a high-temperature booster air preheater.
- (6) Use of bled-steam air preheaters.

COMBUSTION CONTROL

The method of reducing corrosion by limiting the excess air to the point where there is control of the amount of SO_3 formed is being demonstrated with favorable results in England and in Germany. For example, Lees⁽¹¹³⁾ reported a decrease in dewpoint from 345 to 280 F, corresponding to an increase in the CO_2 content of the flue gas from 10% to 13.5%. Actual measurements of air-preheater tube wastage, by Lees, proved very graphically that a reduction from a corrosion rate of 50 mils per 1000 hours to about 5 mils per 1000 hours could be effected by this lowered dewpoint, which is a measure of the reduced SO_3 content. Figure 6 illustrates the decrease in corrosion rates for two rows of tubes in the air preheater at the Bankside Station, which is compared with the easily measured increase in carbon dioxide. The Annual Report of BCURA⁽²⁰⁾ presented results showing that the SO_3 content in the flue gas rose from 5 to 80 ppm as the excess oxygen increased from 0.5% to 3.0%. The corresponding corrosion-rate curve was found to be parallel to the SO_3 curve.

Variation in SO_3 Content

An extensive laboratory study of low-temperature corrosion under carefully controlled conditions is being conducted by Ward, et al., at the Central Electricity Research Laboratories in Leatherhead, England⁽²¹⁰⁾. In a study of the formation and deposition of SO_3 , it was shown that the pilot boiler responds to changes in the proportion of excess air in much the same way as in large-sized boilers, with the added advantage that very low excess air can be used. Continuous recordings of SO_3 and oxygen over a period of 2000 hours, where the amount of oxygen in the flue gas was varied, indicated a direct correlation between SO_3 and oxygen. Figure 7 shows that the SO_3 varies from about 2 ppm at 0.2% oxygen to about 35 ppm near 2% oxygen.

In 1959, Crossley⁽⁴³⁾ summarized the results from full-scale investigations with several power stations in England. At Marchwood, where the SO_3 content was about 20 ppm and the dewpoint was near 300 F, a reduction in excess oxygen from 3% to about 0.5% caused a reduction in SO_3 to about 3 ppm and a dewpoint near 250 F. Similar results were given for three other stations, as shown in Table 2.

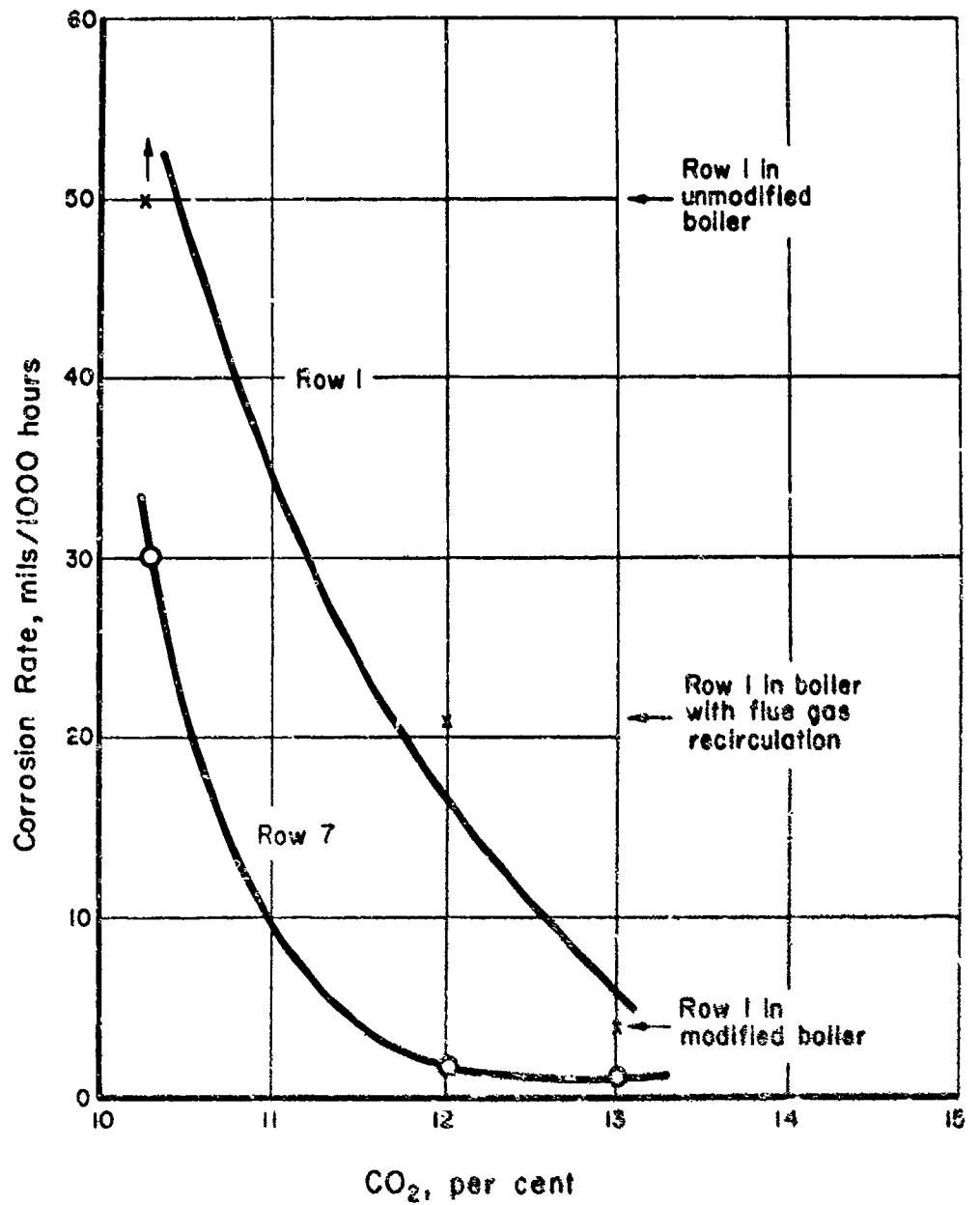


FIGURE 6. RATE OF WASTAGE OF TWO ROWS OF AIR-INLET TUBES⁽¹¹³⁾

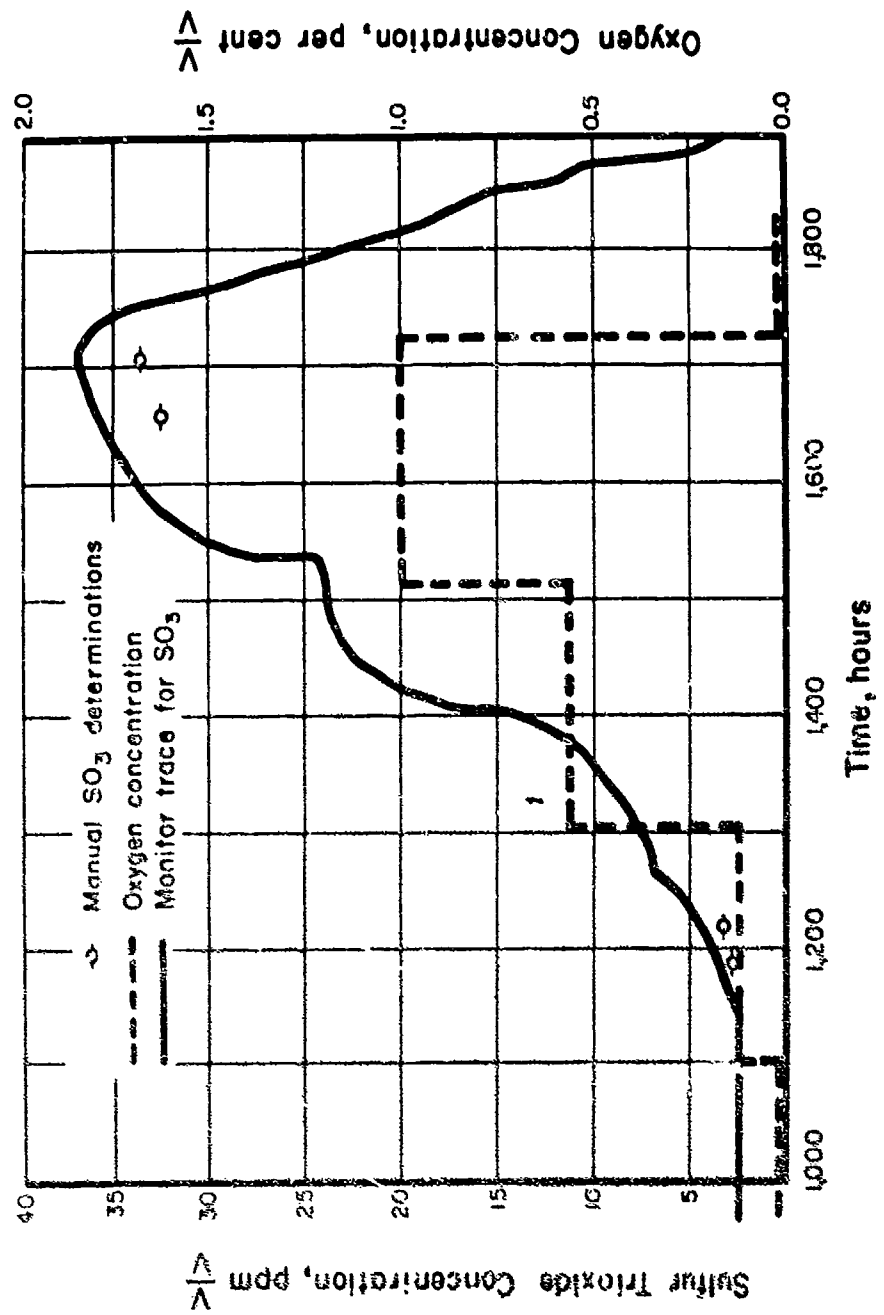


FIGURE 7. EFFECT OF OXYGEN CONCENTRATION ON THE CONCENTRATION OF SO₃ IN FLUE GAS(210)

TABLE 2. EFFECT OF EXCESS OXYGEN ON SO₃ CONTENT AND DEWPOINT(43)

	Excess O ₂ , %	SO ₃ , ppm	Dewpoint, F
Marchwood	3	20	270-320
Marchwood	0.5	2-7	240-255
Poole	<0.6	5	180
Poole	4	45	320
S. Denes	1.7	--	260
Ince	4.5	18	--
Ince	1.0	7	--

Glaubitx has presented two fairly complete papers^(68,69), in Germany, describing the benefits derived from careful control of combustion air in oil-fired boilers. By means of special equipment and burner design, he was able to reduce the oxygen content to about 0.2%. It is stated that after 12,000 operating hours, the boiler had never been cleaned. Highly efficient rates of heat transfer were maintained throughout the experiment. Figure 8 [taken from Glaubitx⁽⁶⁸⁾] shows that the acid dewpoint tends to approach the water dewpoint as the oxygen is reduced to 0.2% in the flue gas.

In addition, it should be noted that the dewpoint with controlled excess air is essentially independent of the sulfur content of the oil.

More recently, Rosborough⁽¹⁷²⁾ summarized (in Figure 9) the trend resulting from this technique of combustion control. The data suggest that there may be a maximum in the SO₃ conversion curve and that both high and low values of excess air tend to reduce the reaction. It is surmised that large amounts of excess air act by causing dilution and by lowering the flame temperature.

Alexander⁽²⁾ and associates indicate a tenfold increase in SO₃ over the range 1.5 to 4.5% oxygen in the flue gas. In a discussion on this paper, Grant brought out the point that in his opinion a reduction in excess air could accomplish the same results as are achieved by additives. Another point was that air-preheater corrosion is lowered if the tubes or plates are cleaned often so that deposits are not allowed to accumulate.

Very recently, Manny⁽¹²¹⁾ has reported that the Central Electricity Generating Board, in England, has applied low-excess-air combustion to all its oil-fired stations (about 12). In addition, the CEGB is designing four very large oil-fired steam generators which will use low-excess-air combustion and will incorporate 32 specially designed burners.

Carter, in his discussion of the paper by Alexander, et al.⁽²⁾, suggests that the thermal loss be accepted, and that flue-gas temperature be maintained above the acid dewpoint to be sure no acid smut is evolved.

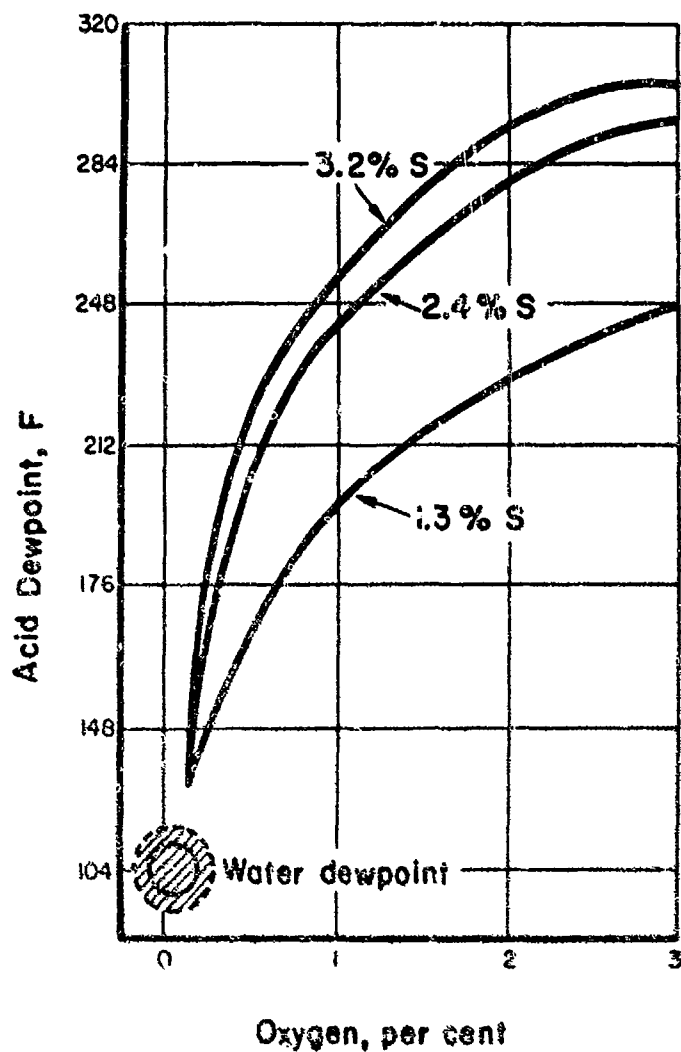


FIGURE 8. EFFECT OF EXCESS OXYGEN ON ACID DEWPOINT⁽⁶⁸⁾

The minimum point is at about 1% excess air and 15.6% carbon dioxide.

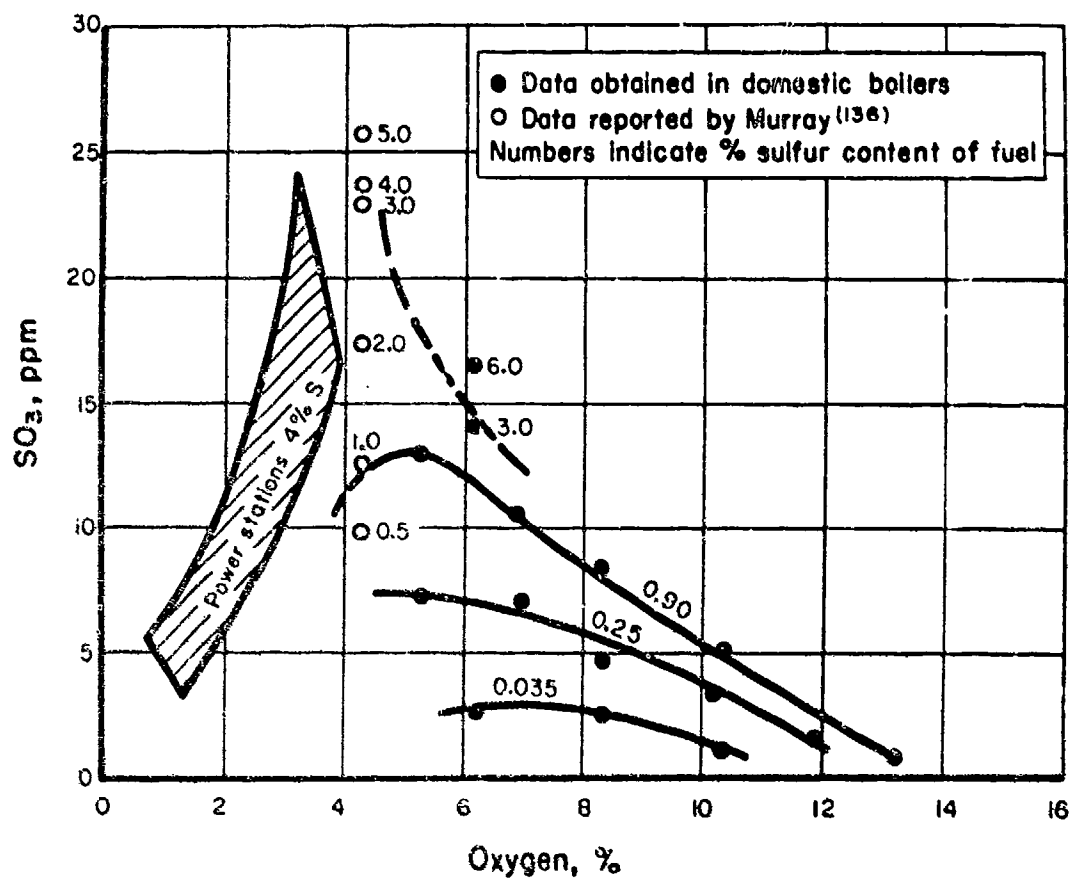
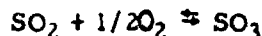


FIGURE 9. RELATION BETWEEN SO_3 AND BOILER OXYGEN WITH FUELS OF DIFFERENT SULFUR CONTENT⁽¹⁷²⁾

Very recently, MacFarlane⁽¹²⁰⁾ used the established equilibrium data for the reaction



to calculate values for the percentage conversion of SO_2 to SO_3 at various conditions of excess air and temperature in a boiler burning fuel oil. His results (summarized in Figure 10) show graphically the decided decrease in SO_3 formation effected by reductions in excess air.

Although the residence time in an actual boiler may be too short to permit equilibrium conditions indicated in Figure 10 to be entirely valid, it should be pointed out that the data are useful for showing the importance of excess air in the problem under discussion in this report.

Boiler Efficiency

From the efficiency standpoint, it is advantageous to operate the boiler in the proper range of excess air. Table 3, presented by Latham⁽¹¹²⁾, shows the relationship between excess air, boiler efficiency, and percentage of oxygen in the flue gas. The data obtained during operation of Navy boilers were recalculated for a constant stack temperature of 500 F.

TABLE 3. EFFECT OF EXCESS AIR ON BOILER EFFICIENCY AND CO_2 CONTENT⁽¹¹²⁾

Excess Air, %	Boiler Efficiency at Full Power, %	CO_2 in Flue Gas, %
15	79.0	14.0
20	78.2	13.3
30	77.0	12.5
50	74.0	10.5
100	69.5	8.0
200	64.5	5.2

It can be seen that it is most economical to operate at the minimum amount of excess air. It is most fortunate that this condition is also favorable for producing the minimum amount of SO_3 in the flue gas, and consequently the lowest corrosion rates. Thus, the need is further emphasized for operating under combustion conditions resulting in 13 to 14% of CO_2 in the flue gas.

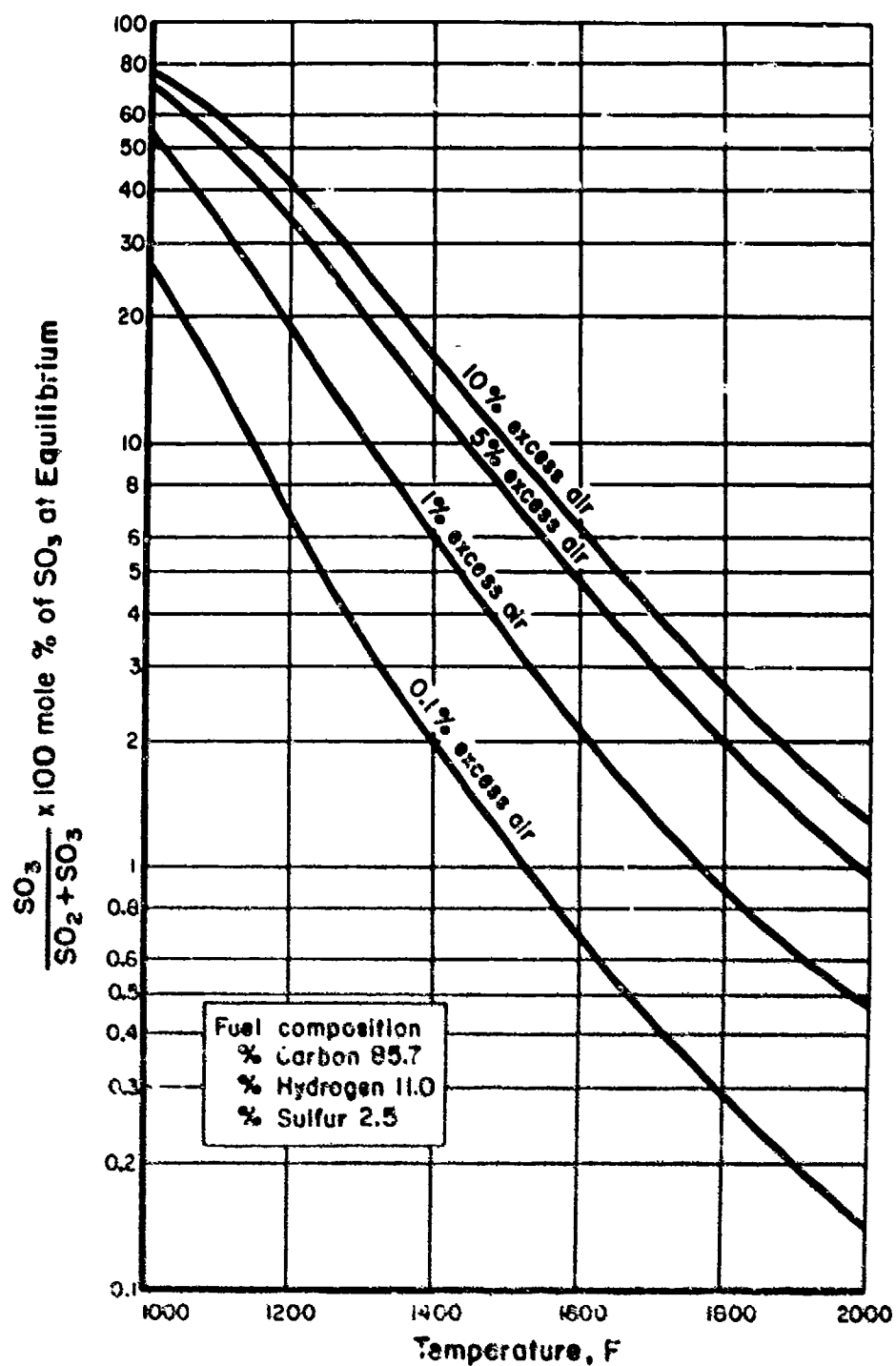


FIGURE 10. THE EFFECT OF TEMPERATURE AND EXCESS AIR ON THE SULFUR TRIOXIDE CONTENT OF COMBUSTION GASES AT EQUILIBRIUM(120)

CONSTRUCTION MATERIALS AND PROTECTIVE COATINGS

Metals and Alloys

An extensive study of materials for low-temperature areas of boilers was conducted about ten years ago by Barkley(8) and associates. They evaluated forty uncoated metals and several coatings by subjecting panels to the flue gas in a regenerative-type air preheater in a coal-fired steam generator. Because the observed corrosion was due largely to sulfuric acid, the results are of pertinent interest in a discussion of oil-fired units.

Barkley assigned a rating of 100 to Corten, which is a low-alloy steel. Other low-alloy steels, Mayari-R and Croloy, were similar in durability. Metals more resistant than Corten were Hastelloy B, Hastelloy C, L-605, Inconel, and Carpenter 20. High-alloy steels were less resistant than Corten.

Corrosion studies conducted at extremely low metal temperatures, where HCl as well as H_2SO_4 were formed, were reported by Piper and VanVliet(151) for an operating station. Low-alloy steels were found to have a higher corrosion resistance than stainless steels, hot-rolled steel, and aluminum.

Haneef(80) recently conducted corrosion tests on metals exposed in a pilot-scale furnace burning oil containing 2.9% sulfur. In general, he confirmed the results of the rating arrived at by Barkley, et al., at the Bureau of Mines(8). Assuming that the corrosion index of Corten was 100, he derived indexes for other materials as shown in Table 4.

TABLE 4. CORROSION INDEXES OF METALS EXPOSED IN
PILOT-SCALE FURNACE BURNING OIL
CONTAINING 2.9% SULFUR(80)

Specimen Surface Temperature, F	Corrosion Index				
	Corten	Stainless Steel	Carbon Steel	Cast Iron	
				Normalized	Annealed
356	100	25	113	148	162
284	100	59	126	146	158
230	100	135	148	166	183

It will be noted that the stainless steel was more resistant than Corten at 356 F and at 284 F, whereas at 230 F the reverse was true.

One of the most recent studies concerning construction materials for low-temperature areas in boilers was reported in 1962 by Wiedersum and associates(221). Their results were obtained in an economizer in a pulverized-coal-fired unit, but are also useful to oil-fired equipment. The results summarized in Figure 11 are taken from their paper. It can be seen that the Types 304 and 316 stainless steels were more durable than the other materials.

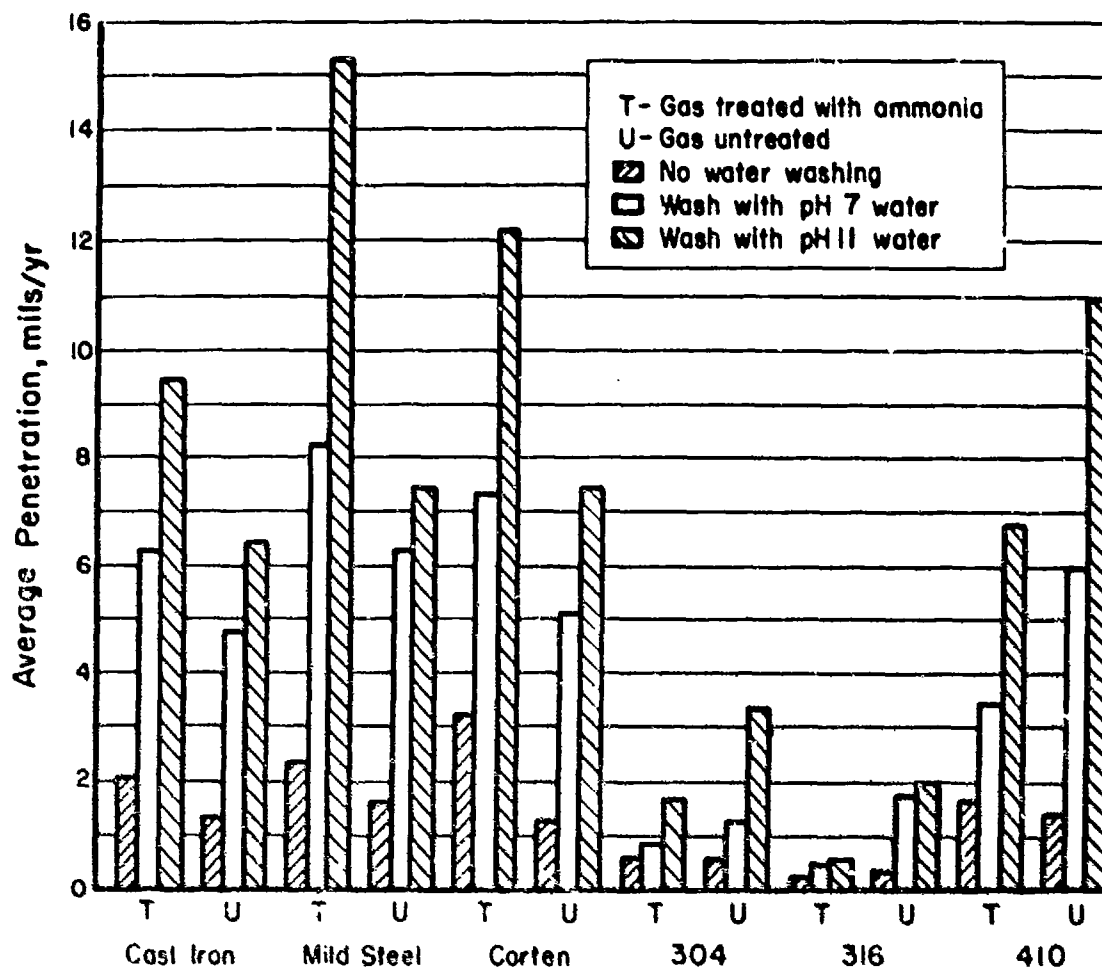


FIGURE 11. PENETRATION RATES OF ALLOYS IN LOW-TEMPERATURE FLUE GAS⁽²²¹⁾

A rating based on both corrosion and economics, however, placed the materials in the following order in relative annual cost:

Cast iron	1 (least expensive)
Mild steel	2
Corten	2
Stainless steels	
Type 304	4-1/2
Type 316	5
Type 410	18

It should be pointed out that studies of Barkley and associates⁽⁸⁾ and earlier studies of Piper and VanVliet⁽¹⁵¹⁾ indicated that low-alloy steels were actually more resistant than stainless steels under similar conditions. Thus, the question of construction materials appears to be unresolved.

Miscellaneous Materials

Teflon, Hanley brick tile, and Olean white tile showed no loss by corrosion⁽⁸⁾.

In 1955, Hoge and Plotter⁽⁸⁹⁾ reported results for over fifty organic and inorganic coatings. The phenol-formaldehyde type of coatings showed good resistance but were limited by temperature deterioration. Porcelain-enamel coatings also showed good promise.

Glass Tubing

It is interesting that QVF Limited⁽¹⁶⁵⁾, of Fenton, England, and McKay⁽¹³²⁾ have reported that an air preheater retubed with glass showed good results after an 18-month trial. Minor amounts of deposits were found on the tube surfaces. Heat transfer was satisfactory.

Protective Coatings

Protective coatings have also been recently studied as a means of resisting the corrosion. Wiedersum⁽²²¹⁾ reported some encouraging results for a phenolic-type coating. A preliminary estimate indicates that the cost of the economiser units would be increased by about one-third.

Vitreous Enamels

Encouraging results were reported for vitreous enamels. Recent field trials, reported by Grames and Huffcut⁽⁷⁰⁾, concerning enameled coatings in operating stations, indicate that porcelain enameling is a practical application of a corrosion-resistant coating for heat exchangers.

Wingert, in discussion of that paper, suggests that the solution of the corrosion and deposit problems is in sight through the use of porcelain enamels in the air-preheater sections.

CHAPTER 2. CHEMISTRY OF BURNING RESIDUAL FUEL OIL AND OIL-ASH DEPOSITS

CHARACTERISTICS OF RESIDUAL FUEL OIL

The residual fuel oil known as No. 6, or Bunker C, comprises the residue or bottoms from distillation of crude oils. To meet specifications, it may be blended with other oils, such as a higher grade distillate or used lubricating oils. The quality of the residual fuel oil partly depends on the fractions that have been removed as distillates (gasoline, kerosene, and the lighter fuel oils) and partly on the source of the original crude oil. In some cases, only 10% of the crude may end up as residual oil, while in other cases, it may be as much as 50%. Competition has encouraged refiners to use processes which result in higher yields of gasoline and distillates from the crude. In general, higher yields of light fractions are accompanied by poorer quality residual oils.

Specifications

Commercial No. 6 oil must meet three ASTM specifications: (1) a viscosity range of 45 to 300 seconds SSF (122 F), (2) a minimum flash point of 150 F, and (3) a maximum water and sediment content of 2.0%. The specifications for U. S. Navy Heavy Grade oil, designed for use in shore-based power plants, are much more stringent, requiring that ten conditions be satisfied as shown in Table 5. The maximum ash content of 0.12% is the item considered of most importance to this discussion.

TABLE 5. SPECIFICATIONS FOR U. S. NAVY RESIDUAL OIL, HEAVY GRADE(142)

Gravity, °API	Min 10.0
Viscosity, SSF, 122 F	Max 150
Flash Point, P-M, F	Min 150
Fire Point, OC, F	Min 200
Pour Point (Upper), F	Max 50
Ash, %	Max 0.12
Sediment by Extraction, %	Max 0.15
Water, by Distillation, %	Max 0.5
Thermal Stability (NBTL)	Pass (No. 2 tube or better)
Explosiveness, %	Max 50

Oil Ash

The ash-forming constituents in the original crude oil go through the refining process practically unchanged and are concentrated in the so-called bottoms. Residual fuel oil usually has an ash content of about 0.1%, although in some exceptional cases it has been found as high as 1 to 2%. Nevertheless, this small amount of ash can be the cause of serious deposit and corrosion problems in boilers.

Ash-forming constituents in the crude oil are introduced (a) by the animal and vegetable matter from which the oil was formed, (b) from contact of the oil with underground rock structures and brines, and (c) during production, storage, and handling. Four classes of contaminants can be distinguished:

- (1) Oil-soluble compounds formed with the crude oil.
- (2) Water-soluble compounds dissolved in water and emulsified in the crude oil. This would include connate brine and sea water.
- (3) Reaction products of the acidic compounds of the oil with metal surfaces such as pipes, tanks, and processing equipment.
- (4) Solid contaminants such as sand, rust, and scale which are picked up during production and handling.

During the refining process, the emulsions (Item 2) are broken and the water is driven off, leaving the inorganic salts suspended in the residual oil.

Chemical Composition

The principal ash-forming elements found in crude oil, as given by Bowden et al. (18), are listed in Table 6. Both inorganic and organometallic, oil-soluble forms have been observed for several of the elements. No matter which form these elements are in, the important point is that they are retained essentially intact during the refining process and are found concentrated in the residual oil. Trace amounts of as many as 25 elements have been detected by Thomas in petroleum by spectrographic analysis⁽²⁰⁵⁾.

Chemical analyses of the ash from crude oils obtained from various sections of the United States and also from Iran are presented in Table 7⁽²⁰⁵⁾. It is obvious from these data that the percentage of each constituent varies widely in oils from different fields. These variations in composition tend to affect the properties of the corresponding residual oils. Typical differences in the important properties of residual oils are illustrated in Table 8^(85, 107, 176). Of particular interest to this discussion are the wide ranges shown for the amount of ash and the content of sulfur, vanadium, and sodium. The main deposit and corrosion problems that occur in boilers result from oxides of vanadium and sodium in the ash combining with oxides of sulfur in the gaseous combustion products.

TABLE 6. PRINCIPAL ASH-FORMING ELEMENTS IN CRUDE OIL⁽¹⁸⁾

Element	Type	Solubility in Oil	Probable Chemical Form
Aluminum	Inorganic	Insoluble	Complex aluminosilicates in suspension
Calcium	Organic	Soluble	Not identified
	Inorganic	Insoluble	Calcium minerals in suspension; calcium salts in suspension or dissolved in emulsified water
Iron	Organic	Soluble	Possible iron porphyrin complexes
	Inorganic	Insoluble	Finely sized iron oxides in suspension
Magnesium	Organic	Soluble	Not identified
	Inorganic	Insoluble	Magnesium salts dissolved in emulsified water or in suspension in microcrystalline state
Nickel	Organic	Soluble	Probable porphyrin complexes
Silicon	Inorganic	Insoluble	Complex silicates and sand in suspension
Sodium	Inorganic	Insoluble	Largely sodium chloride dissolved in emulsified water or in suspension in microcrystalline state
Vanadium	Organic	Soluble	Vanadium porphyrin complexes
Zinc	Organic	Soluble	Not identified

TABLE 7. ANALYSES OF ASH FROM CRUDE OILS⁽²⁰⁵⁾

	Per Cent by Weight						
	California	Mid-Continent	Texas	Pennsylvania	Kansas	Iran # 1	Iran # 2
SiO ₂	38.8	31.7	1.6	0.8	10.0	52.8	12.1
Fe ₂ O ₃	17.3	31.8	9.9	97.5	19.1	13.1	18.1
Al ₂ O ₃							
TiO ₂							
CaO	3.7	12.6	5.3	0.7	4.8	6.1	12.7
MgO	1.8	4.2	2.5	0.2	1.3	9.1	0.2
MnO	0.3	0.4	0.3	0.2	Tr	Tr	Tr
V ₂ O ₅	5.1	Tr	1.4	--	0.4	14.0	38.5
NiO	4.4	0.5	1.5	--	0.6	1.4	10.7
Na ₂ O	9.5	6.9	30.8	0.1	23.6	--	--
K ₂ O	--	--	1.7	--	0.9	--	--
SO ₃	15.0	10.8	42.1	0.9	36.4	2.6	7.0
Chloride	--	--	4.6	--	0.1	--	--

TABLE 8. VARIATION IN PROPERTIES OF NO. 6 RESIDUAL FUEL OILS

Property	Canadian Refineries(176)	U. S. Refineries I(107)	U. S. Refineries II(85)
Specific Gravity, 60 F	0.945 - 1.046	0.959 - 0.990	0.92 - 1.02
Flash Point, F	175 - 300	150 - 285	160 - 410
Viscosity, centistokes, 122 F	105 - 420	140 - 400	85 - 650
Pour Point, F	+10 - +65	0 - +50	+15 - +85
Water and Sediment, per cent	--	0.02 - 0.50	0.05 - 2.0
Water, by Distillation, per cent	0 - 0.2	Tr - 0.2	--
Carbon Residue, per cent	5.86 - 14.3	7.27 - 13.7	5 - 13
Ash, per cent	0.01 - 0.12	0.004 - 0.086	0.01 - 0.50
Sulfur, per cent	0.67 - 3.00	0.75 - 3.61	0.7 - 3.0
Heat of Combustion, Gross, Btu per lb	--	18,200 - 18,740	18,329 - 18,993
Vanadium, ppm in oil	0 - 146	2 - 144	--
Vanadium, per cent ash	--	0.8 - 62.8	--
Sodium, ppm in oil	1.6 - 290	--	--
Ash Fusion Temperature, F	--	1085 - 1330	--

TROUBLESOME ELEMENTS IN OIL-ASH

Vanadium

There is considerable interest in the source of the vanadium in crude oil. It is believed that some marine animals are capable of concentrating in their bodies the vanadium present in sea water and in ocean-bottom muds. Crude oils containing appreciable amounts of vanadium are associated in their origin with the sediments of prehistoric oceans(205).

Occurrence in Petroleum

As noted in Table 6, the vanadium occurs in petroleum as an oil-soluble porphyrin complex. These complexes are insoluble in water and are stable to heat treatment in the presence of water. They undergo decomposition at about 840 F. Absorption spectra of these vanadium complexes indicate that their structure is similar to that of the vanadium derivative of mesoporphyrin IX dimethyl ester(188). The structure of the latter is shown in Figure 12. Undoubtedly, the complexes existing in the crude oil undergo structural changes during the refining process, and when they are concentrated in the residual fraction they are often present as high-molecular-weight products, probably polymeric in nature(66).

The vanadium is associated with the asphaltic portions of the crude oil. The asphaltic-base crudes from areas such as Venezuela, the Middle East, and California contain relatively high concentrations of vanadium. Paraffin-base crudes, such as those

from Pennsylvania and Mid-Continent Fields contain only trace amounts of vanadium. Consequently, the vanadium content of a residual oil can vary from a negligible amount to several hundred parts per million.

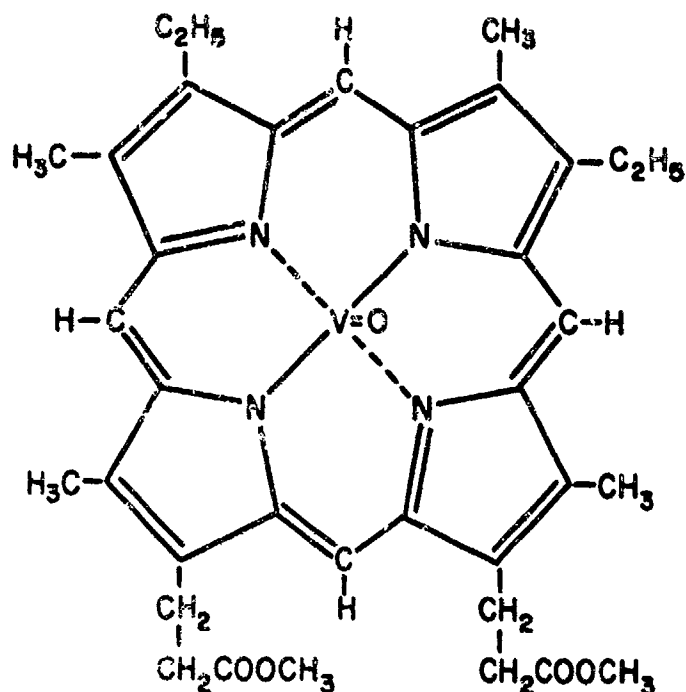


FIGURE 12. VANADIUM COMPLEX OF MESOPORPHYRIN IX DIMETHYL ESTER⁽¹⁸⁸⁾

Combustion Reactions

During combustion, the vanadium complexes in a droplet of fuel oil are decomposed. The vanadium is oxidized in steps: first to the stable and nonvolatile V_2O_3 and V_2O_4 and finally, after all the carbon in the oil has been consumed, the vanadium is oxidized to V_2O_5 ⁽²⁰⁰⁾. The vapor pressure of V_2O_5 was originally measured by Poliakov⁽¹⁵²⁾ and later was corrected by Lloyd and Probert⁽¹¹⁸⁾. These latter investigators found values ranging from about 0.1 mm of mercury at 1800 F to 1 mm in the vicinity of 2500 F. They calculated the amount of V_2O_5 that would be vaporized, in relation to the vanadium content of oils and found that volatilization of a substantial portion of the V_2O_5 would be expected at the flame temperature.

Although the V_2O_5 is slightly volatile, very little of it is carried through the boiler as such, because it reacts with other metal oxides. The sodium, calcium, nickel, and iron present in the oil have been shown to be capable of reacting with the V_2O_5 to form a variety of vanadates which are less volatile than the V_2O_5 ⁽¹¹⁸⁾. The chemical formulas and melting points of possible vanadate compositions which might

form during combustion are shown in Table 9. Most of the vanadium which is found in boiler deposits is present as one or other of the sodium vanadate compositions listed.

Sodium

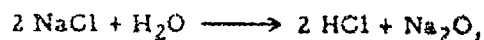
As with other elements, the amount of sodium present in crude oils varies widely, depending on (a) the source and (b) the method of transport to the refinery. Sea water is a common contaminant in crudes delivered by oil tankers. It is a general refinery practice to desalt the crude oil. This procedure removes about 90% of the sodium, most of which is present as sodium chloride. The remaining sodium ends up in the residual-oil fraction, the concentration depending on the proportion of distillates removed from the crude. The residual oil, if transported by ship, is further contaminated by sea water. As delivered to the consumer, a residual oil sometimes contains a few hundred parts per million of sodium.

Combustion Reactions

Sodium chloride has sufficiently high vapor pressure (about 10 mm of mercury at 1800 F) to be volatilized during the combustion process. However, there is a chemical reaction as well. Brinsmead and Kear⁽¹⁹⁾ conducted experiments in which pellets of carbon containing a known amount of sodium chloride were burned in a tubular furnace. Temperature and time were varied independently, and the loss of sodium and chlorine was determined. Their results can be summarized as follows:

- (1) Over the range of temperature studied, 1290 to 1832 F, the proportion of chlorine released, always as HCl, was substantially greater than that of sodium.
- (2) Humidification of the combustion air slightly decreased the amount of sodium released and increased the loss of chlorine.
- (3) The release of sodium, but not that of chlorine, was greatly reduced by the addition of kaolin* (essentially a hydrated aluminum silicate).

These results indicate that water vapor plays a significant role in the combustion reaction. A molecular reaction between NaCl and H₂O vapors is very unlikely, because for the postulated reaction



the free-energy change would be +80 kilocalories at 1800 F, which means that the reverse reaction is strongly favored. On the other hand, dissociation of water vapor at this temperature would provide enough hydrogen atoms to promote a chain reaction in which $\text{NaCl} + \text{H} \longrightarrow \text{Na} + \text{HCl}$, and in the presence of oxygen the sodium would form Na₂O. The reduced loss of sodium in the presence of kaolin points to the formation of silicates of low volatility under these conditions.

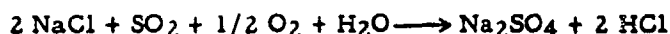
*Additives are discussed in Chapter 4.

TABLE 9. POSSIBLE VANADATE COMPOSITIONS
FORMED DURING COMBUSTION OF
RESIDUAL OIL(a)

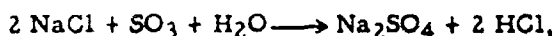
Compound	Melting Point, F
V_2O_5	1274
$3Na_2O \cdot V_2O_5$	1562
$2Na_2O \cdot V_2O_5$	1184
$10Na_2O \cdot 7V_2O_5$	1065
$Na_2O \cdot V_2O_5$	1166
$2Na_2O \cdot 3V_2O_5$	1049
$Na_2O \cdot 2V_2O_5$	1137
$5Na_2O \cdot V_2O_4 \cdot 11V_2O_5$	995
$Na_2O \cdot 3V_2O_5$	1150
$Na_2O \cdot V_2O_4 \cdot 5V_2O_5$	1157
$Na_2O \cdot 6V_2O_5$	1215
$2NiO \cdot V_2O_5$	>1652
$3NiO \cdot V_2O_5$	>1652
$Fe_2O_3 \cdot V_2O_5$	1580
$Fe_2O_3 \cdot 2V_2O_5$	1571
$MgO \cdot V_2O_5$	1240
$2MgO \cdot V_2O_5$	1535
$3MgO \cdot V_2O_5$	1175
$CaO \cdot V_2O_5$	1145
$2CaO \cdot V_2O_5$	1432
$3CaO \cdot V_2O_5$	1860

(a) Compiled from a number of sources.

Fletcher and Gibson⁽⁵⁷⁾ have shown that NaCl will react with both SO₃- and SO₂-oxygen mixtures to form Na₂SO₄. Their data are shown in Figure 13, which includes reactions catalyzed by Fe₂O₃. In the absence of Fe₂O₃, more of the sodium sulfate was formed from SO₃ than from SO₂ between 570 and 1100 F. Above 1100 F the rate of sulfate formation from SO₂ increased rapidly with temperature, while the rate of sulfate formation from SO₃ remained almost constant. The catalytic effect of Fe₂O₃ was much greater for the reaction with SO₂. In this case the reaction



is thermodynamically favorable, the free energy change being -10 kilocalories at 1500 F. The reaction of SO₃,



is slightly less favorable, -4.5 kilocalories at 1500 F. Hence the large difference in the yield of sulfate at this temperature must be an effect of reaction kinetics. The important part played by sulfates in the corrosion and deposit problems of boiler systems requires that consideration be given to the presence of sulfur in the residual oil.

Sulfur

The presence of sulfur in crude oil creates problems in connection with the handling and processing of the crude as well as in the use of refinery products. For heavy fuel oils, sulfur is a significant factor in boiler problems involving:

- (1) The formation, in combination with metallic constituents of the ash, of deposits and corrosive slags in high-temperature sections of the boiler
- (2) Corrosion of metal components in low-temperature sections of the system.

Form of Sulfur in Oil

In recent years about 40 per cent of the crude oil produced in the United States has contained more than 0.5 weight % of sulfur. The crude oils imported from South America and the Middle East contain significantly larger amounts of sulfur, usually 1.5 to 2.5%. Although some elemental sulfur is found in petroleum, the bulk of the sulfur is contained in hydrocarbon molecules. Table 10 summarizes the principal types of sulfur compounds identified in crude oils, distillates, and cracked products⁽¹⁸²⁾. A variety of molecular types are represented, and as many as 50 specific sulfur-containing compounds have been identified in a typical petroleum sample.

Although some of the sulfur compounds are converted to hydrogen sulfide during the refining of the crude and are removed along with the lighter fractions of the petroleum, much of the sulfur is concentrated in the residual oil. This increase of sulfur content is illustrated in Table 11, which shows that the residual oil from a Middle East crude contains a substantially higher percentage of sulfur than did the original crude

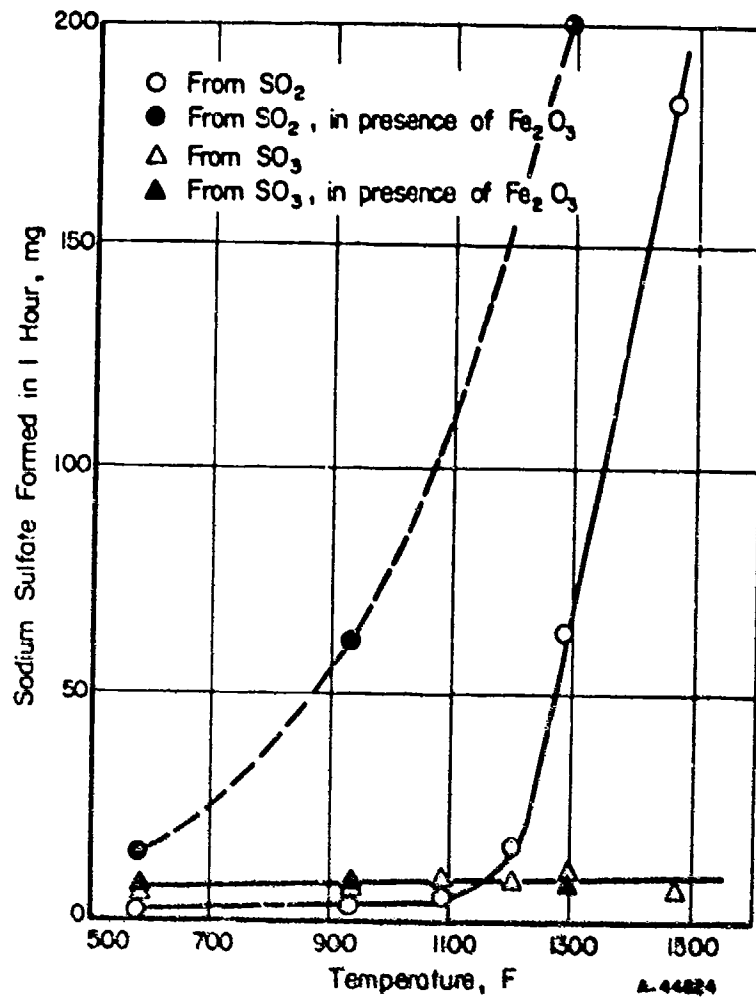


FIGURE 13. FORMATION OF SODIUM SULFATE FROM SODIUM CHLORIDE, SULFUR DIOXIDE, AND SULFUR TRIOXIDE(57)

TABLE 10. TYPES OF SULFUR COMPOUNDS IN CRUDE OIL AND DISTILLATES^(a)

Type	Formula	In Crude Oil?	In Straight-Run Products?	In Cracked Products?
Elemental sulfur	S	Yes	Yes	Yes
Hydrogen sulfide	H ₂ S	Yes	Yes	Yes
Mercaptans				
Aliphatic	RSH	Yes	Yes	Yes
Aromatic	RSH	Yes	Yes	Yes
Naphthenic	RSH	No	No	No
Sulfides				
Aliphatic	R - S - R	Yes	Yes	Yes
Aromatic	R - S - R	No	No	No
Cyclic	$\begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ (\text{CH}_2)_n - \text{CH}_2 \end{array}$	Yes	Yes	Possibly
Disulfides				
Aliphatic	R - S - S - H	Yes	Yes	No
Aromatic	R - S - S - H	?	No	Yes
Thiophene and homologues				
	$\begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{HC} \quad \text{CH} \\ \quad \\ \text{HC} \text{ --- } \text{CH} \end{array}$	Yes	Yes	Yes
Polysulfides	R - S _n - S - R	?	Yes	Yes

(a) Reference (182) revised to include later studies.

TABLE 11. SULFUR CONTENT IN FRACTIONS OF KUWAIT CRUDE OIL⁽⁸⁷⁾

	Distillation Range, C	Total Sulfur, weight %
Crude oil	--	2.55
Gasoline	51-123	0.05
Light naphtha	125-149	0.05
Heavy naphtha	153-197	0.11
Kerosene	207-238	0.45
Light gas oil	247-269	0.85
Heavy gas oil	281-306	1.15
Residual oil	309-498	3.70

oil⁽⁸⁷⁾. A typical average sulfur content of No. 6 residual oil produced in U. S. and Canadian refineries is 1.5%.⁽¹⁴⁾ However, the values contributing to this average ranged between the extremes of 0.3% at an eastern refinery to 5.3% at two western refineries.

Sulfur Dioxide

During combustion most of the sulfur in the fuel oil appears as sulfur dioxide in the flue gases. Thus, in a typical situation, 92% of the sulfur content of a residual fuel oil appeared in the flue gases at the air preheater as SO_2 , and 2% as SO_3 .⁽¹⁰⁶⁾

In the process of combustion of a sulfur compound in the oil, the reactions go through a number of fairly specific steps. As the compound approaches the flame zone, heat radiating from the flame zone causes some pyrolysis and some preliminary, cool-flame oxidation reactions to occur. In the flame zone, temperatures are high, and the oxidation of the sulfur compounds proceeds primarily to SO_2 . As the products leave the immediate neighborhood of the flame zone, temperatures fall rapidly, and some workers believe that SO_2 may be oxidized to SO_3 .

The bulk of sulfur as SO_2 may pass through the entire boiler system as such, and normally does no harm. The small amount of SO_2 which is converted to SO_3 or which reacts with metal compounds to form sulfates can cause serious corrosion and deposit problems. The case in which the SO_2 reacts with NaCl and oxygen from the excess air to form Na_2SO_4 has been discussed in the section on sodium. In the analysis of flue gas at the air preheater (already cited), in addition to SO_2 and SO_3 , 1% of the sulfur in the oil was detected as Na_2SO_4 . Besides NaCl , other metal chlorides (such as CaCl_2 or MgCl_2) are present in the fuel oil. They can also react to form sulfates. However, calcium and magnesium compounds are seldom present to the same extent as those of sodium. The remaining metals, which are found in residual oils, exist mostly as organic complexes. They probably are first converted to oxides and then react with SO_3 to form sulfates.

Sulfur Trioxide

The most important reaction which SO_2 undergoes in the flue gas is the conversion to SO_3 . Only a relatively small amount of the SO_2 is further oxidized to SO_3 . The results of a study by Matty and Diehl⁽¹²⁴⁾ are given in Table 12. These data indicate that 1 to 3% of the SO_2 present was converted to SO_3 . It is also of interest to note that the SO_2 content of the gas stream decreased between the superheater and the air preheater*, whereas the SO_3 content increased slightly in traversing the same distance. This observation shows that conversion of SO_2 to SO_3 continued as the flue gases progressed through the boiler system. The same order of magnitude for SO_3 concentration in a power-station boiler was reported by Crumley and Fletcher⁽⁴⁴⁾, who found SO_3 values in the range 0.002 to 0.007 volume % of the total flue gases.

There have been two schools of thought regarding the mechanism by which the SO_2 is oxidized to SO_3 . Whittingham and his associates have done considerable work to support the theory that the reaction is a homogeneous oxidation occurring in the flame. Harlow has promoted the view that the reaction is heterogeneous, being dependent on catalytic surfaces.

*Probably because of air leakage through the furnace casing.

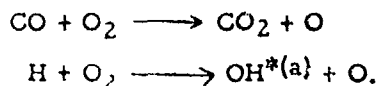
TABLE 12. SULFUR OXIDES FOUND IN THE FLUE GASES
OF AN OIL-FIRED BOILER⁽¹²⁴⁾

Constituent	Percentage of Constituent at Indicated Location and Temperature		
	Super- heater 1800 F	Air Preheater	
		Inlet	Outlet
		700 F	300 F
<u>Sampling Station A</u>			
SO ₂ by volume (dry basis)	0.148	0.124	0.114
	0.152	0.129	0.128
SO ₃ by volume (dry basis)		0.133	0.123
	0.0034	0.0039	0.0033
	0.0039	0.0038	0.0023
Total sulfur gases by volume (average)		0.0043	0.0032
Theoretical total sulfur gases by volume ^(a)	0.154	0.133	0.124
	0.149	0.139	0.126
Difference	0.005	0.006	0.002
<u>Sampling Station B</u>			
SO ₂ by volume (dry basis)	0.220	0.201	0.193
	0.215	0.205	0.189
SO ₃ by volume (dry basis)	0.0022	0.0032	0.0020
	0.0025	0.0030	0.0019
Total sulfur gases by volume (average)	0.218	0.206	0.193
Theoretical total sulfur gases by volume ^(a)	0.217	0.199	0.190
Difference	0.001	0.007	0.003
<u>Sampling Station C</u>			
SO ₂ by volume (dry basis)	0.100	0.087	0.087
	0.096	0.096	0.089
SO ₃ by volume (dry basis)			0.089
	0.0028	0.0031	0.0020
	0.0029	0.0033	0.0014
Total sulfur gases by volume (average)			0.0017
Theoretical total sulfur gases by volume ^(a)	0.100	0.090	0.090
	0.091	0.085	0.086
Difference	0.009	0.005	0.004

(a) Calculated from fuel analysis and combustion data.

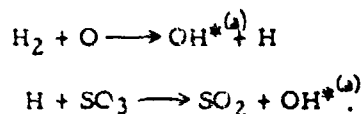
Oxidation in the Flame. The oxidation of SO_2 in town gas (coal gas) flames was studied by Dooley and Whittingham.⁽⁴⁹⁾ They showed that the amount of SO_3 formed is dependent on SO_2 concentration, the nature of the gas burned, the position in the flame, and the presence of materials that trap atomic oxygen. The decrease in SO_2 oxidation with increased concentration of SO_2 which they observed is shown in Table 13. It is known that SO_2 functions as a chain-breaker in the sequence of reactions in which sulfur vapor is oxidized, and it is possible that a similar inhibitive mechanism occurs in this case. The profile of SO_3 formation as a function of distance in the flame zone is presented in Figure 14. The profile was obtained on an aerated flame containing 0.05% SO_2 . The important feature of the data is that the maximum rate of SO_3 formation occurs in the cooler regions of the flame. This result is consistent with the thermodynamics of the SO_2 - SO_3 system, as illustrated in Figure 15⁽⁵²⁾, where the equilibrium conversion of SO_2 to SO_3 is shown as a function of temperature. At equilibrium below 900 F, over 90 mole % of the sulfur oxide mixture is SO_3 . Above 1600 F, less than 15% of the oxidized sulfur is SO_3 . With increase in temperature in this range, the SO_3 concentration decreases rapidly. Consequently, this production of SO_3 in flames must be the result of atomic oxygen combining with SO_2 . The work of Gaydon⁽⁶⁵⁾ on flame spectra also demonstrated that the extent of oxidation of SO_2 could be related to the concentration of atomic oxygen in the flames.

The oxidation of SO_2 in diffusion flames of methane, hydrogen, and carbon monoxide was also examined by Whittingham.^(49, 213, 214) Relatively large amounts of SO_3 , up to 0.008 volume %, were formed, depending on the nature of the flame and the amount of added SO_2 . The percentage of oxidation of SO_2 in these three flames is shown in Figure 16⁽⁴⁹⁾. The lowest degree of oxidation occurred in the luminous methane flame and the highest in the carbon monoxide flame. Both the carbon monoxide and the hydrogen flame are sources of atomic oxygen via the reactions



Hence, one might expect the oxidation of the SO_2 to be enhanced in these flames.

The effect of water vapor on the degree of oxidation of SO_2 in carbon monoxide flames was just the opposite. Apparently, hydrogen from the water competes successfully with SO_2 for available oxygen atoms. A mechanism of this type should result in the formation of more OH radicals:



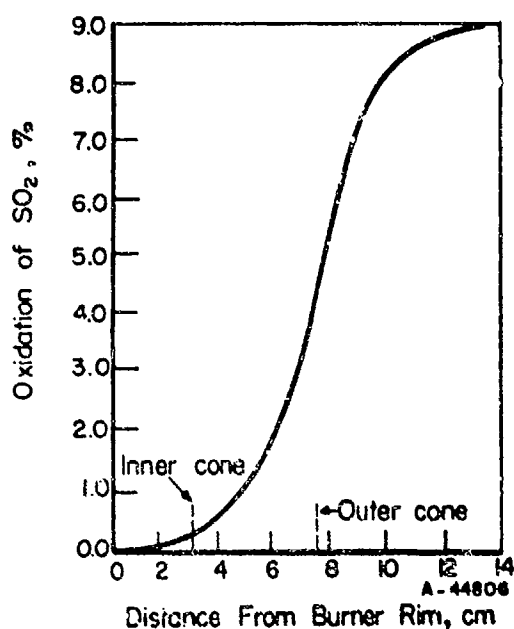
However, this buildup of OH was not observed, so additional mechanisms should be investigated to explain the apparent contradiction.

Another study by Whittingham⁽¹¹⁷⁾ on the decomposition of sulfuric acid injected into gas flames showed that the reduction of SO_3 occurred in the inner cone of the flame, probably by reaction of SO_3 with hydrogen atoms as shown above. In the lower temperature of the upper cone, dissociation of SO_3 was significantly reduced.

(a) OH^* = free radicals.

TABLE 13. THE OXIDATION OF SO_2 IN TOWN-GAS FLAMES⁽⁴⁹⁾

SO_2 in Exit Gases, %	Oxidation to SO_3 , %
0.02	10.0
0.04	8.2
0.11	4.5
0.15	3.8
0.50	1.8
1.00	1.0

FIGURE 14. THE OXIDATION OF SO_2 IN A TOWN-GAS FLAME⁽⁴⁹⁾Initial SO_2 concentration = 0.05%.

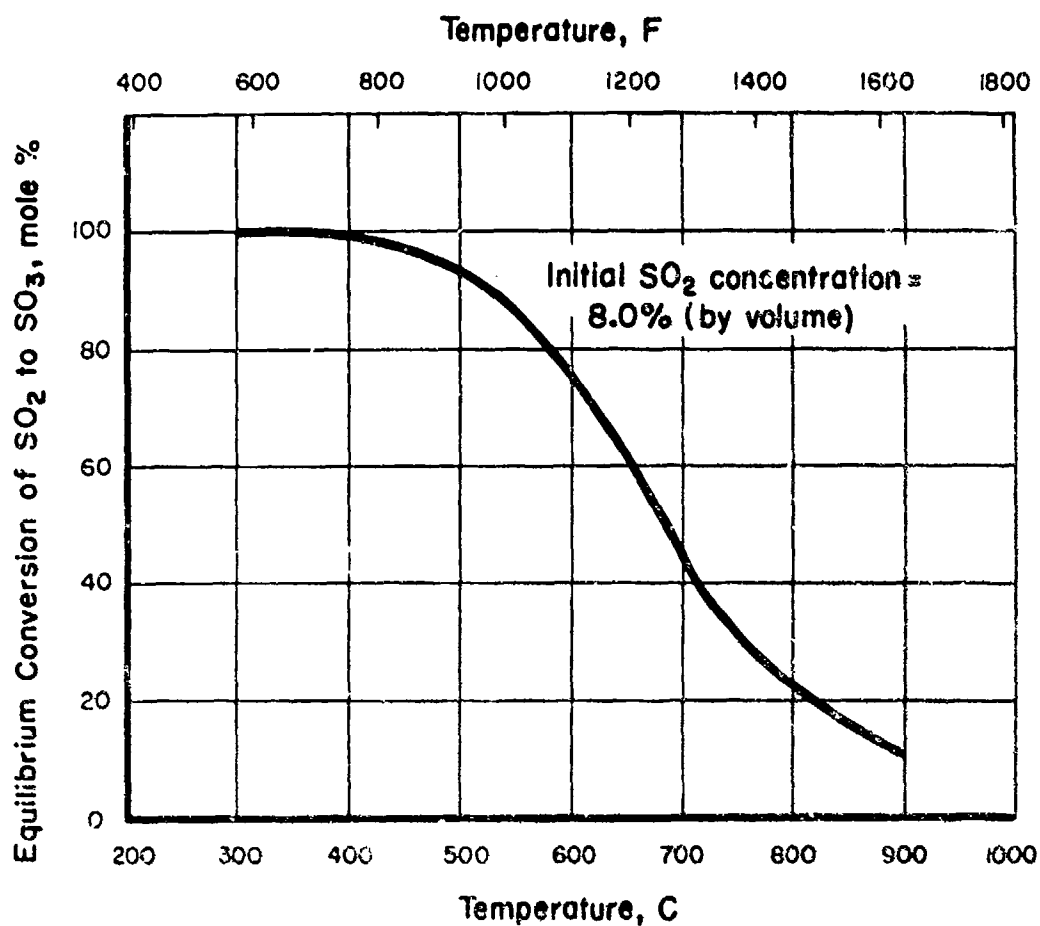


FIGURE 15. EFFECT OF TEMPERATURE ON THE EQUILIBRIUM CONVERSION OF SO_2 TO SO_3 (52)

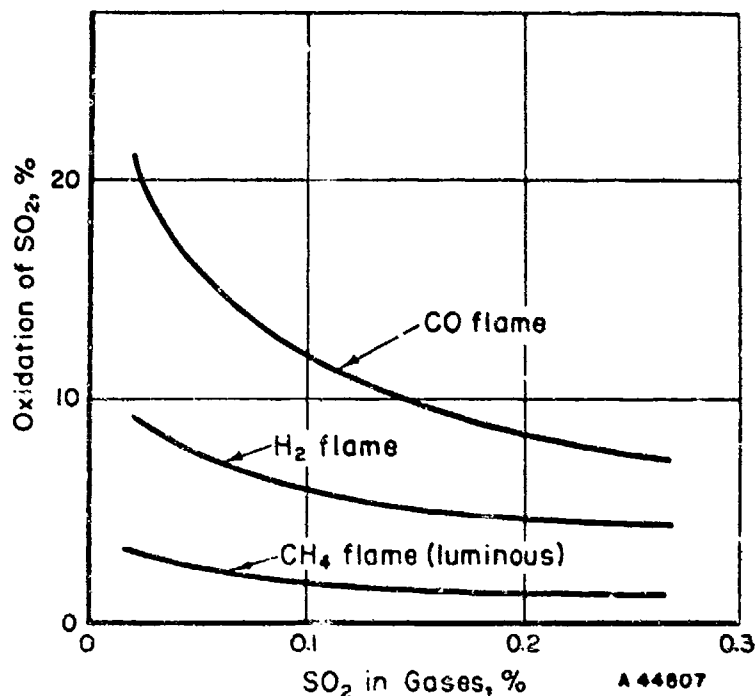


FIGURE 16. OXIDATION OF SO₂ IN VARIOUS FLAMES⁽⁴⁹⁾

Hence, it appears to be fairly well established that SO₃ can be formed from SO₂ in the cooler regions of the flame. What remains to be determined is the relative amount of SO₃ produced by this means, as compared to that which may be formed on downstream catalytic surfaces in the boiler. Levy and Merryman⁽¹¹⁴⁾ have presented an analysis of probable conversion of SO₂ to SO₃ with and without catalysts in the flame zone. They concluded that the SO₃ in the flue gases passing through a hot zone in the boiler, containing iron oxide as a catalyst, would be a minimum at 2000 F and reach a maximum at 1100 F. [Also see A. B. Healey "Sulfur Trioxide in Combustion Gases", Fuel Society Journal, Univ. of Sheffield 13, 45-54 (1962).]

Oxidation on Catalytic Surfaces. The principle of catalytic oxidation of SO₂ to SO₃ has been known for many years and has been the basis for the contact process for sulfuric acid manufacture.

Corroded Steel. Harlow⁽⁶¹⁾ was the first to attribute SO₃ formation in boiler systems to catalytic oxidation of SO₂ on heating surfaces at high temperatures. In his experiments, flue gases were passed through a mild-steel duct containing sample specimens of boiler tubes. The duct, through which the gases were passed, was divided so that half the gases passed over the boiler-tube samples and the other half could be used as a control. The whole apparatus was heated in a manner that gave a temperature pattern like that in a boiler. It was found that when the gases were passed over rusty steel scrap or oxidized superheater-tube sections at 1000 F, a rise in the sulfuric acid dewpoint, indicative of increased SO₃ concentration, resulted. The gases from this

half contained more SO_3 than the control section. In Figure 17, the data for sulfuric acid production over the rusty steel surfaces are shown as a function of temperature. The amount of SO_3 formed began to increase rapidly at 800 F and reached a maximum at 1100 F.

Later, Harlow⁽⁸²⁾ demonstrated that surface reactions on superheater-tube sections raised temperatures still further, and that if the maximum surface temperature was kept low enough, very little sulfuric acid was formed. In another study⁽⁸³⁾, he found that heating flue gases to 1000 F resulted in a downstream maximum of 801 mg of H_2SO_4 , whereas those heated to only 640 F yielded at most 133 mg of H_2SO_4 . Other investigators have also reported catalytic activity of steel surfaces in oxidizing SO_2 to SO_3 .^(88, 206)

Oxide Deposits. A number of oxides are also known to be catalysts for the oxidation of SO_2 , and each of them has a characteristic temperature range in which the conversion is most effective. The per cent conversion of SO_2 to SO_3 as a function of temperature is shown in Figure 18 for several oxides.⁽¹⁶⁾ At low temperatures platinum is the only efficient catalyst. However, above 900 F, significant conversion of SO_2 to SO_3 can be brought about by several oxides which are encountered on boiler surfaces or in deposits, namely V_2O_5 , Cr_2O_3 , and Fe_2O_3 .

Oil-Ash Deposits. Similar studies by Wickert^(215, 216), who passed air containing 5% SO_2 over fuel-oil ash components and possible additives, demonstrated the high catalytic activity of V_2O_5 and Fe_2O_3 , although the maximum conversion obtained was not quite so high in his apparatus as those shown in Figure 17. His results are shown in Figure 19, which also includes the effects of some boiler deposit materials and synthetic combinations. One such mixture containing 60% V_2O_5 with Na_2SO_4 showed greater activity than pure V_2O_5 , indicating the potential danger of SO_3 formation over deposits containing these compounds. On the other hand, it was noted that SiO_2 brings about a maximum SO_2 to SO_3 conversion of only 10% at 1600 F and that Al_2O_3 effects a conversion of 4%, at most, at temperatures above 1800 F.

In another investigation, Wickert⁽²¹⁷⁾ noted that CaO also catalyzed SO_2 oxidation, starting at 400 F and reaching a maximum at 1100 F. Mixtures of V_2O_5 with SiO_2 or CaO gave significant conversions of SO_2 to SO_3 in the vicinity of 1050 to 1250 F.

The use of V_2O_5 as a catalyst for SO_2 oxidation dates back to 1900, and several patents have been issued for such an application.^(21, 37, 208) The interest in this reaction arose in the course of the development of the contact process for the manufacture of sulfuric acid. Postnikov and associates⁽¹⁵⁸⁾ found that the temperature interval for intensive contact catalysis was 825 to 1025 F. At all SO_2 concentrations an increase in gas velocity required a rise in temperature to maintain optimum conversion of SO_2 to SO_3 . At the present time, for the manufacture of sulfuric acid, SO_2 is passed over V_2O_5 at 800 to 1150 F. The contact time is 2 to 4 seconds, and the conversion of SO_2 to SO_3 is 90 to 98%. A typical oil-fired boiler has the corresponding temperature range needed to promote this reaction but unfortunately there is less catalyst, less air, and a shorter contact time than is required for ideal reaction conditions. Nevertheless, the contribution of V_2O_5 and vanadates to SO_3 production in a boiler cannot be discounted.

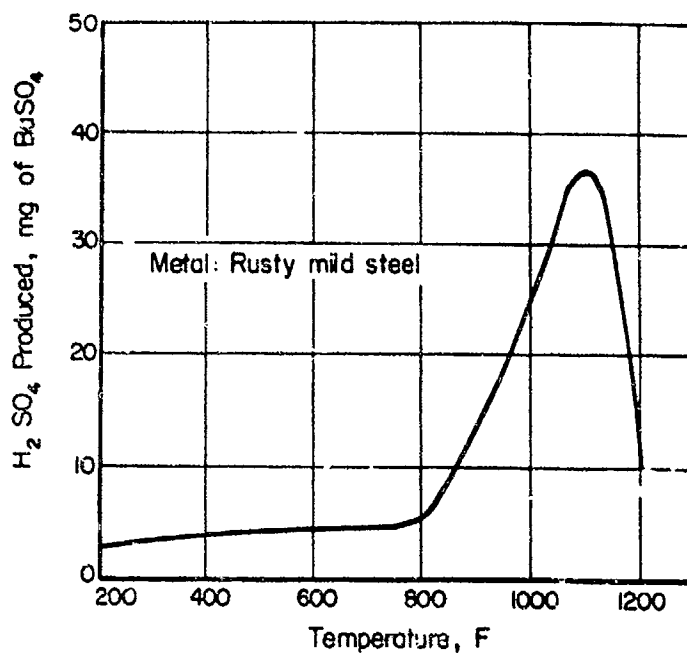


FIGURE 17. SULFURIC ACID PRODUCED FROM SO₂ IN FLUE GASES AS A FUNCTION OF TEMPERATURE OF METAL SURFACE⁽⁸¹⁾

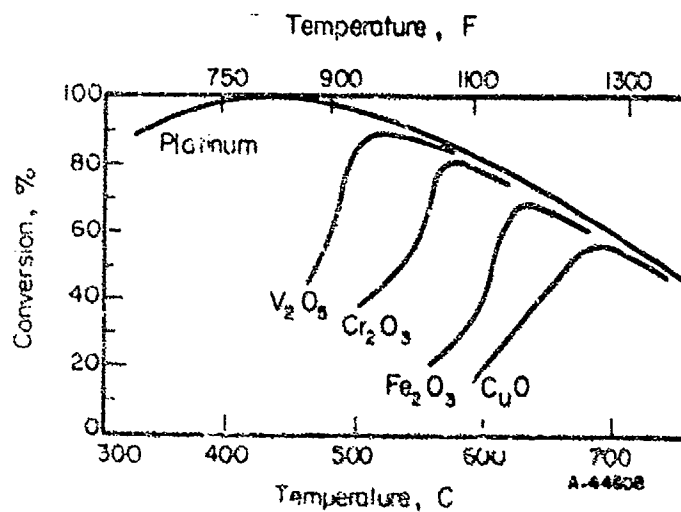
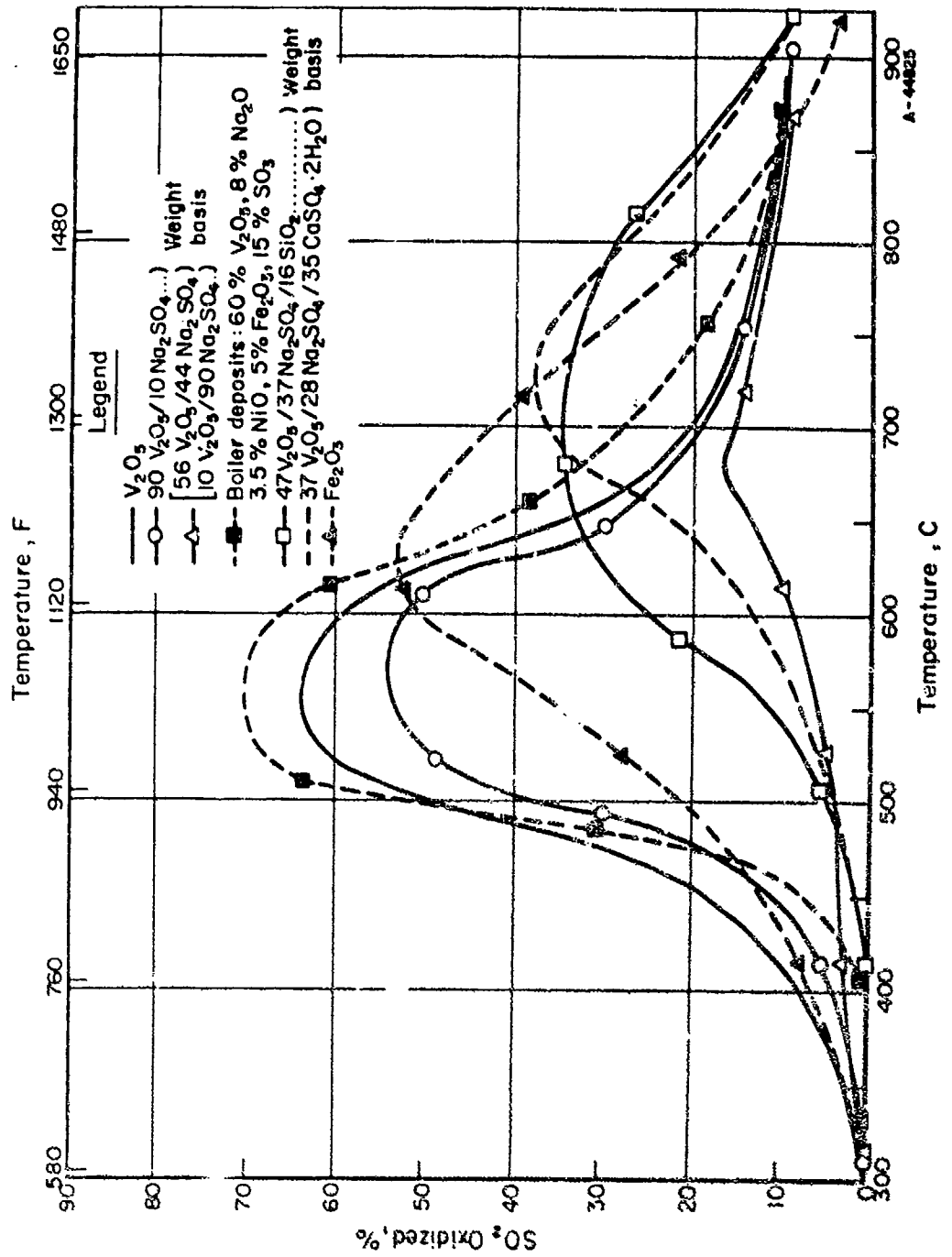


FIGURE 18. CONVERSION OF SO₂ TO SO₃ IN THE PRESENCE OF SEVERAL CATALYSTS⁽¹⁶⁾

FIGURE 19. CATALYTIC OXIDATION OF SO₂ TO SO₃ BY VARIOUS MATERIALS (215)

Apparently the V_2O_5 must be present as a deposit over which the SO_2 passes in order to effect significant catalytic action, because Taylor and Lewis⁽²⁰⁴⁾ found no additional SO_3 when 0.045 wt % of V_2O_5 was added to oil in the form of a soluble naphthenate. In these laboratory experiments, very light V_2O_5 deposits were formed on the ductwork, but the lack of SO_3 formation can be attributed to the small surface-to-volume ratio of the system and the fact that metal temperatures were lower than commonly found in boilers. Similarly, Rendle and Wilsdon⁽¹⁶⁶⁾ found no effect on sulfuric acid dewpoint in an experimental furnace burning oils with significant vanadium content. However, their combustion chamber was operated at 1830 F, where conversion of SO_2 to SO_3 by V_2O_5 is very low, and their system also had a small surface-to-volume ratio. Hence these observations are not valid objections to catalytic effects of the vanadium in oil.

An effort to closely approximate boiler conditions was made by Burnside, Marskell, and Miller⁽²⁹⁾, who used a pilot-scale unit. It consisted of a horizontal combustion chamber, a swirl chamber for mixing, and a vertical flue on which was placed a bank of superheater tubes. The unit was fired with coal gas to which SO_2 was added in controlled amounts. The rate of firing was such as to maintain a gas temperature below the tube bank of approximately 1500 F. The surface temperature of the superheaters was varied as desired between 850 and 1250 F by passing air through the tubes. The SO_2 and SO_3 levels were determined by chemical analysis of samples of gas withdrawn below and above the tube bank. In addition, the dewpoint was measured at both points. The results of a series of tests are presented in Figure 20, showing SO_3 concentration above and below the tube bank as a function of tube-metal temperature. The data are somewhat scattered, but show clearly that SO_3 concentration increased above the tube bank as the metal temperature rose. It is significant that the SO_3 level below the tube bank, about 50 ppm, was great enough to cause boiler problems. This amount of SO_3 probably resulted from oxidation of SO_2 in the flame zone.

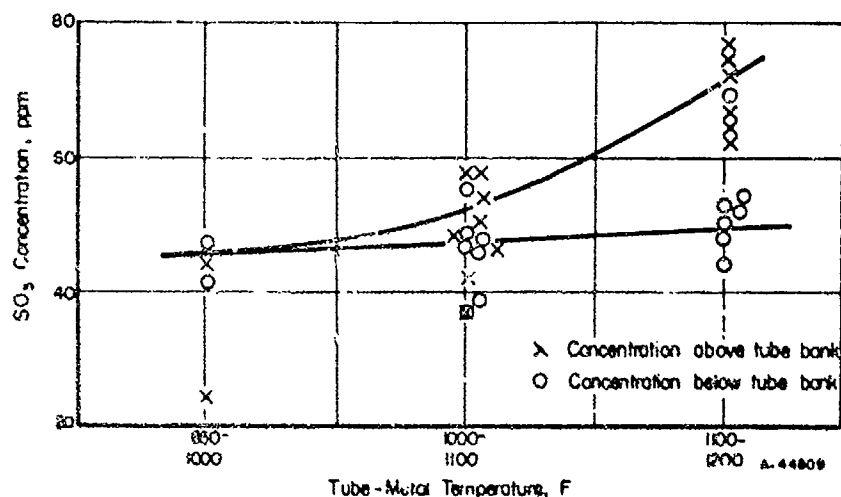


FIGURE 20. CONVERSION OF SO_2 TO SO_3 ACROSS TUBE BANK⁽²⁹⁾

Test conditions: Flue-gas temperature, 1300 to 1400 F, CO_2 , 7 to 8%; excess air, 60%; SO_2 concentration, 9.11 to 0.14%.

B A T T E L L E M E M O R I A L I N S T I T U T E

Experiments were performed with an oil-fired residential heating boiler by Anderson and Manlik⁽⁶⁾ to examine SO_3 formation in different parts of the system. SO_2 was injected successively at four points in the boiler: with the combustion air, in the furnace, in the flues, and in the stack. From the corrosion resulting on steel specimens mounted in the stack, it was estimated that the amount of acid formed in each of the four zones was approximately equal, with slightly less forming in the stack.

With CS_2 added to distillate fuel oil to give 1% sulfur, the effect of individual ash constituents on the oxidation of SO_2 was studied. The ash constituents (sodium, vanadium, nickel, and iron) were added separately as oil-soluble compounds at a concentration of 200 ppm. The following conclusions were reached:

- (1) So long as the ash was suspended in the flue gases, it inhibited corrosion due to SO_3 . When fired in a clean boiler, the additions resulted in lowered corrosion, up to 37% for the vanadium.
- (2) Ash deposits form catalytic surfaces. The conversion of SO_2 to SO_3 , as indicated by corrosion on the steel sample, was increased by the accumulation of the deposits, except in the case of sodium. Under the test conditions, the iron gave the greatest increase, 15%.
- (3) Ash deposits formed from sodium and vanadium mixtures (1 to 1 and 1 to 3) catalyzed SO_3 formation to a greater extent than did the individual constituents. The 1-to-3 mixture resulted in a 42% increase in corrosion, while the 1-to-1 mixture gave a 23% increase.

These experiments demonstrated that suspended oil ash, formed in burning residual fuel oil, can scavenge SO_3 from the gas stream. However, as soon as the ash has accumulated on boiler surfaces, the catalytic effect of the ash deposit overshadows the inhibitive effect in the gas stream, whether it be reaction or adsorption, and the net result is increased SO_3 in the gas stream. The enhanced catalytic activity indicated for the sodium vanadate deposit is particularly noteworthy because both these elements are commonly encountered in residual oils. This study is the most complete one reported to date that has been performed under actual boiler conditions. It constitutes an important contribution because it has verified many of the ideas suggested by results of earlier research. Extrapolation of the data to a large boiler would be more reliable, perhaps, if SO_3 had actually been measured in the gas stream rather than estimated from corrosion damage.

The temperature dependence of these catalytic effects has been brought out in full-scale boiler operation also. Coward⁽⁴¹⁾ reported that in the initial operation of Ripple Power Station in England the surface temperature of the superheater tubes was 1100 F, with a steam temperature of 850 F at the superheater outlet. This temperature is the optimum for Fe_2O_3 catalysis of SO_2 oxidation, and the excessive amount of SO_3 in the flue gases was made evident by perforation of one air preheater surface after only 8 weeks of operation. Reduction of the temperature of the superheater surface to 900 F was brought about by reducing gas velocity through the superheater and regulating air controls to produce a higher heat release in the furnace. As a result of these modifications and consequent temperature lowering, air preheater blockage and corrosion were reduced to the point where it became possible to operate from one annual inspection to the next without stoppage.

From the mass of data which has been accumulated regarding SO_3 formation in boilers, it appears that both oxidation of SO_2 in the flame zone and the catalytic oxidation contribute to the total SO_3 in the flue gases. Widell⁽²¹⁹⁾ showed by thermodynamic and kinetic considerations that both types of reactions probably do occur in practice. The relative contributions depend on the specific conditions which exist in a given boiler system. Some additional facts which have been reported regarding the effects of the various factors in boiler operation on the production of SO_3 are given in the next section.

Other Factors in SO_3 Formation. Data published by Rendle and Wilsdon⁽¹⁶⁶⁾ on the relation of the SO_3 content of the combustion gases and of the dewpoint of the gases to the sulfur content of fuel oils are presented in Figure 21. Results of several other investigations also have been plotted. Consequently, the type of oil, ash content, and combustion conditions differ for the various sets of points. Although the plot of SO_3 content shows considerable scatter, it is apparent that with more than 0.5 per cent sulfur in the oil, the SO_3 content of the gases does not increase in direct proportion to the increase in sulfur.

The dewpoint plot brings out two important points: (1) There is a rapid initial rise in dewpoint with the first increment of sulfur in the fuel. For an estimated dewpoint of 100 F with no sulfur (the water dewpoint), an increase to 260 F (H_2SO_4 dewpoint) is found with 1% sulfur. (2) There is a relatively small rise in dewpoint as the sulfur in the fuel oil increases beyond 1 to 6%. Even if an economical method of removing sulfur from oil were available, a reduction from 6 to 1% would lower the dewpoint only from 300 F to 260 F. It would be necessary to achieve almost complete removal of the sulfur to obtain a significant drop in dewpoint.

The effect of flame temperature on SO_3 formation was reported by Crumley and Fletcher⁽⁴⁴⁾ for a laboratory furnace burning two different fuels. Their results, shown in Figure 22, indicated a tenfold increase in SO_3 concentration in the flue gases with an increase of flame temperature from 2800 F to 3100 F, after which the SO_3 content leveled off. In this instance it is likely that catalysis of SO_2 at the refractory wall as a result of the higher temperature was responsible for the increase in SO_3 .

Crumley and Fletcher also noted that at the same combustion temperature, an increase of excess air from 9 to 70% approximately doubled the percentage of SO_2 that was oxidized to SO_3 . Lees⁽¹¹³⁾ obtained data on a large boiler at the Bankside station by variation of the flow of primary air while operating at constant load. An increase in excess air as represented by a decrease of the flue-gas CO_2 content from 13 to 10% resulted in a rise in dewpoint from 300 to 345 F. Glaubitz^(68,69) carried this approach to the practical limit by operating refinery boilers at Emoland with a mere 1% of excess air. He reported that SO_3 formation was negligible, as evidenced by the lack of problems with deposits and corrosion.

Large changes in the water-vapor content of flue gases cause only slight changes in acid dewpoint. The variation of dewpoint with sulfuric acid content of gases having different water-vapor concentrations is shown in Figure 23, where the range from 0.5 to 15% water vapor changes the dewpoint only 30 to 40 F for the medium to high acid contents indicated.

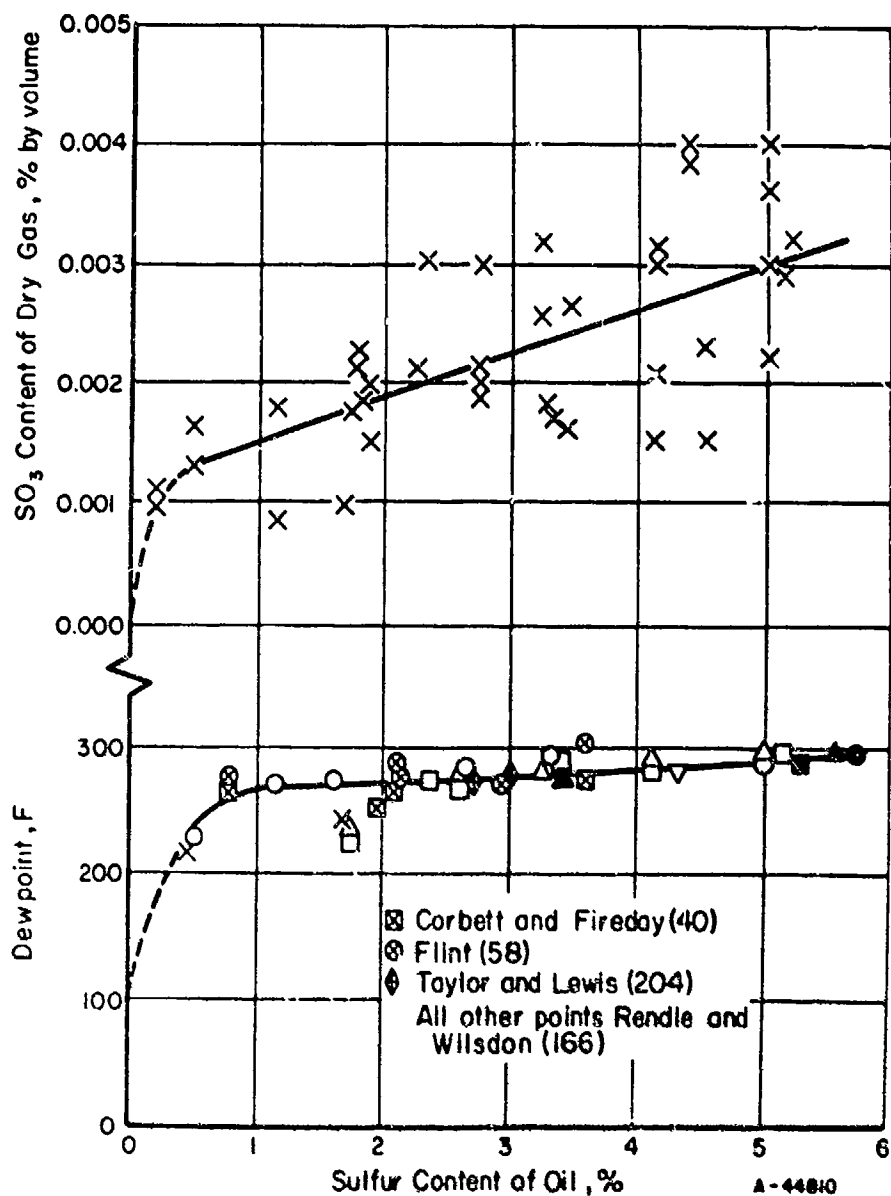


FIGURE 21. RELATION OF DEWPOINT AND SO₃ CONTENT OF COMEUSTION GASES TO SULFUR CONTENT OF OIL⁽¹⁶⁶⁾

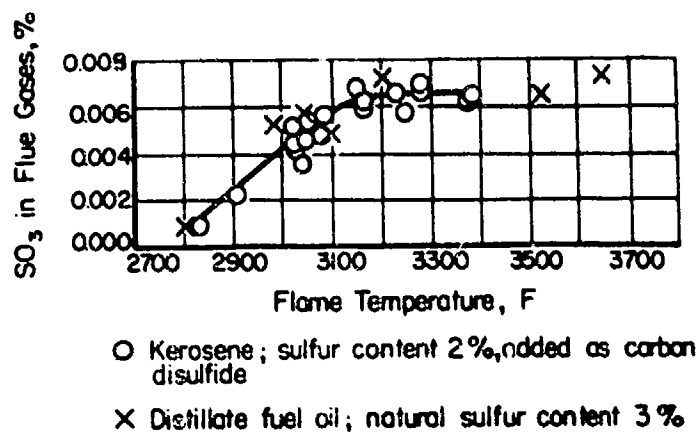
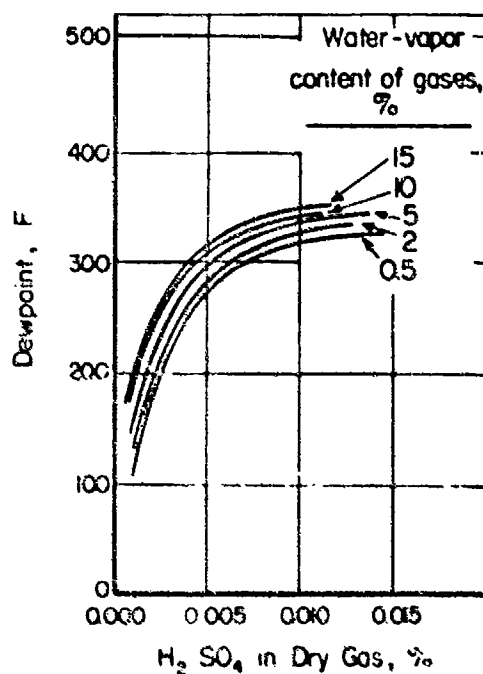


FIGURE 22. VARIATION OF SO₃ CONTENT OF FLUE GASES WITH FLAME TEMPERATURE⁽⁴⁴⁾

Flue gases contained 12% CO₂.



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FIGURE 23. VARIATION OF DEWPOINT WITH H₂SO₄ CONTENT FOR GASES HAVING DIFFERENT WATER-VAPOR CONTENTS⁽¹²⁵⁾

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HIGH-TEMPERATURE OIL-ASH DEPOSITS

Effect of Flue-Gas Temperatures

Fire-side deposits in boilers have been the source of considerable difficulty because they (1) reduce the rate of heat transfer through the boiler and steam tubing and (2) increase the draft pressure needed to conduct the combustion gases through the boiler. The higher tube-metal temperatures are often found to lead to increased corrosion of the heat-receiving surfaces for several reasons. First, the formation of deposits appears to be closely related to the temperature of the metal surfaces, and secondly, at higher temperatures deposits react more rapidly with the metal.

The maximum temperature in the boiler system occurs in the active combustion zone, where the gases range from 2700 to 3100 F. As heat is extracted from the combustion gases by the furnace-wall tubes, the gas-temperature drops, so it is 1500 F to 2200 F as the gases leave the radiant section. These gases then pass through the superheater section where they are further cooled to between 900 F and 1400 F. Following this, the gases usually pass through an economizer and an air preheater, further cooling them until they are discharged to the stack at a temperature generally lower than 325 F.

Effect of Metal Temperatures

The heat-receiving surfaces, however, are not at the same temperatures as the combustion gases. The exposed surface of the steam-generating tubes in the furnace and boiler sections may be at temperatures between 400 F and 800 F, while the temperature of the superheater elements may range from 900 F to 1300 F, depending on the final steam temperature. The economizer and air-preheater metal surfaces may be at temperatures anywhere from 500 to 600 F down to about 200 F. The discussion in this section is concerned with the external deposits which form in the high-temperature areas: the radiant, convection, and superheater sections of the boiler.

Formation of Deposits

The oxidation of metal surfaces is essentially a corrosion reaction that results in the formation of a scale on the metal. The oxide film, or scale, is not a coating deposited from the surrounding environment but is the result of a reaction between the metal and the gaseous components of the environment. In the absence of other effects, oxidation can, in extreme cases, be severe enough to seriously affect the performance of the metallic components in the boiler.

Normally, oxidation is not a major problem. The external, or fire-side, deposits that are formed from the solid and gaseous combustion products are of far greater concern in boiler operation. These deposits cause difficulties due to loss in heat transfer to the water or to the steam, and under certain conditions the gas passages may plug completely. At high temperatures the deposits react with the oxide and metal surfaces, causing pitting and other types of corrosion.

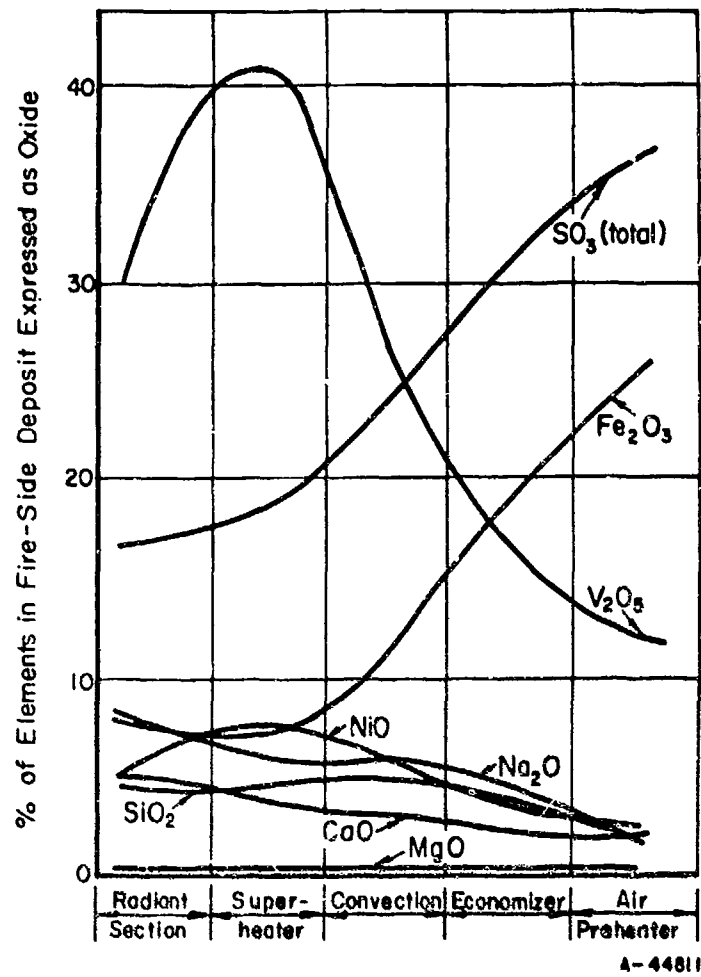


FIGURE 24. TYPICAL DISTRIBUTION OF DEPOSITS IN OIL-FIRED BOILERS(91)

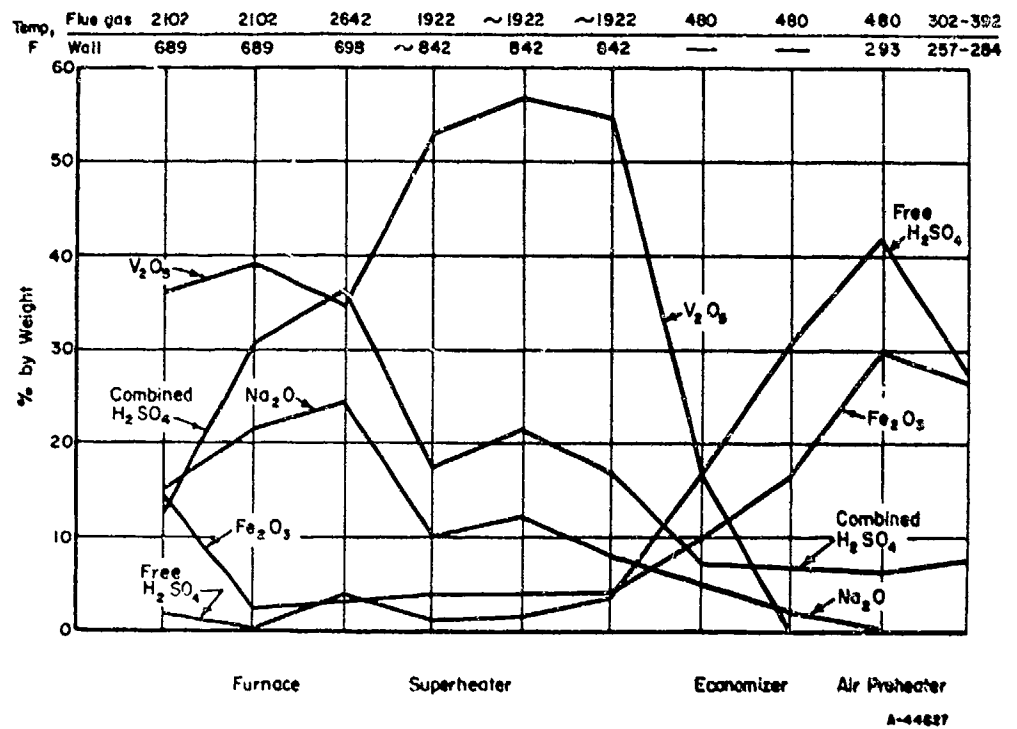
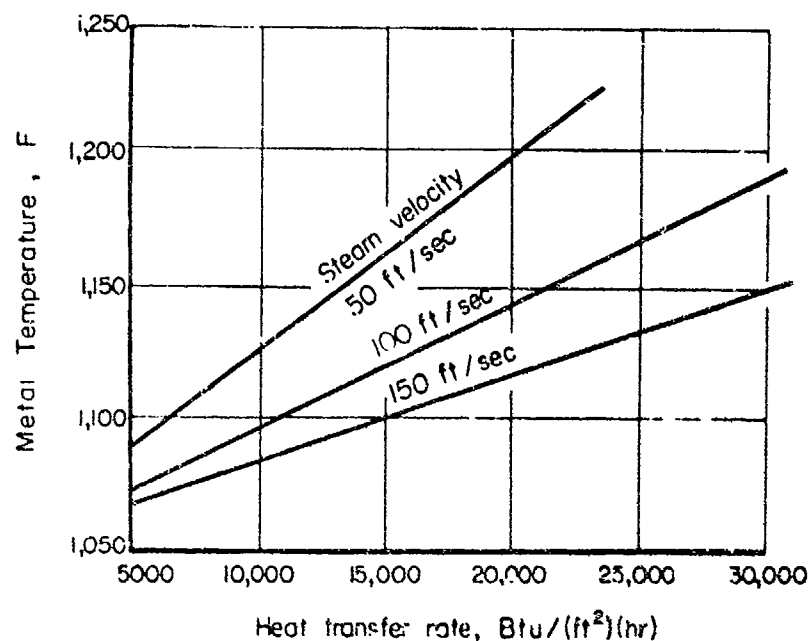


FIGURE 25. GRAPHICAL REPRESENTATION OF THE ANALYSIS OF DEPOSITS IN AN OIL-FIRED BOILER⁽¹⁰⁵⁾

Composition and Distribution

It already has been explained that the main harmful constituents of the oil ash are sulfur, vanadium, and sodium. However, most of the other elements that occur in residual fuels also will be found in the deposit. The proportion of these constituents varies a great deal from one section of the furnace to another. A number of factors influence the composition of the deposits in the various sections of the boiler, with the analysis of the original fuel and the gas and metal temperature probably being the most important variables. The distribution of deposits has been reported by Jacklin, Anderson, and Thompson⁽⁹¹⁾, as shown in Figure 24, and by Kirsch and Pruss⁽¹⁰⁵⁾, shown in Figure 25. Both figures indicate essentially the same distribution of ash components, although it should be noted that the actual percentages differ somewhat in the two illustrations. The vanadium content rises to its maximum value in the superheater zone, while the iron and sulfur are highest in the air preheater. Figure 25 also shows the flue gas, and metal or wall temperatures existing in the various zones. Crancher⁽⁴²⁾ pointed out that the superheater-tube temperature is a function of gas temperature, gas velocity, and steam velocity, as well as steam temperature. Thus, there is no specific relationship between tube temperature and steam temperature, but in conventional plants, 100 F temperature difference between the outside of the superheater-tube wall and the outlet steam is a practical minimum. The influence of steam velocity is shown in Figure 26. The relationship between gas temperature and metal temperature has been discussed by Phillips and Wagoner⁽¹⁴⁹⁾ in connection with corrosion studies on superheater alloys. They reported that while increasing metal temperature will cause more corrosion, a higher gas temperature for a given metal temperature will have a similar effect.



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FIGURE 26. VARIATION IN TUBE-METAL TEMPERATURE WITH TRANSFER RATE AND STEAM SPEED⁽⁴²⁾

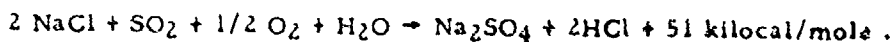
Steam conditions, 800 psig, 1050 F.

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Two main types of deposits occur in oil-fired units. (3) They may be classified as sulfate and vanadate deposits, signifying their basic components. Clarke⁽³⁷⁾, and Collins and Knox⁽³⁹⁾ have distinguished these two distinct types of deposits by their color, physical characteristics, and water solubility. A granular to powdery deposit, varying in color from greenish white to green, is usually found on the coolest generating tubes. These deposits are high in both sodium and sulfur, and they are water soluble. On passing inward towards the hotter tubes, the character of the deposit changes, becoming less granular, with lower sulfate content. Approaching the rear of the furnace, the deposits are fused black slags, higher in vanadium content and having low water solubility. Some superheater deposits are layered, with the high-vanadium-type slag adjacent to the tube, overlaid with the granular, sulfate-type deposit. The latter type has sometimes caused complete blocking in the superheater sections. Clarke indicated that other deposition patterns also have been observed. Wigan⁽²²⁾ considers that sulfur is the prime culprit in fouling and corrosion. He reports that tests indicate that maximum sulfate buildup occurs at a metal temperature of a little over 1000 F. This is within the optimum range for the catalytic oxidation of SO₂ to SO₃ on Fe₂O₃ surfaces. A surface scale can form that is said to provide an ideal surface for continued buildup of deposits. Vanadium's contribution is also believed to lie in its role as a catalyst for SO₂ to SO₃. In making the above statements Wigan is obviously referring only to relatively low-temperature boilers. In other discussion he acknowledges the fact that vanadium is a corrosion factor in high-temperature operation.

Whittingham⁽²¹²⁾ discussed deposit formation, and possible mechanisms involved, in oil-fired boilers. He classifies high-temperature deposits as those occurring at metal temperatures above about 750 F and suggests that SO₃ in the flue gas may be involved in the reactions. Deposits are the end products of a complicated sequence of reactions in burning droplets of oil, in hot gases, and on heating surfaces. The deposit may form from a combination of stack solids associated with coked residues of oil droplets, volatilized compounds, and soft or molten particles. Whether deposits form as loose dusts or in a bonded form is determined by the extent to which a liquid or plastic phase is produced in the primary layer. If the metal temperature is above the softening or sintering temperature of the depositing particles, the initial film will adhere to the metal or oxide surface.

Sulzer⁽¹⁹⁶⁾ distinguished between three possible kinds of reactions to account for the final ash product. Primary reactions, after all the carbon has been burned, occur between ash constituents within the oil droplet at high temperatures. Secondary reactions occur in the gas stream between the flame zone and the place of deposition. Chances of reaction between vapor-phase ash constituents and SO₂ or SO₃ are considered to be good. However, because of high flow velocities, chemical equilibrium probably is not attained. One such reaction is that between vaporized NaCl and SO₂, according to the following equation:



Sulzer considered that the heat generated by the above reaction might be enough to cause the Na₂SO₄ to be deposited in a plastic or semimolten state. However, it should be remembered that if sufficient V₂O₅ is present, several other low-melting compounds could form that would melt at superheater temperatures. Fletcher and Gibson⁽⁵⁷⁾ demonstrated the progress of this reaction over a range of temperature, showing the amount of Na₂SO₄ formed from either SO₂ or SO₃ alone and in the presence of Fe₂O₃.

(Figure 13). The tertiary reactions are those occurring at the deposition surface, between the ash and the metal surface, or between the deposits and SO_2 or SO_3 .

Whittingham⁽²¹²⁾ also recognized the possibility of deposition of very small solid particles by molecular diffusion or by migration through a thermal gradient. Preliminary calculations indicated that the rate of deposition possible by thermal diffusion was of the same order as that observed in practice. Very little work has been done along this line, but the subject was discussed in Chapter 3 of the ASME publication⁽³⁾, where suggestions for experimental programs are given.

Melting Characteristics of Deposits

Concern over the melting behavior of ash compounds has prompted a number of investigators to try various experimental techniques in an effort to obtain reliable data on actual or synthetic ash mixtures. In addition to the interest in explaining bonding of deposits, as discussed above, the problem is of importance in studying high-temperature corrosion and means for overcoming it.

Whittingham⁽²¹²⁾ investigated the sintering and flow characteristics of laboratory ashes over a range of vanadium to sodium ratios. Compressed pellets of the laboratory ashes were heated in a furnace, and the temperatures for initial deformation, partial melting, and complete melting were observed. Figure 27 is a graph of the ratio of vanadium to sodium in the ash versus the temperature at which the three end points occurred in an oxidizing atmosphere. The initial deformation temperature denotes the onset of sintering of the ash, and the minimum apparently is at a 1-to-1 ratio of vanadium to sodium. This coincides approximately with the formation of NaVO_3 (melting point, 1166 F) according to the reaction



In Figure 28, the importance of the furnace atmosphere is indicated. The temperature for initial deformation is affected considerably by a change in the oxidizing potential of the gaseous atmosphere, and it fluctuates over a wide range with changes in the vanadium/sodium ratio. Whittingham noted, however, that these wide variations occurred under controlled laboratory conditions, whereas selective deposition of components could occur in a boiler. Also, the presence of sulfur oxides in flue gases might result in the formation of compounds with lower sintering temperatures. Adhesion of ash to the metal will be more likely in the primary layer if the ash particles are plastic or molten as they strike the metal or oxidized surface. Whittingham also noted that even an initially solid layer could be converted to a plastic form by reaction with SO_3 that might be present near the metal surface.

Wickert⁽²¹⁶⁾ used a Leitz heating microscope to study the melting behavior of V_2O_5 - Na_2SO_4 mixtures by observing the sinter point, the partly molten point, and the flow point. These results were correlated with the adhesion of the mixtures at these various temperatures to a platinum sheet surface. The melting behavior was plotted as a function of the mole ratios of the components as shown in Figure 29. These curves are similar, although not exactly the same as those shown by Whittingham in Figure 27. A very slight indication of adhesion of the deposit began at about the sintering temperature. With further increases in temperature, the mixtures spread over

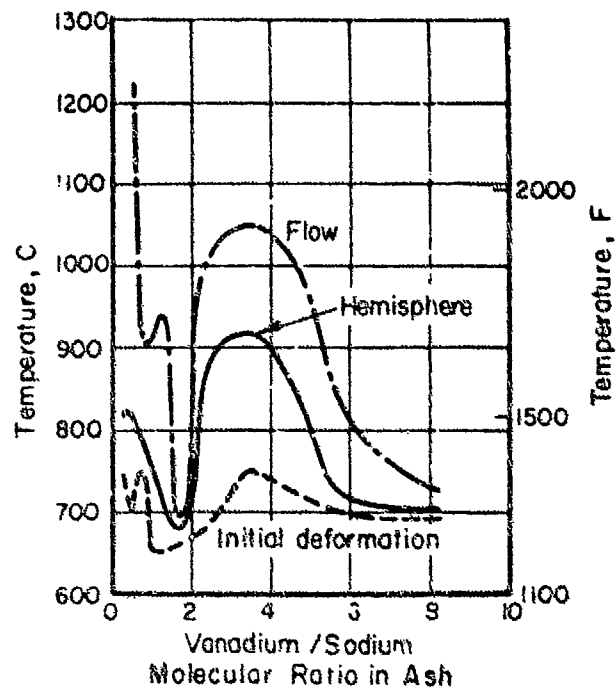
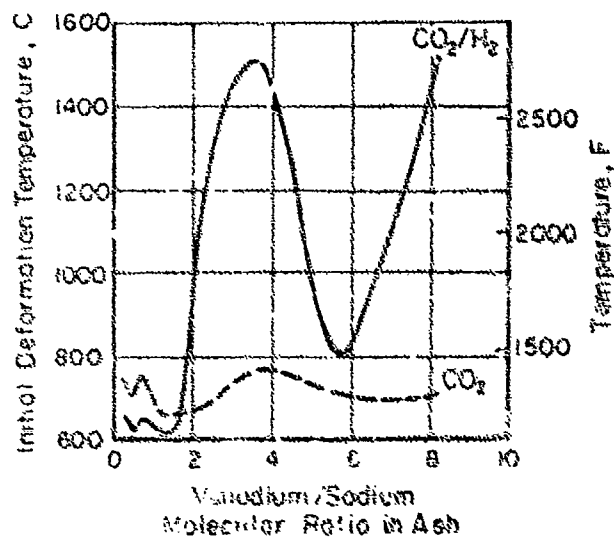


FIGURE 27. HIGH-TEMPERATURE FLOW CHARACTERISTICS OF FUEL-OIL ASH IN OXIDIZING ATMOSPHERE(212)



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FIGURE 28. EFFECT OF ATMOSPHERE ON INITIAL DEFORMATION TEMPERATURE OF FUEL-OIL ASH(212)

the platinum surface and adhered more strongly as the fully molten condition was approached.

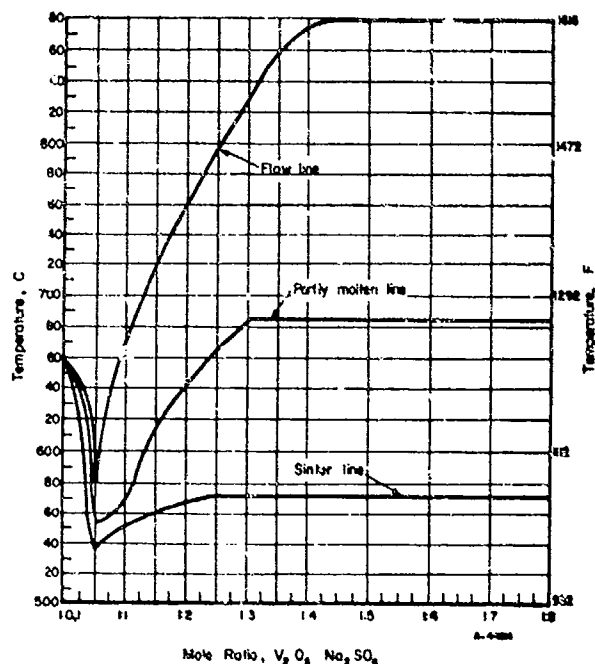


FIGURE 29. MELTING BEHAVIOR OF V_2O_5 - Na_2SO_4 MIXTURES(216)

The procedure was used to determine the effect of several additives on the melting behavior (see also the section on additives in Chapter 4). It was shown that SiO_2 raised the melting point of a V_2O_5 - Na_2SO_4 - SiO_2 mixture at 1-to-1/2-to-1/2 mole ratio to over 1800 F. In a natural oil ash containing 73% V_2O_5 , 8.45% Na_2O , and 0.45% K_2O , silica additions also raised the partly molten point and flow point to over 1800 F, but the first effect was to lower the sinter point to about 1000 F. Therefore, some deposition can be expected on boiler tubes where the metal temperature is in the 1000 F range. Similar results were obtained with kaolin. This test did not indicate any beneficial effect for MgO additions up to a 1-to-1-to-1 mole-ratio mixture of V_2O_5 - Na_2SO_4 - MgO . Partial melting occurred at about 1100 F, and the deposit became strongly bonded on cooling.

Niles and Sanders⁽¹³⁸⁾ used the Leitz heating microscope to determine the melting characteristics of a few compounds as follows:

Compound	Sodium/Vanadium Mole Ratio	Sinter Point, F	Initial Melting Point, F	Final Melting Point, F
NaVO_3	1/1	984	1095	1150
$\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5$	1/3	1030	1150	1235
$\text{Na}_2\text{O} \cdot 6\text{V}_2\text{O}_5$	1/6	1095	1215	1295
$2\text{MgO} \cdot \text{V}_2\text{O}_5$	--	1300	1535	1965
$3\text{MgO} \cdot \text{V}_2\text{O}_5$	--	1790	2175	2270

These figures are used in discussing the mechanism of oil-ash corrosion to be mentioned later.

Phillips and Wagoner⁽¹⁵⁰⁾ and Johnson⁽⁹⁴⁾ have used differential thermal analysis to study melting and freezing points of a number of compounds and mixtures possibly involved in oil-ash corrosion. This procedure is used to detect whether reactions such as fusion, freezing or decomposition occur in the sample while being heated or cooled. Phillips and Wagoner noted that freezing temperatures were significantly lower than melting temperatures. The following tabulation shows the differences observed.

Compound	Liquidus Temperature, F	
	Heating	Cooling
V_2O_5	1220	1165
$\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$	1185	1060
$\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5$	1040	1020
NaVO_3	1040	1020
Na_2SO_4	1625	1625

This is an important observation in view of the possible connection between corrosion and molten ash compounds. Corrosion could occur at temperatures below those indicated by melting-point data. This is significant because boiler deposits occur as a result of solidification of liquid ash on metal surfaces. Evidence was found of a eutectic, between NaVO_3 and $\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5$, having a solidification temperature of 895 F. The melting point of this eutectic determined by other means had been reported to be 1011 F. Variations of this order of magnitude have also been reported for other vanadium compounds. The explanation for these differences may be in the inherent accuracy of the various methods of measurement, or perhaps in the method of sample preparation. In Johnson's paper, the emphasis was on compound formation and the determination of the effect of possible additive metal oxides on the melting point of sodium-vanadium mixtures.

Sulfate Deposits

Form of Deposits

The analyses of deposits formed in oil-fired boilers show that the major constituents of the oil ash predominate in the deposits. However, the proportions of these constituents tend to vary a great deal from one section of the furnace to another and seldom agree with the distribution in the ash. Deposits in the high-temperature section of a boiler generally exhibit a transition in properties and appearance from the burner end to the rear of the furnace. Clarke⁽³⁷⁾ and Collins^(38,39) both have found that the light-colored granular deposits that occur at the burner end are high in both sodium and sulfate. They are hygroscopic to such an extent that free sulfuric acid has been observed by Slater and Parr⁽¹⁹⁰⁾ during shutdown of marine boilers having this type of deposit. The sulfate deposits are soluble in water up to 90%, and the resulting solution is extremely acid. There is a gradual transition in the composition of the deposits as the rear tubes are approached, with less sulfate and lower acidity.

An extreme case of sulfate separation was reported by McCoy⁽¹²⁶⁾, who found 13.2% Na₂O and 30.2% SO₃ in deposits from the radiant section of a boiler but none of either in the superheater deposits.

The rear tubes usually have layered deposits, vanadium being concentrated in the first layer and sodium sulfate predominating in the outer layer. The existence of sodium sulfate as such in the deposits has been verified by X-ray diffraction studies of the fire-side deposits from some U. S. Navy vessels.^(30,169) Minor amounts of the sulfates of other metals are undoubtedly formed in the deposits also. Part of the calcium and magnesium present in the fuel oil and nickel and iron from the boiler materials are found in the deposits. It is believed they occur as sulfates. However, it is generally agreed that chiefly sodium sulfate is involved in the fouling of oil-fired boilers.

Table 14 shows data from Clarke⁽³⁷⁾ on the composition of typical bilayered deposits where sulfates predominate in the outer layer, while vanadium is concentrated in the layer next to the tube.

TABLE 14. COMPOSITION OF BILAYERED DEPOSIT IN OIL-FIRED BOILERS⁽³⁷⁾

Probable Constituent	Primary Black		White Overlay	
	Destroyer	Stationary	Destroyer	Stationary
	Superheater	Boiler	Superheater	Boiler
Na ₂ SO ₄	35.95	23.99	42.39	46.78
NaHSO ₄	--	8.92	--	28.36
CaSO ₄	0.71	--	6.56	8.73
MgSO ₄	1.87	--	10.72	4.26
NI	Trace	1.01	5.19	2.62
V ₂ O ₅	49.34	57.21	16.73	5.16
Fe ₂ O ₃	2.26	2.36	3.20	2.95
SiO ₂	0.67	0.53	0.74	1.41
H ₂ O	3.44	0.97	8.55	0.59
CaO	--	--	--	0.12
MgO	--	--	--	1.23
NiSO ₄	--	--	--	3.14

Although it is the combination of sodium and sulfur oxides from combustion of the oil that is chiefly responsible for the formation of sulfate deposits, there is normally more than enough sulfur in the oil to combine with all of the sodium present. Consequently, the sodium content is commonly used as an index of the tendency of an oil to form sulfate deposits.

A typical distribution of materials as determined by analyses of 75 fire-side deposits in the different sections of an oil-fired boiler, as reported by Jacklin and associates(91), was shown in Figure 24. In this case, large variations in deposit composition with position in the boiler are found for sulfur, iron, and vanadium. The Fe_2O_3 and total SO_3 content of deposits became greater as the boiler was traversed, while the other metal oxide concentrations decreased, indicating that ferric sulfate was the chief deposit material beyond the superheater. The V_2O_5 concentration was greatest in the highest metal temperature region, the superheater, where the melting point of the vanadates is most likely to be reached and cause deposits to adhere.

Sulfur Trioxide Content. An SO_3 concentration gradient through the deposit has been noted also. Harlow(82) found 25% SO_3 in the portion of the deposit adhering to the superheater tubes and only 3% at the surface of the deposit. Weintraub and his associates(211) confirmed this finding, observing a gradient from 19.5% SO_3 to 6.7%. These results point to sulfate formation by reaction of SO_3 formed catalytically at the surface of the tubes.

Initiation of Deposits. The initiation of deposits by alkali metals in combination with oxides of sulfur is the most-widely-accepted theory for the formation of these deposits. Analytical data showing selective deposition of sodium and potassium sulfates have been published in recent years by Carlile(34), Marskell and Miller(122), and Jackson and Ward(92). In an effort to establish the relative importance of various metals in forming deposits in gas turbines, oil-soluble organometallic compounds were added to distillate fuel in a study by Bowden, Draper, and Rowling(18). The results, shown in Figure 30, indicate that sodium is by far the worst in causing both rapid and continued deposit formation. The same effect was observed by Pasman(144) when synthetic sea water containing 2.5% sodium chloride was added (0.4% by volume) to a distillate fuel burned in a small open-cycle gas turbine. Deposits, which were primarily sodium sulfate, were sufficiently heavy after 64 hours of operation to cause a 27% decline in power output.

Bonding of Deposits. Some have speculated as to whether the initial bonding of a deposit requires contact with the pure metal beneath the oxide film that is present on metallic surfaces. If that is the case, a purely physical phenomenon may also be important. Electron photomicrographs of the oxidized surface of steel by Pfefferkorn(146) have shown a grasslike structure of Fe_2O_3 , indicating that particles larger than 5 microns would not reach the pure metal surface of the boiler tube. However, sublimation products 0.7 micron in diameter could penetrate the interlaced needles of oxide, and it is possible that sublimed sodium and potassium compounds do reach the true surface. A few written reports(5, 130) and a good deal of hearsay evidence indicate that newly commissioned boilers and those cleaned to bare metal by water washing experience periods of immunity to deposit. These observations suggest there is an

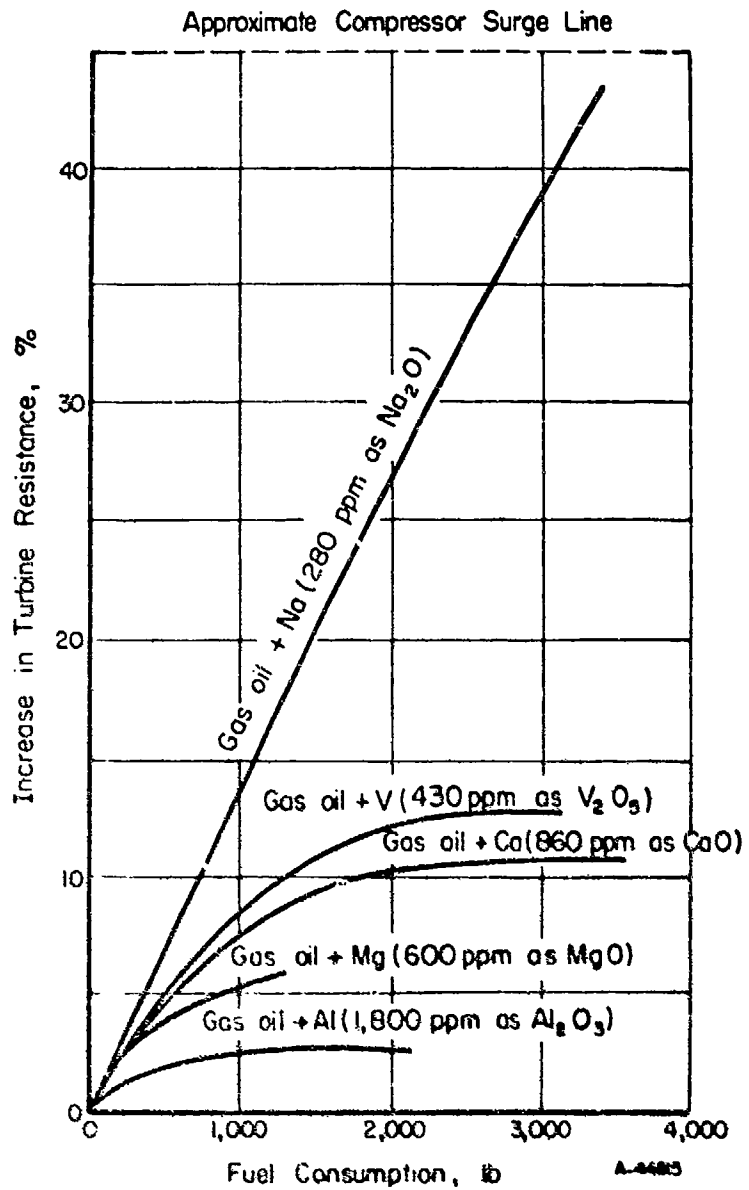


FIGURE 30. EFFECT OF INDIVIDUAL ASH COMPONENTS ON DEPOSIT FORMATION IN A GAS TURBINE(16)

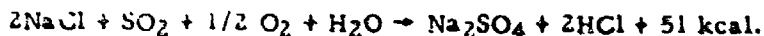
induction time in deposit buildup during which (a) diffusion through the oxide layer may occur or (b) a material having a structure close to that of the oxide may be formed. After the initial reaction, a more rapid accumulation of deposit would be expected.

Mechanism of Formation. The work of Anderson and Diehl⁽⁵⁾ pointed out the most likely mechanism for sulfate deposit formation:

- (1) The alkalis in the ash deposited on the clean tubes are converted to sulfates by reaction with SO_2 and SO_3 from the gas stream.
- (2) Iron oxide and aluminum oxide react with the alkali sulfates and additional SO_3 to form alkali iron sulfates and alkali aluminum sulfates. These complex sulfates have low melting points, 1000 F to 1500 F, which is the range of surface temperatures of the tubes. Thus, a tightly adherent bond to the metal is formed.
- (3) The inner layer increases in thickness, and fly ash from the flue gases adheres to the sticky surface.
- (4) Finally, as the thickness increases and the temperature of the outer surface rises, alkali silicates are formed, and the outer layers are fused into a strong glassy deposit.

It was further demonstrated in the study by Anderson and Diehl that it is possible to form sodium iron sulfate, $\text{Na}_3\text{Fe}(\text{SO}_4)_3$, at 1000 F and potassium iron sulfate, $\text{K}_3\text{Fe}(\text{SO}_4)_3$, in the range 1000 to 1200 F in an atmosphere containing only SO_2 and no SO_3 . This reaction is attributed to the catalytic effect of Fe_2O_3 at these temperatures. These data substantiate the findings of Fletcher and Gibson⁽⁵⁷⁾, who studied the reaction of SO_2 and SO_3 with NaCl , using radioactive sulfur, and showed that sodium sulfate can be formed from SO_2 , particularly in the presence of Fe_2O_3 , as discussed previously.

This same viewpoint has been advanced by Sulzer^(196, 197), in his studies of residual-oil combustion in gas turbines. He suggests that the following reaction plays a large part in sulfate formation:



It is his contention that the heat evolved in this reaction may bring the particle temperature sufficiently above the ambient temperature to melt the fine particles of Na_2SO_4 formed. Dense, partly molten deposits, consisting of over 95% Na_2SO_4 , have been observed on turbine blades even at temperatures of about 1200 F, although the melting point of Na_2SO_4 is 1630 F.⁽¹⁹⁸⁾ Such an explanation for turbine systems may be questioned, however, on the basis of observations by Widell and Juhasz⁽²⁰⁰⁾, who found that the softening temperatures of mixtures of Na_2SO_4 and V_2O_5 were 1050 to 1100 F. This was true even when the mixtures contained as little as 10% V_2O_5 , which is usually present also. So, it is possible that a low-melting eutectic composition may have been formed instead of a highly exothermic reaction occurring.

A list of sulfate compositions which may be encountered in boiler systems, with their respective melting points, is presented in Table 15. Several of these materials

have sufficiently low melting points to be fused onto superheater tubes. Five polymorphous forms of Na_2SO_4 have been identified by Lambertson⁽¹¹¹⁾ in superheater deposits from a naval boiler, and Simons, et al. (187), found CaSO_4 as well.

TABLE 15. MELTING POINTS OF SULFATE COMPOSITIONS^(a)

System	Melting Point, F	Remarks
Na_2SO_4	1623	
K_2SO_4	1969	
Na_2SO_4 -75%, K_2SO_4 -25%	1530	
$\text{K}_2\text{SO}_4(\text{s})$ - $\text{SO}_3(\text{g})$	635	
$3\text{K}_2\text{SO}_4$ - $\text{Na}_2\text{SO}_4(\text{s})$ - $\text{SO}_3(\text{g})$	535	
$\text{K}_3\text{Fe}(\text{SO}_4)_3$	750	
$\text{Fe}_2(\text{SO}_4)_3$	896	Decomposes to Fe_2O_3 and SO_3
$\text{Al}_2(\text{SO}_4)_3$	1418	Forms Al_2O_3 and SO_3
CaSO_4	2642	
CaSO_4 -42%, K_2SO_4 -31%, Na_2SO_4 -27%	1400	
Na_2SO_4 , K_2SO_4 , $\text{Fe}_2(\text{SO}_4)_3$	1030	
Na_2SO_4 , K_2SO_4 , $\text{Al}_2(\text{SO}_4)_3$	1030	
MgSO_4	2055	Forms MgO and SO_3
NiSO_4	1544	Forms NiO and SO_3
NaHSO_4	482	Forms $\text{Na}_2\text{S}_2\text{O}_7$
$\text{Na}_2\text{S}_2\text{O}_7$	752	
ZnSO_4	1364	Forms ZnO and SO_3
Na_2SO_4 - CaSO_4 eutectic	1675	Mixtures melt from 1620 F to 1740 F

(a) Compiled from various sources.

Sulzer⁽¹⁹⁹⁾ has offered CaSO_4 formation as an explanation for heavy deposit formation when calcium compounds are used as additives to residual oils. He proposes a mechanism as follows: CaO forms during combustion and collects on metal surfaces, where it reacts exothermally with the SO_3 in the gas stream to form CaSO_4 . Sulfur dioxide in the gases may be oxidized catalytically to SO_3 by V_2O_5 formed from the combustion of the oil.

Although CaSO_4 has a reported melting point of 2640 F, Sulzer believes that the heat of formation may raise the temperature sufficiently to cause a sticky surface. It should be pointed out, however, that the dissociation of CaSO_4 begins at about 1850 F, which is significantly below this melting point. Simons noted that mixtures of Na_2SO_4 and CaSO_4 melt in the range 1600 to 1750 F, depending on their composition, and it is likely that one of these mixtures is involved whenever calcium is found in bonded deposits. The phase diagram for the Na_2SO_4 - K_2SO_4 - CaSO_4 ternary system⁽¹⁰³⁾ shows a eutectic at 1400 F, so that other relatively low-melting mixtures are possible as well, to account for mixed deposits.

Magnesium sulfate seems to play little part in deposit formation, although Lewis⁽¹¹⁵⁾ found it to be present in deposits from residual-oil ash when magnesium

compounds were used as additives to combat vanadium corrosion. However, experience at the Gas Turbine Division of the Westinghouse Electric Corporation has shown that no MgSO_4 is found in deposits, although there is more magnesium present in the additive than would be required to react with all of the vanadium present⁽¹⁶²⁾.

Vanadate Deposits

Form of Deposit

The relatively large amount of vanadium which occurs in many residual oils accounts for a sizable portion of the deposits in oil-fired systems. Vanadium was found by Clarke⁽³⁷⁾ in the compact, black, crystalline deposits on the high-temperature rear tubes of a marine boiler, in a form which he believed to be one of the lower oxides of vanadium. As shown in Table 14, whenever a two-layered deposit occurs, the vanadium-rich, black layer is found adjacent to the tube. In the form V_2O_5 , the vanadium has been reported in deposits on the final stage of a gas turbine, as shown by X-ray analysis⁽¹⁴⁸⁾. However, it is more common to find the vanadium in combination with sodium, as a vanadate. Sodium vanadyl vanadates ($\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$ and $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 11\text{V}_2\text{O}_5$) have been observed in deposits on marine-boiler tubes and in the high-temperature regions of gas turbines. The vanadate deposits are characterized by low water solubility, as compared with the sulfate deposits, one analysis showing 10% of a soluble portion to be V_2O_5 , as compared with 72% of the insoluble portion.⁽¹⁶⁹⁾

Selectivity in the deposition of vanadium compounds was noted also by Lloyd and Probert⁽¹¹⁸⁾, as a typical analysis of a gas-turbine deposit showed 33% V_2O_5 on a stator blade as compared with 45.2% on a rotor blade, from an oil ash containing 62% V_2O_5 .

There is evidence from the study of Zoachak and Bryers⁽²²⁶⁾ that vanadium-containing deposits are initiated by condensation of V_2O_5 on tube surfaces and are built up by subsequent reaction with other ash components and with SO_3 in the flue gases. Occasionally, V_2O_5 as such has been observed in X-ray diffraction studies of deposits, and this type of deposit undoubtedly forms by condensation of V_2O_5 from the gaseous phase. However, sodium and sulfur are invariably present in the oil-ash also, and interactions of vanadium with these elements results in more complex deposits.

Vanadium and Sodium. The effect of the ratio of vanadium to sodium has been studied by Evans and associates⁽⁵⁴⁾, who found that both deposits and corrosion were decreased when the vanadium-to-sodium ratio was reduced. At the same time the deposits became increasingly water soluble and easily removed. Table 16 shows the analyses of the fuels and the improvement obtained by lowering the vanadium-to-sodium ratio of the fuel from 11:1 to 1:1.

TABLE 16. EFFECT OF THE VANADIUM-SODIUM RATIO ON DEPOSITION AND CORROSION BY RESIDUAL OILS(54)

Fuel	Venezuelan	Middle East
<u>Analyses</u>		
Total Ash, wt %	0.060	0.045
Vanadium, wt %	0.022	0.009
Sodium, wt %	0.002	0.009
<u>10-Hour Turbine-Test Results</u>		
Gas Temperature, F	1305	1267
Average Stator Blade Deposit, g	0.165	0.043
Deposit Type	Strongly bonded, ceramic-like, hard to remove	Largely water soluble
Corrosion Wt Loss, g	0.154	0.068

These results indicate that there are some combinations of sodium and vanadium oxides which adhere more readily to the heated metal surfaces, probably because they are lower melting. A detailed study of the phase equilibria in systems involving Na_2O , SO_3 , and V_2O_5 was conducted by Foster and associates(62). They demonstrated that Na_2SO_4 and V_2O_5 are not compatible with each other either in the crystalline or in the molten state. These two compounds react upon heating, with evolution of SO_3 , to form NaVO_3 and complex vanadates. Foster concluded:

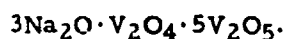
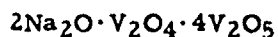
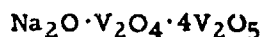
- (1) Na_2SO_4 exists only in mixtures containing less than 56% V_2O_5 .
- (2) SO_3 is liberated from all mixtures, partially up to 56% V_2O_5 and completely beyond 56% V_2O_5 .
- (3) The 56% V_2O_5 mixture consists entirely of $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_5$.
- (4) The 80% V_2O_5 mixture consists entirely of $\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5$.
- (5) The 88% V_2O_5 mixture consists entirely of the complex $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$.
- (6) Free V_2O_5 exists only in mixtures containing in excess of 88.8% V_2O_5 .

The data of Niles and Sanders(138) were similar, showing the existence of compounds having Na_2O -to- V_2O_5 ratios of 1 to 1 and 1 to 3 and almost 1 to 6 ($\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$). It was observed that the 1-to-6 ratio was maintained in the molten salt, but oxygen was evolved on cooling, resulting in the oxygen-deficient structure.

Another intermediate composition, $5\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 11\text{V}_2\text{O}_5$, was investigated by Phillips and Wagoner(150) by using differential thermal analysis. They found evidence for a eutectic having a solidification temperature of 900 F. A material melting at a temperature this low could act as a bonding agent for deposits in boilers operating at

moderate steam temperatures. Another study by these investigators⁽¹⁴⁹⁾, in which metallic contaminants were added to a gas flame, showed that increasing the sodium-to-vanadium ratio resulted in soft, bulky, loosely bonded deposits. This result confirmed the previously cited work of Evans and associates, which was carried out on a gas turbine.

Additional oxygen-deficient sodium vanadate compositions have been reported by Canneri⁽³²⁾, who claimed to have prepared



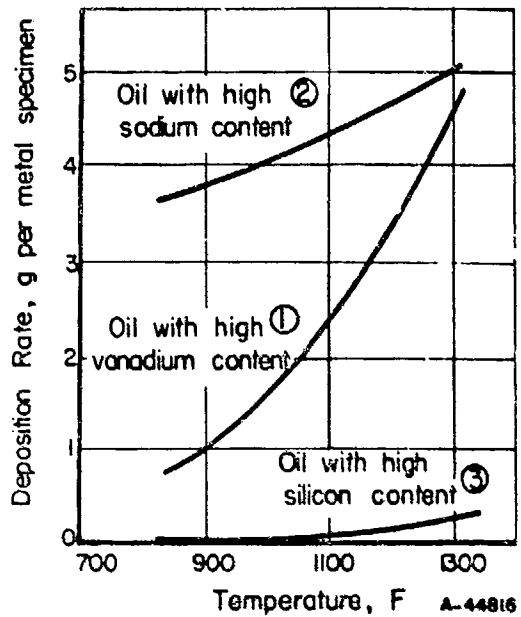
Systems similar to the first two are reported with potassium replacing the sodium. It is possible that complex vanadates of this nature occur in boiler and turbine deposits and account for the inability of investigators to identify all the deposit components by X-ray diffraction. There have been several reports of "unidentified lines" in X-ray patterns which do not conform to any compounds listed in standard tables.

The formation of vanadyl sulfate, $(\text{VO}_2)_2\text{SO}_4$, by the interaction of V_2O_5 and SO_3 at temperatures above 650 F was claimed by Wickert⁽²¹⁶⁾. Maximum formation of this compound occurred at 850 F and dissociation began at 930 F. Vanadyl sulfate proved to be very insoluble in water and perhaps may account for the insoluble portion of many boiler deposits containing vanadium.

In an effort to come closer to actual conditions than is achieved by using mixtures of Na_2SO_4 and V_2O_5 , Wickert⁽²¹⁸⁾ examined the combination of Na_2O and V_2O_5 in an SO_2 -oxygen atmosphere. Under these conditions he found that SO_3 would react with $\text{Na}_2\text{O} \cdot 6\text{V}_2\text{O}_5$ to produce the combination $\text{V}_2\text{O}_5 \cdot 2\text{SO}_3$. This compound is probably better formulated as vanadyl pyrosulfate, $(\text{VO}_2)_2\text{S}_2\text{O}_7$. In addition he found evidence for the existence of $2\text{V}_2\text{O}_5 \cdot \text{SO}_3$, which most likely is a combination of vanadyl sulfate and V_2O_5 , as $(\text{VO}_2)_2\text{SO}_4 \cdot \text{V}_2\text{O}_5$.

Melting-point diagrams for the sodium vanadate and potassium vanadate systems have been reported by Canneri⁽³²⁾. A thermal-arrest diagram for the Na_2SO_4 - V_2O_5 system has been prepared by Cunningham and Brasunas⁽⁴⁵⁾, and the phase diagram for the calcium vanadate system is given by Morosov⁽¹³⁴⁾. The thermal-arrest diagram for Fe_2O_3 - V_2O_5 mixtures has been reported by Monkman and Grant⁽¹³³⁾. All of these diagrams are characterized by the presence of low-melting components which would contribute to deposit problems in steam-generating systems.

The nature of vanadate deposits in boilers and the mechanism of their formation is obviously complex. The conditions in each boiler system vary sufficiently that no single explanation can be offered that will cover most cases. However, from the mass of data which have been accumulated, it appears that vanadate deposition is a potential problem in boilers operating with tube temperatures anywhere above 650 F. The likelihood of difficulty increases with tube temperature, as observed by Sulzer⁽¹⁹⁶⁾ while experimenting with deposition rates of three fuels at various temperatures. His results are shown in Figure 31. The high-sodium high-sulfur fuel had the highest deposition rate at all temperatures, but the vanadium-containing fuel showed the greatest



Ash Compositions, per cent			
	①	②	③
Ash	0.05	0.2	0.18
S	1.9	2.5	0.5
V ₂ O ₅	0.025	-	-
Na ₂ O	0.01	0.09	-
SiO ₂ + Al ₂ O ₃	-	-	0.14

FIGURE 31. EFFECT OF COMPOSITION AND TEMPERATURE ON THE DEPOSITION RATE OF SOME RESIDUAL OILS(196)

Duration of test 12 hours; pressure 21 atm abs.

temperature dependence. The rates became very nearly equal at 1300 F, which is the maximum tube temperature encountered in present-day practice. In the absence of sodium and vanadium, deposits were negligible.

Low-Vanadium Fuels. Noteworthy is the fact that there are some residual fuels sufficiently low in vanadium and sodium that they do not cause deposit or corrosion problems. An example of this situation has been reported⁽¹⁶⁰⁾ in work on Canadian residual oils. Only negligible amounts of deposits and corrosion were observed in 1000-hour tests when using residual oils from crudes of the Leduc oil fields in Alberta. The fuels contained from 0.7 to 13.5 ppm of vanadium and from 3.8 to 54.7 ppm of sodium. The highest rate of ash deposition was only 5 mg/sq cm in 1000 hours at 1300 F gas temperature. However, as yet no one has reported the maximum allowable concentrations of vanadium and sodium that will be compatible with deposit- and corrosion-free operation of a steam-generating system.

CHAPTER 1. HIGH-TEMPERATURE CORROSION REACTIONS

This chapter reviews the reactions that cause deterioration of the metal components at high-temperature areas in the boiler as a result of burning residual fuel oil. Materials of construction are exposed to oxidation and other reactions by corrosive flue gases and attack by molten deposits of the oil-ash mixtures.

OXIDATION OF METALS

There has been a vast amount of research conducted on various aspects of the oxidation of metals at high temperatures. A complete survey of this work is beyond the scope of this report. However, a brief review of the mechanism of film formation and of the laws governing its growth is presented here as an introduction to the discussion of the behavior of metals in boilers.

Mechanism of Oxide-Film Formation

Practically all metals and alloys have a tendency to react with a surrounding gaseous environment. Because the rate of chemical reactions increases considerably with increasing temperature, the problem of oxidation of a metal becomes particularly important at higher temperatures. Generally, the first result of a metal-gas reaction is the formation of a solid film on the metal surface. If the surrounding gas is air or oxygen, the film could be an oxide of the metal. This film, in a sense, separates the metal from the gas environment, but does not necessarily stop continued oxidation. Diffusion, or some other mechanism, permits the passage of oxygen ions through the film to react at the metal-oxide interface. Wagner(209) has listed four factors that influence the progress of oxidation: (1) thickness of the layer, (2) concentration or partial pressure of the oxidizing gas, (3) temperature, and (4) composition of the alloy. A complete review of the fundamental considerations involved in the mechanism and kinetics of oxidation of metals is given in the book by Kubaschewski and Hopkins(108).

Kinetics of the Reaction

Oxidation may proceed at varying rates, and several different relationships have been discovered empirically between weight increase per unit area caused by oxidation (Δm) and time of exposure (t).

Four of these relationships are:

$$(1) \Delta m = k_L t$$

$$(2) \Delta m^2 = k_p t$$

$$(3) \Delta m^3 = k_C t$$

$$(4) \Delta m = k_E (\log at + t_0),$$

representing the (1) linear, (2) parabolic, (3) cubic, and (4) logarithmic relationships. A schematic plot of Δm versus t , shown in Figure 32, helps to visualize the progress of oxidation with time. When the corrosion product is volatile or when the scale is porous and nonprotective, the linear law will determine the progress of oxidation. In this case, oxidation is proportional to time with no noticeable stifling, or slowing down. Figure 32 shows that in the other three cases oxidation rates are high at first but tend to slow down as the film formed on the metal interferes with the passage of ions and electrons. The parabolic rate law is a common one, describing the situation where the oxidation reaction is controlled by diffusion of the reacting materials through the film. It should be noted that a metal may start to oxidize according to one law, and then continue according to another law. Also, a change in temperature may result in a different kinetic relationship.

Metal Sulfide and Sulfate Formation

While the above comments refer to oxidation air or oxygen atmospheres, metals and alloys will also react to form films with other gases, such as carbon dioxide, sulfur dioxide, or hydrogen sulfide. This is of interest because these gases may be present in the combustion products of fuel oil. The mechanisms of film formation and the rate-of-growth laws are fundamentally similar to those applicable in air atmospheres. Kubaschewski and Von Goldbeck(109) discussed the mechanism of sulfidation in gaseous sulfur compounds. Metal sulfides are formed which may have different properties than the oxides. If oxygen is also present, sulfates and perhaps other sulfur-oxygen metal compounds may form to complicate the situation. The relatively low melting points of some sulfides and metal-sulfide eutectics are responsible for some of the deleterious effects that have been observed. If the temperature is high enough to melt the compound present in the film, the liquid sulfide tends to penetrate the metal or alloy along its grain boundaries. This type of intergranular attack has been observed in high-nickel alloys exposed to sulfur-containing gases under reducing conditions.

Oxidation of Metals by Hot Combustion Gases

Combustion-Gas Formation

The gaseous portion of the combustion products of a fuel oil, under conditions of complete combustion with the stoichiometric quantity of air, should consist of CO_2 , H_2O , SO_2 , and N_2 . This situation is not likely to exist in actual boiler operation. In practice, the gas mixture may also contain some O_2 , H_2 , CO , and SC_2 . The quantity of each component in the gas stream will depend on the original composition of the fuel and on the combustion conditions.

Metal-Gas Reactions

When the gas mixture, resulting from fuel-oil combustion, sweeps over the hot metal surfaces in the boiler, there will be a tendency for reactions to take place between

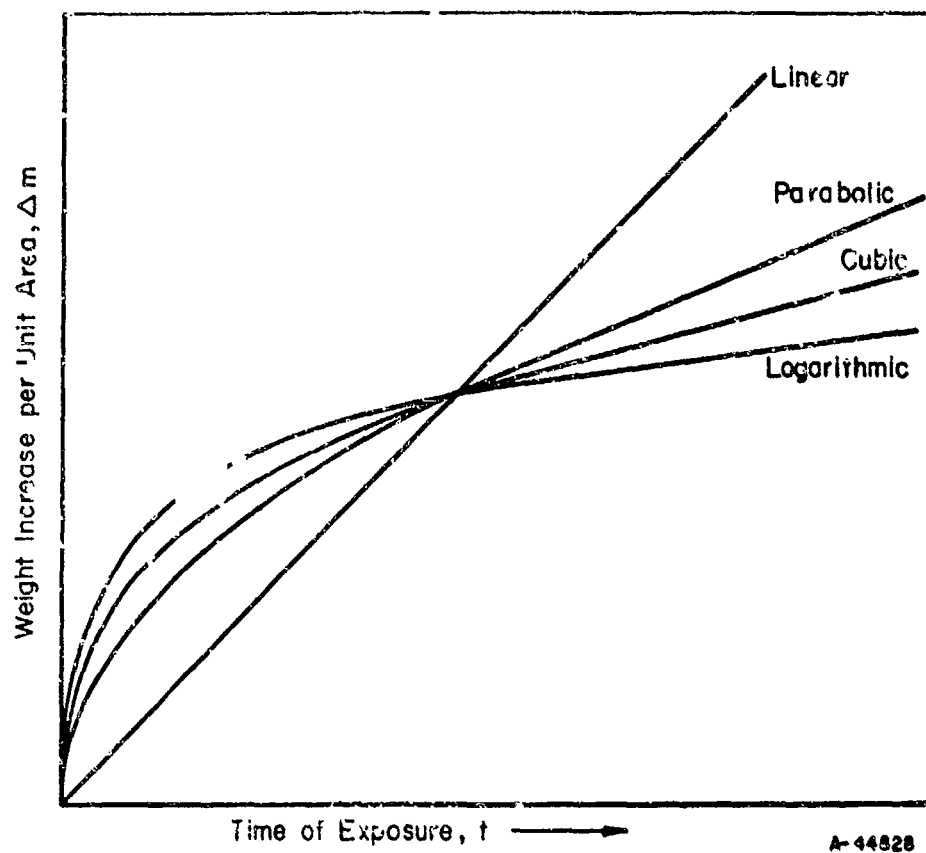


FIGURE 32. THE OXIDATION - TIME RELATIONSHIPS(108)

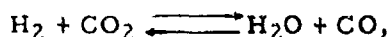
the metal surface and some of the components of the gas mixture. If the mixture is oxidizing, oxide films will form on the metal surfaces and continue to grow according to one or more of the rate laws. (See discussion of Figure 32, under "Kinetics of the Reaction". At low temperatures and steady operating conditions, the rate of oxidation may decrease to a relatively low value. Under more severe conditions, thicker films will be formed. These often develop into heavy scales that may crack or spall. Also, in some cases, oxides or sulfides may penetrate the metal along its grain boundaries. If this surface and subsurface attack continues, the result will be a reduction in the effective metal thickness and strength of the boiler tubes and other boiler components.

The behavior of metal surfaces in contact with hot combustion gases is of interest, not only because oxidation and sulfidation are themselves harmful corrosion reactions, but also because oxide films have been suspected of being involved with the buildup of thick undesirable deposits in the hot zones of a boiler. For example, in the operation of a new boiler, or a clean boiler, it is reported that a period of immunity against deposit formation often exists, during which time an oxide film is being formed on the metal surfaces. As discussed on page 106 of the ASME report⁽³⁾, several explanations for the buildup of deposits have been offered. The exact nature of the starting surface required for the initiation of bonded deposits has not been established.

Factors in Oxidation and Scaling

In addition to the gaseous components of the combustion products of fuel oil, mentioned above, other factors such as temperature, time of exposure, gas velocity, and composition of the metal will affect the extent of oxidation and the properties of the oxide or sulfide film. Many investigations have been conducted to obtain empirical data on the effect of single gases, and some gas mixtures, on the oxidation of carbon and alloy steels.

In some early work, Marston and Cobb⁽¹²³⁾ showed that one of the requirements for heating without scaling is the absence of oxygen. However, the combustion products of completely burned fuel also contain CO₂, H₂O, and N₂. Nitrogen is neutral to mild steel, but CO₂ and H₂O are capable of oxidizing steel. Angus and Cobb⁽⁷⁾ discussed the reaction



which proceeds vigorously above 1100 F. They also considered the possibilities of eliminating oxidation caused by CO₂ or H₂O by the addition of CO or H₂, respectively. From a practical standpoint, the amounts of H₂ or CO that would be required to reduce scaling to a negligible value would be so large that much of the combustible portion of the fuel would remain unburned.

Preese, et al.⁽¹⁵⁹⁾ reviewed the previous literature, and their summary indicates that below about 1300 F, scale formation is rather slow in CO₂, oxygen or steam, and largely independent of the scaling medium. Scaling in SO₂ becomes very rapid above 1500 F, and this is associated with the formation of a ferrous sulfide-ferrous oxide eutectic at the metal-oxide interface.

The report by Preese, et al.⁽¹⁵⁹⁾ also included a summary of their experimental work on the scaling of steels at about 1800 F in synthetic gas mixtures, based on a

"neutral" composition of 80% N_2 - 10% CO_2 - 10% H_2O to which CO , H_2 , and SO_2 were added. The addition of CO up to 4% had little effect, whereas scaling rapidly increased with additions of O_2 up to 1% to the neutral mixture. Additions of fractional percentages of SO_2 led to a rapid increase in scaling in the neutral or reducing atmospheres. SO_2 also increased scaling in the atmospheres containing O_2 , becoming less harmful at higher O_2 concentrations. With 4% O_2 in the mixture, even 0.30% SO_2 had no further effect. It will be noted that these tests were conducted at temperatures somewhat above those generally expected in boilers. The data may be of interest however, in helping to explain reactions that may occur unexpectedly at hot spots.

Bourggraff(17) conducted an extensive series of tests in various gas mixtures over a wide range of temperature. He found that scale formation was not very great below 1100 F. He classified the gases into the following categories.

Oxidizing: O_2 , SO_2 , and those fractions of CO_2 and H_2O not in equilibrium with CO and H_2

Reducing: The fractions of CO and H_2 not in equilibrium with CO_2 and H_2O

Neutral: N_2 , and the mixture of CO , CO_2 , H_2 , and H_2O in equilibrium over the metal surface at the existing temperature.

Preece, et al. (159) also reported on some tests conducted at 1200 F, a temperature of interest in boilers. At this relatively low temperature, most of the steels tested scaled at about the same rate in atmospheres free from sulfur dioxide. Up to about 0.6 addition of oxygen to the neutral mixture rapidly increased the rate of scaling, but further additions had little effect. The effect of SO_2 was similar to that observed at higher temperatures, but with one important difference. At the lower temperature, the oxide-sulfide eutectic was distributed as small particles in the scale, rather than being present at the scale-metal interface.

The few references that have noted the effect of gas velocity on oxidation indicate that the effect is minor, providing that a certain minimum value is exceeded. However, this minimum is different for each gas component, and it is difficult to apply to a flue-gas mixture the reported results for individual gases.

CORROSION BY OIL ASH

Nature of the Attack

The corrosion of metals at high temperature that is attributed to residual oil ash is particularly severe and proceeds at such a rapid rate that it has been termed "accelerated" or "catastrophic" oxidation. The scale is bulky and not protective, sometimes showing evidence of exfoliation. The oxidation proceeds at a rate even faster than that indicated by the linear rate law described under "Kinetics of the Reaction". Under these conditions, metal is consumed very rapidly. For example, Lloyd and Probert(118) have

reported that the presence of vanadium-containing ash caused a tenfold increase in metal loss.

Temperature Limits

The lower temperature limit for the onset of high-temperature corrosion is not definitely established. The early investigators were concerned with the severe attack of metals in gas turbines and of superheater tubes and supports in boilers producing 1050-1100 F steam. Therefore, metal-surface temperatures above about 1200 F were considered necessary for this type of corrosion to occur. For example, in 1949, Schläpfer, Amgwerd, and Preis⁽¹⁸¹⁾ studied the corrosion of heat-resisting steel by vanadium-containing oil ashes in the 1200-1380 F temperature range. One of their conclusions was that rate of scaling was markedly accelerated when the test temperature was above the melting point of the ash. Many subsequent workers have confirmed that ash mixtures in the molten state promoted this type of attack, but the reported melting points of possible ash constituents indicates that accelerated corrosion could occur even below 900 F.

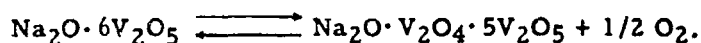
Schläpfer made some general observations that have been confirmed by later workers in more refined experiments. Intensity of corrosion was said to increase with time and temperature of exposure and with the quantity of the ash. An estimate of these factors, especially the metal temperature, in specific applications, should give some idea of whether oil-ash corrosion would become a serious problem. For example, Edwards⁽⁵¹⁾, in a review concerned mainly with naval steam-raising installations, concluded that within the scope of the boiler systems surveyed, corrosion was at present a lesser problem than deposits. Similarly, McClimont⁽¹²⁷⁾ felt that there has been a tendency to place too much emphasis on the vanadium-corrosion problem in merchant ships. He indicated that the maximum superheater tube temperatures to be expected in such installations would not exceed 950 F, and therefore corrosion would be a problem only on uncooled superheater supports. Whittingham⁽²¹²⁾ also reported that corrosion of superheater tubes is not a problem in present steam power plants because operating temperatures are below the softening point of ash deposits. In many of these cases, however, uncooled parts or assemblies (such as brackets, hangers, or supports) will still be susceptible to attack because they attain temperatures above the ash's melting point.

Mechanisms of Attack

Harmful Ash Compositions

It was established quite early that the presence of molten compounds on the metal surface was necessary to promote accelerated oxidation, but the mechanism of attack was not clear. By analysis of ash deposits and the residual oil, it was soon determined that the principal elements causing catastrophic oxidation were vanadium, sodium, and sulfur. The manner in which these elements were combined was not known, and many of the early empirical studies were made with simplified synthetic mixtures of V_2O_5 and Na_2SO_4 . Results of corrosion tests began to point to a mixture containing approximately 12% Na_2SO_4 and 88% V_2O_5 as being the most corrosive. The relationship between the character of the mixtures and the mechanism of corrosion and deposit formation was only partly clarified by these investigations.

More-advanced studies were undertaken, involving the establishment of phase and equilibrium diagrams for pertinent systems. Foster, Leipold, and Shevlin⁽⁶²⁾ suggested that the ash be considered in terms of the ternary system $\text{Na}_2\text{O}-\text{SO}_3-\text{V}_2\text{O}_5$. Through the use of compatibility diagrams, they were able to indicate the compounds that should be formed from varying proportions of Na_2SO_4 and V_2O_5 . The phases that they proposed as possible corrosive agents were Na_2SO_4 , V_2O_5 , SO_3 , NaVO_3 , $\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5$, and $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$. Oxygen may also contribute to the attack by these corrosive agents. Oxygen may come from the equilibrium mixture of $\text{SO}_3-\text{SO}_2-\text{O}_2$ at the temperature under consideration, or from the reaction



Hale and Starnes⁽⁷⁸⁾, by studies of the physical properties of the ash, arrived at the same conclusion, that $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$ was one compound that could be responsible for corrosion. Niles and Sanders⁽¹³⁸⁾ conducted experiments that verified the formation of the three sodium-vanadium complexes suggested by Foster when the corresponding molar ratios of Na_2SO_4 and V_2O_5 were reacted. They also showed that nonstoichiometric proportions of the reactants resulted in mixtures of NaVO_3 and $\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5$ being formed when the ratio of V_2O_5 to Na_2SO_4 was greater than 1 but less than 3, and of $\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5$ plus $\text{Na}_2\text{O} \cdot 6\text{V}_2\text{O}_5$ when the ratio was greater than 3 but less than 6. This approach to the problem has led to a clarification of the chemical reactions occurring between certain ash constituents at elevated temperatures. The correlation between this information and corrosion will be discussed in a following section.

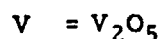
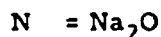
Oil-Ash Phase Diagrams

Other workers have extended the study of phase diagrams to include compounds that conceivably would be formed from corrosion of alloys by the ash. Also, the technique has been used to study the phases formed in mixtures of ash components and inorganic compounds that are possible additives to inhibit the high-temperature corrosion, or modify the character of the deposits.*

Cirilli, et al. (27, 28, 35, 36) have tried to correlate phase diagrams and corrosive attack of V_2O_5 with components of stainless steels and with minor additions of alloying metals, such as aluminum, silicon, manganese, molybdenum, beryllium, zirconium, and copper. The variety of vanadates formed are discussed with some comments about the relation to corrosion. Manganese, molybdenum, and copper are not suitable additions because they tend to form complex low-melting or volatile vanadates. Beryllium and zirconium have favorable corrosion effects, but any vanadates that are formed decompose to the oxide. Aluminum forms an orthovanadate melting at 1280 F and has no favorable effect. Silicon did not form compounds with V_2O_5 . The authors concluded that knowledge of phase diagrams of V_2O_5 and metallic oxides can aid in the selection of more resistant materials by a consideration of their ability to develop stable protective films on their surface and also to form vanadates with high melting points. These are rather general statements that have been substantiated only by limited experimental results.

The research by Johnson⁽⁹⁴⁾ provided information on the eutectic composition and temperature for a large number of binary and ternary systems composed of $\text{NV}_3 + \text{MO}$, or $\text{NV}_6 + \text{MO}$ and $\text{NV}_3 + \text{MO} + \text{Fe}_2\text{O}_3$ or $\text{NV}_6 + \text{MO} + \text{Fe}_2\text{O}_3$. These compound designations have appeared in several publications and are abbreviations for the vanadium complexes as follows:

*See Chapter 1 for a discussion of additives.



MO = metal oxide.

It is interesting to note that all of the mixtures investigated had a eutectic melting below about 1170 F, ranging from 960 to 1166 F. The conclusions drawn from these studies by Johnson are:

- (1) The oxides of iron and magnesium form definite compounds with NV_3 and NV_6 and may therefore have definite value as additives.
- (2) The oxides of silicon and chromium do not form compounds with NV_3 and NV_6 but form only mechanical mixtures and are believed to have no possible use as additives.
- (3) Results with aluminum and calcium left uncertainties. Mixtures containing CaO bonded to anything they touched. Al_2O_3 showed evidence of forming a high-temperature compound with NV_3 , which is unstable at lower temperatures.

Equilibrium diagrams were also used by Brubaker, Foster, and Shevlin⁽²²⁾ to determine possible corrosion products which would be found in equilibrium with vanadium ash components. These results are shown as equilibrium diagrams of the systems $Na_2O-Fe_2O_3-V_2O_5$, $Na_2O-Cr_2O_3-V_2O_5$, and $Na_2O-NiO-V_2O_5$. The effects SO_2-SO_3 -air mixtures on the corrosion process were also studied.

The identification of deposits taken from oil-fired naval boilers given in the recent report by Pollard⁽¹⁵³⁾ is of interest. On screen tubes, a chalky white, water-soluble coating, sometimes hidden by carbon, was found. This is either sodium sulfate or a mixture of sodium sulfate with sodium vanadate. Purple-black layers on screen tubes and superheater tubes are invariably $Na_2O \cdot V_2O_4 \cdot 5V_2O_5$, sometimes mixed with $Na_2O \cdot 2V_2O_5$ or sodium sulfate. These layers are difficult to remove because they are only slightly water-soluble. They also are excellent solvents, when molten, for materials of construction of boilers.

Generating-tube deposits are similar to superheater deposits but show fewer signs of high-temperature effects. Next to the metal surface, however, there usually is a small amount of white ferrous sulfate present which turns yellow on being exposed to air. Massive deposits on top of water drums are composed of a water-soluble portion that is usually high in sodium and iron sulfates, and the purple-black layer near the tubes is mostly $Na_2O \cdot V_2O_4 \cdot 5V_2O_5$. This classification verifies the presence of the compounds, associated with corrosion, in boilers.

Other chemical compounds, isolated and identified from deposits taken from various locations in boilers, reported by Pollard⁽¹⁵³⁾, were:

- (1) $\beta-Na_2O \cdot V_2O_4 \cdot 5V_2O_5$ (approximately)
- (2) $\gamma-Na_2O \cdot 2V_2O_5$
- (3) Na_2SO_4

- (4) CaSO_4
- (5) Fe_3O_4
- (6) CaCO_3
- (7) $\text{Fe}_2(\text{SO}_4)_3$, carbon, sulfuric acid, and $\alpha\text{-SiO}_2$.

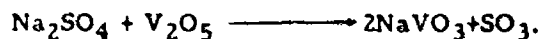
The phase diagrams from Illarionov⁽⁹⁰⁾, shown in Figure 33 and 34, were used in the study of the oil-ash deposits. Pollard emphasized the need for more information about a knowledge of compounds formed between vanadium compounds found in oil ash and oxides of potential additives. Relatively little work has been reported so far on this subject. In the appendix to his report, Pollard has given a compilation of sources of data for a number of vanadium oxide-metal oxide systems. Part 2 of the report contains X-ray powder diffraction pattern data for crystalline components of oil ash. This investigation is continuing and should provide additional valuable information pertinent to the problem.

The Role of Oxygen

Cunningham and Brasunas⁽⁴⁵⁾ reviewed previous investigations and theories that have been proposed to explain accelerated corrosion. The explanation that the molten material at the metal-oxide interface destroys the protective layer by a fluxing action did not appear adequate, and Cunningham conducted the necessary experiments to prepare a thermal-arrest diagram for the $\text{Na}_2\text{SO}_4\text{-V}_2\text{O}_5$ system. He noted the oxygen absorption and evolution ascribed to the reversible reaction:



Oxygen evolution has been known to cause the "spitting" which occurs when molten vanadates solidify and are converted to the vanadyl vanadate. However, the oxygen-absorption reaction was also thought to have some bearing on the corrosion problem, and some experiments were conducted to investigate this point. Temperature-pressure determinations were made in closed systems containing oxygen and mixtures of either Na_2O and V_2O_5 or Na_2SO_4 and V_2O_5 . Typical pressure-temperature curves are shown in Figure 35. The significant features shown by the curves is the decrease in pressure (Curve C) caused by absorption of oxygen into the melt, above the melting point of the mixture $\text{Na}_2\text{O} + \text{V}_2\text{O}_5$. Curve D, for the $\text{Na}_2\text{SO}_4 + \text{V}_2\text{O}_5$, shows an initial pressure drop, just as in Curve C, followed by a reversal and a pressure increase which was attributed to evolution of sulfur trioxide from a reaction of the type



It was observed that the most severe corrosion reported by other investigators occurred within the composition range showing maximum absorption of oxygen. This appears to be good evidence for suggesting that oxygen, continually being absorbed from the surroundings, passes through the molten film and sustains the rapid oxidation of the metal underneath. The oxide formed in the presence of these contaminants is very porous and does not interfere with the passage of oxygen through it. Research by Johnson⁽⁹⁵⁾ supported the conclusion by Cunningham and Brasunas, that the molten layer appears to act as an oxygen carrier and destroyer of protective films. Johnson heated and cooled a 1-to-6 mole ratio of $\text{Na}_2\text{O-V}_2\text{O}_5$ between room temperature and 1525 F for a number of cycles. The initial melting released 7.9 cc of oxygen per gram of original salt mixture. On

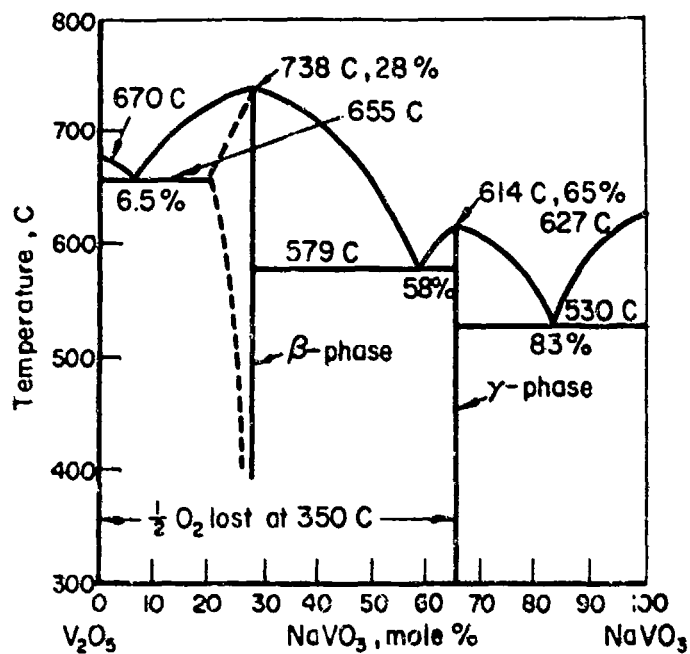


FIGURE 33. PHASE DIAGRAM FOR THE SYSTEM $\text{NaVO}_3 - \text{V}_2\text{O}_5$ (90)

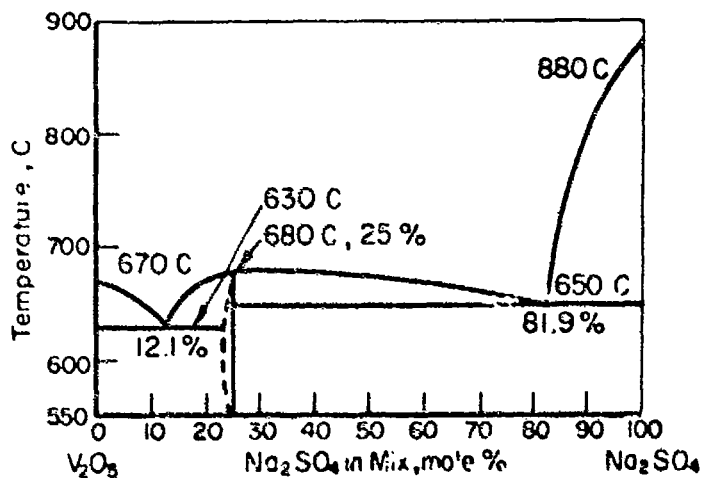


FIGURE 34. PHASE DIAGRAM FOR THE SYSTEM $\text{Na}_2\text{SO}_4 - \text{V}_2\text{O}_5$ (90)

Obtained from heating curves. Systems not at equilibrium.

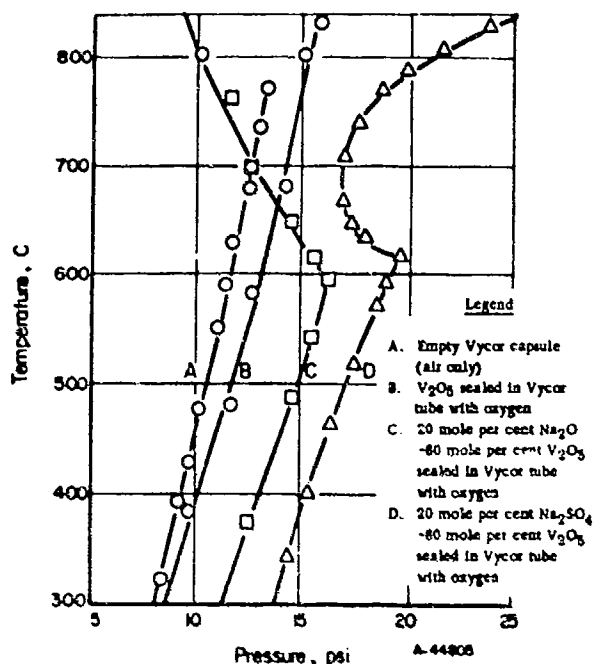


FIGURE 35. TYPICAL PRESSURE-TEMPERATURE CURVES FOR VARIOUS MIXTURES COMPARED WITH THE CURVE FOR A BLANK(45)

cooling below the freezing point (1193 F) an additional 1.3 cc of gas per gram of salt mixture was released. This quantity was subsequently reabsorbed and released each time the mixture was heated beyond the melting point and cooled to the solidification point. Tests run in air, oxygen, argon, and nitrogen showed that oxygen was the only gas that would be reabsorbed. Corrosion experiments were designed to compare the behavior of Type 302 stainless steel specimens under a 1-inch layer of molten salt, in the presence or absence of an oxygen atmosphere. The test specimen heated in salt in the absence of oxygen lost 1 to 2% in weight, while those heated in salt in the presence of oxygen lost 65% in weight. Any oxygen that reached the metal surface had to pass through 1 inch of molten salt.

Phillips and Wagoner(150) verified Cunningham and Brasunas' observation of the release of oxygen during solidification. When the melt was observed under the Leitz heating microscope, gas bubbles were observed escaping during solidification. The temperature difference between melting and freezing was also found to be related to the oxygen-absorption capacity of the compound, as shown in Figure 36. The greatest oxygen-absorption capacity, most severe corrosion, and greatest difference between melting and freezing temperature all occur at approximately the same ash mixture, that is, at the $Na_2O \cdot V_2O_4 \cdot 5V_2O_5$ composition. It would be helpful to be able to predict the type of deposit to expect from a given fuel. While Niles and Sanders(138) have proposed that this can be done, the experiments of Phillips indicate that it is not always possible.

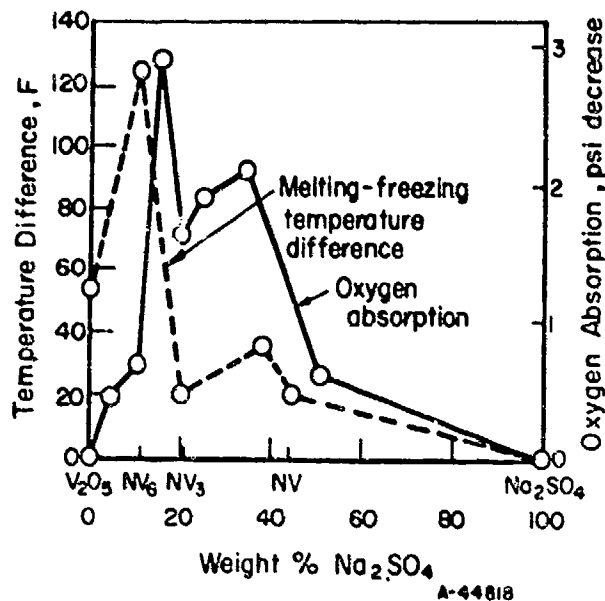


FIGURE 36. CORRELATION OF TEMPERATURE DIFFERENCE (MELTING-FREEZING) AND OXYGEN ABSORPTION WITH ASH COMPOSITION(150)

Figure 37 shows that the Na/V ratio of the deposit can be up to four times that in the fuel. Gas temperature at the point of deposition appears to have something to do with this effect. Gas temperature has been shown to have an appreciable effect on corrosion at constant metal temperature. This is illustrated in Figure 38.

The Role of Sulfur Trioxide

The possible effect of SO_3 in the corrosion mechanism was mentioned by Foster(62). The liberation of SO_3 in the reaction between Na_2SO_4 and V_2O_5 may have an important effect on corrosion. A preliminary experiment in a prefused Na_2SO_4 - V_2O_5 mixture compared with the same mixture which had not been prefused demonstrated the strong corrosive effect of the SO_3 evolved in the reaction. Any tendency for SO_3 to break down into SO_2 and O_2 according to equilibrium requirements would make additional oxygen available for oxidation at the metal surfaces. This oxygen would probably be present in a nascent, highly reactive form.

Nickel and Iron Vanadates

The majority of the investigations reviewed deal only with the sodium, sulfur, and vanadium components of the fuel-oil ash. Miles and Sanders(139) pointed out that when appreciable amounts of other components are present, some of the other metals will react with vanadium, resulting in a higher Na/V ratio in the remaining mixture, and alter the compound that will form. An example was given in which the compound $\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5$ would be expected to form. However, the nickel and iron in the fuel oil reacted with vanadium to form nickel and iron vanadates and left less vanadium to combine with the sodium.

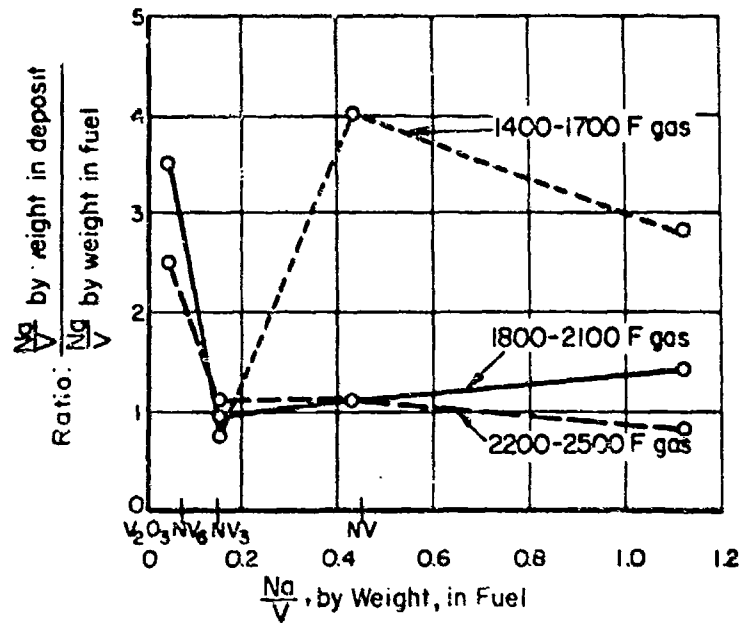


FIGURE 37. CHANGE OF $\frac{\text{Na}}{\text{V}}$ RATIO FROM FUEL TO DEPOSIT AT SEVERAL GAS TEMPERATURES(150)

Specimens at 1200 F.

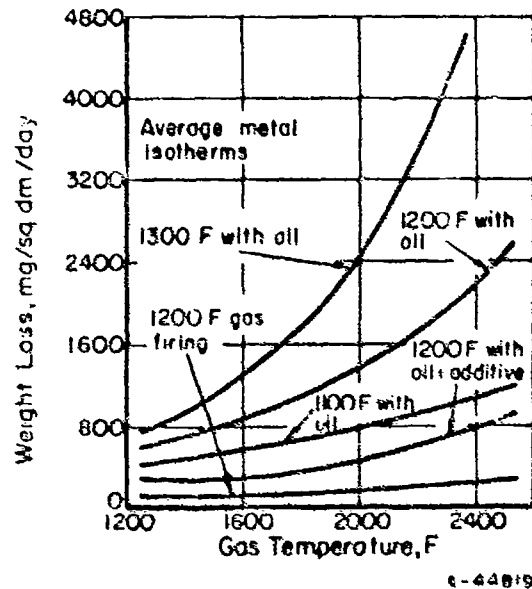


FIGURE 38. EFFECT ON CORROSION OF GAS TEMPERATURE AT CONSTANT METAL TEMPERATURE(150)

One-hundred-hour tests on stainless steel types 304, 316 and 321; oil contained 150 ppm vanadium, 70 ppm sodium, 2.5% sulfur.

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Resistance of Metals to Ash Attack

From a practical standpoint, a primary interest of users of residual fuels was to find materials of construction that would withstand the corrosive environment. Therefore, in many of the early investigations, the objective was to evaluate the high-temperature corrosion resistance of a variety of heat-resistant alloys, with the hope of either finding a useful material or some promising indication that would lead to the development of a more resistant material. This became a formidable undertaking because of the many factors that had to be taken into consideration. The quantity of ash, metal surface temperature, gas temperature, time, velocity of combustion gases, and thermal cycling are among the variables which could influence the corrosion results.

Kind⁽¹⁰⁴⁾ has indicated that it is impossible to reproduce in the laboratory all of the conditions prevailing in practice. The ash-forming constituents can occur in the gaseous, liquid, or solid state, and the different phases cannot be determined because the chemical and physical equilibria are changing continually. For this reason, simple laboratory tests have been condemned as being unrealistic; however, Frederick and Eden⁽⁶⁴⁾, among others, have found them to be almost indispensable guides to determine the course of more elaborate experiments.

One simple test that has been used consists merely of placing a small quantity of ash, or ash component, on an alloy specimen and heating in air. In another procedure, specimens are wholly or partially immersed in ash mixtures contained in a crucible and heated to various temperatures for selected periods of time.

Schläpfer, Amgwerd, and Preis⁽¹⁸¹⁾; Evans⁽⁵³⁾; Buckland, Gardiner, and Sanders⁽²⁵⁾; and Skinner and Kozlik⁽¹⁸⁹⁾ were among the early investigators who used these tests in exploratory work for screening of alloys and observing the effect of some variables. Their results cannot be compared quantitatively because of other differences in test procedures, and some contradictory results were noted. Some of their general conclusions are in agreement, however, and have been verified by later work. For example, Skinner and Kozlik⁽¹⁸⁹⁾ reported that nickel-base alloys were resistant to vanadium pentoxide but were severely corroded in ash mixtures containing large percentages of sodium sulfate. Similarly, molybdenum-containing alloys were severely attacked in vanadium environments at high temperature. On the other hand, the chromium-iron alloys containing about 26% chromium (such as AISI 446) performed better than other alloys under a variety of conditions. These comparisons are relative, and both Evans⁽⁵³⁾ and Buckland et al.⁽²⁵⁾ concluded that no alloy or class of materials which had been tested up to the time of their experiments could be considered to have a satisfactory service life for boilers and gas turbines burning residual fuels.

Nevertheless, the search for a useful material has continued, and a number of additional papers have appeared describing the results of new work. Many of these merely corroborated earlier results and provided corrosion data on additional alloys exposed to vanadium-containing fuel ashes.

Oliver and Harris⁽¹⁴¹⁾, and Harris, Child, and Kerr⁽⁸⁴⁾ used a testing procedure which involved applying vanadium pentoxide on metal surfaces by painting them with a suspension of V_2O_5 in benzene and drying. This was followed by exposure to preheated air for 24 or 70 hours. Corrosion was evaluated by weight loss after descaling. Four and sixteen 70-hour cycles were used. A variety of gas-turbine alloys were tested, and it was shown that a rapid increase in the rate of oxidation occurred at about 1400 F. The

general effects of contamination with V_2O_5 was to lower markedly the useful service temperature of the alloys. Some alloys were comparatively better than others. G39 (a 65Ni-20Cr alloy containing tungsten, molybdenum, niobium, and tantalum) proved to be the most resistant in this test, being corroded at a rate of slightly less than 10 mg/sq cm/24 hr at 1750 F.

Fitzer and Schwab⁽⁵⁶⁾ used a testing procedure in which specimens were scaled at about 1700 F for 15-minute periods in a stream of oxygen, followed by brief immersions in molten V_2O_5 at 1650 F. This cyclic treatment could be continued as long as desired. The use of pure oxygen and 100% V_2O_5 was not thought to affect the mechanism of the corrosive reaction other than to accelerate it greatly. The beneficial effect of silicon as an alloying component was shown by this procedure in an experiment which extended over a relatively short period of 2-1/2 hours. Silicon was present in all of the best alloys. The most resistant material was Sicromal 12, a 23% chromium steel containing aluminum and about 3% silicon. Fitzer and Schwab attributed this to the good resistance of SiO_2 to attack by molten V_2O_5 . In contrast, the chromium-containing scale layers formed on the austenitic chromium steels are said to be destroyed by V_2O_5 .

Betteridge, Sachs, and Lewis⁽⁹⁾ were concerned with the effect of ash attack on the high-temperature mechanical properties of materials of construction. Stress-rupture test bars were painted with water pastes of mixtures of V_2O_5 and Na_2SO_4 and then tested at about 1400 F. It was found that contamination with the mixtures shortened the lifetime under stress of all materials. The decrease in stress-rupture lifetime of iron-base alloys was caused by a reduction in the cross section of the test bar by uniform and progressive scaling. In nickel-base alloys, intergranular penetration led to scattered stress-rupture results. These observations indicate that the effective metal thickness determines the strength of the construction materials and that subsurface attack (which is not so readily detected) may result in serious weakening of the structural parts.

The corrosion behavior of selected heat-resistant alloys suspended in an operating steam boiler was described by McDowell, Raudebaugh, and Somers⁽¹²⁸⁾. The investigation was conducted at the Marion Generating Station of the Public Service Gas and Electric Company. Test racks were suspended from the high-temperature superheater tubes and presumably attained the gas temperature at that location. This varied from 1050 to 1560 F, depending on the boiler load. The boiler was fired with Bunker C fuel oil. Exposure periods of three test racks varied from about 500 to 700 hours. The alloys were rated comparatively from best to worst, and Type 406 (12Cr-3Al iron-base alloy) showed the least corrosion penetration, a fairly uniform metal loss of about 0.1 inch per year. It was thought that Al_2O_3 formed from the aluminum in this alloy provided some protective effect. Corrosion of Inconel was also at a rate of about 0.1 inch per year; but, in this case, sulfidation and intergranular oxide penetration was observed. AISI 446 Incoloy, and AISI 309 were next best in that order. For comparison, AISI 302 corroded at a rate of about 0.4 inch per year. The authors concluded that none of the alloys showed outstanding oxidation resistance, and many of the alloys certainly would be unsatisfactory for application in the high-temperature superheater sections of boilers.

A more recent paper by McDowell and Mihalisin⁽¹²⁹⁾ reported on some laboratory crucible tests, comparing the resistance of 60Cr-40Ni cast alloy with several other alloys. At both 1500 and 1700 F, in a mixture of 15% Na_2SO_4 and 85% V_2O_5 , the 60Cr-40Ni alloy shows considerably less weight loss than the other alloys in 100-hour tests. Inconel "X" is an exception that appears to be somewhat more resistant than the 60Cr-40Ni alloy. However, the authors point out that Inconel "X" is susceptible to sulfidation attack, and there is no evidence that the 60Cr-40Ni alloy is similarly susceptible. A

recent note⁽¹⁸⁶⁾ reports that trial castings of this alloy, exposed for 7000 hours in an aircraft carrier where Bunker C oil was burned, showed very little attack. Also, bracelet hangers made from the new alloy show no sign of corrosion after 6450 hours of exposure at a power-plant installation.

A comprehensive report was published recently by Greenert⁽⁷²⁾ describing work conducted for the U. S. Navy. A large number of alloys and coatings were evaluated for resistance to three different laboratory slags. The slags were selected to simulate the type of corrosion observed in service, as a result of burning fuel oils of varying composition. The test specimens were precontaminated by immersion in the slag at 1600 F for 2 hours. They were then exposed to an oxygen environment in a gantight combustion furnace. The amount of oxygen consumed by the oxidation reaction at various temperatures and time periods was a measure of the extent of corrosion. The results were tabulated in several ways, so that the behavior of specific materials, or classes of materials, could be compared. One such tabulation is shown in Table 17. Greenert summarized his results, with the comments that the high-chromium nickel alloys, and the alloys in the Cr-Al-Fe series, consistently exhibited the best resistance to both vanadium and non-vanadium slags. He indicated that, from a corrosion standpoint, these alloys should show satisfactory performance. However, their use might be limited by poor engineering and physical properties. The Cr-Al-Fe series is also discussed in a report by Srawley⁽¹⁹²⁾. Ductility of the alloys has been improved by vacuum melting and protection by argon during pouring.

Protective Coatings

Relatively little information was found on the application and value of protective coatings against fuel-oil ash. Evans⁽⁵³⁾ tested a number of coatings on carbon and stainless steel specimens by partial immersion for 168 hours in a high-vanadium oil ash at 1350 F. Silicon impregnation by a proprietary process provided the most protection for carbon steel, limiting the oxidation weight gain to that obtained by heating the steel in air. It was reported that the coating would not adhere to heat-resisting steels. Chromizing of carbon steel and AISI 430 was the next most promising treatment. Other coatings such as aluminizing, calorizing, and galvanizing were partially protective. Srawley⁽¹⁹³⁾ tested aluminized AISI 310 steel by contaminating the surface with a mixture of equal parts of V_2O_5 and Na_2SO_4 and heating in a muffle furnace at 1700 F. In this test, aluminizing did not reduce corrosion to any significant extent, but it was indicated that a more extensive investigation should be made before making final conclusions. Frederick and Eden⁽⁶⁴⁾ examined the effect of V_2O_5 plus 10% Na_2SO_4 at 1240 F on nickel and chromium electrodeposits. Nickel offered little resistance to attack. It started to disintegrate after 200 hours of exposure. On the other hand, the chromium electrodeposit was found to be resistant in itself, but it failed by cracking because of the difference in thermal expansion between the coating and the basis metal.

Lewis, in discussing Frederick and Eden's results⁽⁶⁴⁾, reported that a wide range of coating materials had been tested at the Thornton Research Center in England. In their experiments also, the coatings disintegrated either as a result of oxidation through pores in the coatings or as a result of differential expansion between the coating and the basis metal. Lewis thought that chromized layers would diffuse inwards upon prolonged exposure to elevated temperature. Therefore, he suggested better results might be obtained by chromizing alloys having some inherent oxidation resistance.

TABLE 17. RELATIVE RESISTANCE OF SEVERAL ALLOYS AND COATINGS TO CORROSION BY SLAGS⁽¹³⁹⁾
Basis: Oxygen Consumed in 23 Hours of Test

Grouping	Milliliter of Oxygen Consumed	Sulfated- Vanadium Slag, 70% V ₂ O ₅ + 30% Na ₂ SO ₄	Nonsulfated- Vanadium Slag, 79% V ₂ O ₅ + 21% NaVO ₃	Sulfated- Chloride Slag, 90% Na ₂ SO ₄ + 10% NaCl
Excellent	0-50	Hastelloy D Durichlor 25 Cr-5 Al-Fe ^(a) 60 Cr-40 Ni Berylliumized Type 310 SS	Silchrome Hastelloy D Haynes-Stellite 31 Duriron	100 Cr 30 Cr-30 Ni-40 Co 60 Cr-40 Ni 14 Cr-14 Mn-Fe 25 Cr-5 Al-Fe ^(b) 25 Cr-9 Al-Fe CD4MCu Cr ₃ C ₂ cement
		Duriron 50 Cr-30 Ni 100 Cr Inconel "X" Inconel	25 Cr-5 Al-Fe ^(b) Enduro A Durichlor Inconel "X" 100 Cr 50 Cr-50 Ni Berylliumized Type 310 SS Berylliumized HS-31 Berylliumized Inconel	25 Cr-3 Al-Fe Hastelloy D 60 Cr-50 Ni Type 304 SS Type 304 porous compact
Good	100-200	25 Cr-5 Al-Fe ^(b) Cr ₃ C ₂ cement 25 Cr-9 Al-Fe 30 Cr-30 Ni-40 Co Armco 525 Haynes-Stellite 31 14 Cr-14 Mn-Fe (CNC alloy) Silchrome Berylliumized Inconel	25 Cr-3 Al-Fe 30 Cr-30 Ni-40 Co 60 Cr-40 Ni Inconel Type 304, porous compact Cr ₃ C ₂ cement	Haynes-Stellite 31
		Enduro A 25 Cr-3 Al-Fe Type 202 SS Armco 524 Type 304 SS GMR 235	25 Cr-9 Al-Fe 14 Cr-14 Mn-Fe GMR 235 Hadfield steel Armco 524 Type 340 SS N-155	Berylliumized HS-31 GMR 235 Enduro A Ceramesalix
Fair	200-300			
Somewhat better than Type 310 SS	300-400	Armco 519 Hadfield steel Inco, Inco N-155	Armco 525 Hastelloy X Armco 519 Armco 510	Thermaloid Type 202 SS Type 347 SS
Somewhat better than Type 310 SS	400-500	Hastelloy X Berylliumized HS-31		Hadfield steel Type 201 SS Type 202 SS

TABLE 17. (Continued)

Grouping	Milliliter of Oxygen Consumed	Sulfated- Vanadium Slag, 70% V ₂ O ₅ + 30% Na ₂ SO ₄	Nonsulfated- Vanadium Slag, 70% V ₂ O ₅ + 21% NaVO ₃	Sulfated- Chloride Slag, 90% Na ₂ SO ₄ + 10% NaCl
No improvement over Type 310 SS	500-600	Armco 519 Type 201 SS Type 304 porous compact	Type 201 SS	Hastelloy X 12% Cr steel Berylliumized Type 310 SS N-155
No improvement over Type 310 SS	600-700	12% Cr steel CD4MCu		Inconel "X" Duriron
No improvement over Type 310 SS	700-1000	Type 347 SS Thermonol Cerometalix		Inconel Berylliumized Inconel
No improvement over Type 310 SS	1000+		12% Cr steel Type 310 SS CD4MCu Iron, ingot Type 347 SS Type 202 SS Cerometalix	Nimonic 80 Silchro-ne Durachlor (a) Armco 515 Armco 519 Armco 524 Armco 525 Iron, ingot

Note: SS = stainless steel

(a) Cast product.

(b) Wrought product.

Several coated, heat-resistant casting alloys were included in the tests reported by McDowell(128). The coatings were of the ceramic type, consisting of a mixture of oxides applied to the specimens and fired at a high temperature. After exposure of about 700 hours in the superheater zone of an oil-fired boiler, the coatings had chipped and cracked but had not been penetrated completely. Photomicrograph revealed a layer at the metal-coating interface which appeared to have resisted corrosive attack. This type of coating also was shown to be protective in one of the case histories included in the NACE Technical Committee report(137).

Application of protective coatings by metal spraying was considered as a means of preventing the corrosion occurring in mercury boilers. (79) Sprayed layers of 26%Cr-Fe alloys were found to have good inherent resistance to oil-ash corrosion. This is in agreement with the good corrosion resistance of AISI 446 reported earlier. It was indicated, however, that the value of such coatings would depend on proper treatment of the surface to be sprayed, and possibly treatment after spraying, to provide an impervious coating and a metallurgical bond at the metal-coating interface.

Thus, it appears that some relatively ash-resistant materials exist, but the problem of applying them to metal surfaces economically and in a useful form has not been solved. Further work on the development of protective surface coatings may be justified on the assumption that higher concentrations of beneficial elements can be tolerated in surface layers, rather than as alloying ingredients, without excessive harm to the physical properties of the alloy.

Foster(61) summarized the situation with regard to materials and protective coatings with the statement: "No single alloy, protective coating, or ceramic material has been found that by itself will be completely immune to attack by all residual-oil ashes under conditions of gas-turbine operation". However, for something less than complete immunity, the comparative results discussed above show that some metals and coatings are relatively more ash resistant than others. Their application in practice will depend on the service conditions encountered during operation of a boiler and on economic considerations.

CHAPTER 4. CONTROL OF BOILER DEPOSITS AND CORROSION

Methods of operating the boiler for the control of deposits and corrosion have been dealt with in the previous three chapters. This chapter deals mainly with special procedures for the control of deposits and corrosion, especially by additives.

METHODS OF CONTROL BY ADDITIVES

Since the removal of the harmful constituents from residual fuel oil at the refinery is not considered a practical or economical solution to the problem by the petroleum refiners, investigators have given their attention to other methods of corrosion control. Considerable study has been devoted to compounds that can be added to the fuel oil or to the furnace to minimize deposits or change their physical characteristics, and prevent or reduce the corrosion of metallic surfaces.

Control of Flue-Gas Condensate

There are several possibilities for the control of corrosion by flue-gas condensate at the wet end of the boiler. Additives have been studied for the control of corrosion resulting from sulfur compounds in the flue gas. In most cases the objective has been to reduce the amount of SO_3 formed or to deal with the resultant sulfuric acid-bearing condensate. Additions have been made directly to the fuel oil prior to ignition, to the combustion air ahead of the burner, to the gases in the furnace just beyond the burner, and at various points within the boiler up to the air preheater section.

It is generally agreed that the additives for the control of corrosion by sulfur compounds act by one or more of the following mechanisms:

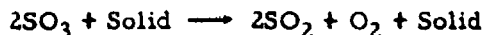
- (1) Retardation of SO_3 formation
- (2) Physical absorption of SO_3
- (3) Neutralization of SO_3 by chemical reaction
- (4) Corrosion inhibition of metal surfaces by passive films.

Oxidation Inhibitors (Retardation of SO_3 Formation)

At the present time, agreement has not been reached as to the mechanism of the oxidation of SO_2 to SO_3 in boilers. There is evidence from several sources that both of the two major mechanisms proposed (i. e., catalytic action and gas-phase oxidation) are effective to some extent. If the action is by catalytic activity from metal oxides or

deposits on surfaces, the inhibition can be effected by coating the surfaces with an inert material. In this connection, Harlow⁽⁸³⁾ has studied the use of sprays of aluminum ethyl silicate.

If the oxidation takes place through a rapid reaction of an active species in the flame, the theory would predict inhibition by the addition to the burner of finely dispersed solids, since the solid surface area would be increased and the reaction



would be favored. As has been pointed out by Whittingham⁽²¹²⁾, carbon and zinc smokes are particularly effective in reducing SO_3 contents.

Physical Absorption of SO_3

Some relatively inert materials have been found to be effective in reducing the SO_3 content of the flue gas when they are added in a finely divided state. Typical examples are silica smoke, clays, and pulverized-coal ash. It appears that their effectiveness is due to the physical absorption of the SO_3 by the particles.

Neutralization of SO_3 by Chemical Reaction

The use of additives to neutralize the SO_3 has been given a broad technical study. Two schemes have been examined: (1) the use of finely divided alkaline particles and (2) the introduction of gaseous ammonia. The finely divided solids include magnesium or calcium compounds, either singly or as dolomite, zinc smoke, or zinc metal. In many cases, the action is probably a combination of absorption combined with chemical reaction or neutralization.

Ammonia. Since the effectiveness of inhibitors is greatly dependent on even distribution and intimate contact between SO_3 and the neutralizing chemical, it is readily apparent that gases afford some advantages over finely dispersed solids. Ammonia will combine readily with SO_3 , and it is economically available as a gas. It has been and is still being seriously considered, both here and abroad, as a means of controlling low-temperature corrosion.

For example, in 1956, Rendle and Wilsdon⁽¹⁶⁶⁾ conducted a study with a variety of inhibitors and concluded that ammonia injection was the most efficient and economical method of lowering the acid dewpoint and reducing corrosion. They injected ammonia at a concentration of 0.06% by weight of the fuel into the combustion gases at a temperature slightly below 600 F. By a proper choice of temperature it is possible to reach conditions where the ammonia reacts only with SO_3 and not with the more prevalent SO_2 . Either ammonium bisulfate, NH_4HSO_4 , or normal sulfate, $(\text{NH}_4)_2\text{SO}_4$, is formed, depending on the concentrations of ammonia. Further tests were described by Rendle, et al.,⁽¹⁶⁷⁾ in 1959 involving full-scale trials in oil-fired boilers. The results in several installations were very encouraging. Figure 39, taken from their paper, shows that the corrosion was reduced to a very low level by the addition of 0.05% by weight of ammonia. The gas was added between the economizer and rotary air preheater.

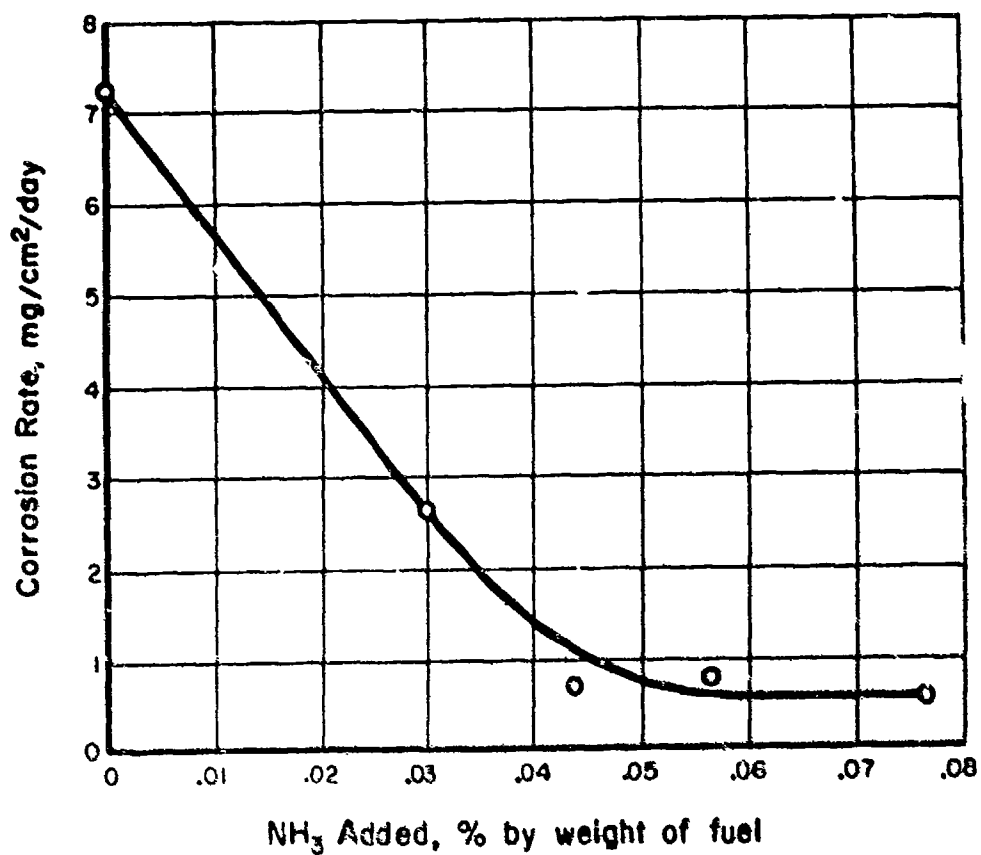


FIGURE 39. EFFECT OF AMMONIA ON THE CORROSION OF MILD-STEEL ROTARY AIR PREHEATERS(167)

Exposure periods were for 6 hours.

Another boiler operated for 8 months using ammonia injection to tubular air preheaters, with biweekly air lancing, showed no evidence of corrosion.

An ammonia-injection installation was also evaluated in a boiler which had required tube replacements every 2 years. It was concluded that the life of the tubes would be increased to about 18 years by the use of ammonia and water washing, and to about 7 years by the use of water washing alone.

Other studies to date have shown that ammonia will effectively reduce the dewpoint but that additions must be made with great care to avoid excessive blockage of the air-heater channels(223). Wiedersum and associates(221) recently concluded that ammonia treatment of the flue gas entering the Eddystone pulverized-coal-fired low-level economizers could not be justified because the corrosion was not significantly reduced and because objectional deposits were formed.

Upmalis(207), in Scandinavia, rejected ammonia because of the very adherent deposits which formed on the heat-exchanger surfaces. Jarvis(93), in 1958, described results from four stations, including one in France. In most instances, rapid blockage of the air heaters was experienced, but sufficient interest was noted that tests were continued.

It should be mentioned that the injection of ammonia into the flue gas from a pulverized-coal-fired boiler at 420 F virtually eliminated corrosion at metal temperatures between 150-420 F, as reported by Kato(96) in 1960. No buildup of deposits was noted after 60 hours.

In laboratory experiments, ammonia was found to reduce V_2O_5 at 1290 F to form the high-melting V_2O_3 . This reaction also occurred when the ammonia was mixed with air, in amounts up to 95% by volume of air, and has been attributed to the lower energy requirement for production of atomic oxygen from V_2O_5 than from oxygen in the air. Ammonia partially reduces alkaline earth sulfates, particularly if they are mixed with V_2O_5 . The injection of ammonia into a high-pressure combustion rig resulted in lowered deposition, with an analysis about 20% less in V_2O_5 and SO_3 . Sulzer(197) felt that the cost of the materials added was out of proportion to the effect obtained. Injection of heavy fuel oil into flue gases at 1290 F in the combustion rig caused about the same reduction in deposits as ammonia. This effect was attributed to the reducing atmosphere produced by unburned carbon and the CO surrounding it. Ash constituents concentrate in the residual carbon, but at the expense of combustion efficiency.

At the present time, it is concluded that ammonia treatment may be most effective when:

- (1) The SO_3 content in the flue gas is relatively low
- (2) The location and the method of injection can be carefully controlled
- (3) Periodic water washing can be employed.

Thus, the process may be of most value to scavenge the residual SO_3 present when a boiler is operating at the minimum of excess air.

Dispersed Solids. Extensive studies have been made with the use of finely divided solids to neutralize the SO_3 in the flue gas.

A comparative survey of many additives was sponsored by the Central Electricity Generating Board when air heater corrosion problems developed as boilers were converted from coal to oil firing, and results were presented in 1959 by Wilkinson and Clarke(223). They reported that an addition of dolomite (20 microns) at the rate of 4 lb/ton of fuel oil reduced the corrosion and deposit formation and caused a drop in SO_3 from 15 to 5 ppm. They also found in another experiment that a proprietary additive (MgCO_3 , Zn, CuO , C), of 200-mesh size, added at the rate of 2 lb/ton of fuel oil reduced the corrosion and deposits by 50% and lowered the SO_3 from 40 to 18 ppm. Magnesium oxide was found to be unsatisfactory because of the difficulties in adding it to the boiler and because adherent deposits were formed.

Black and associates(13) measured dewpoints in flue gas with two additives. A reduction in dewpoint of 10 degrees was observed when magnesium hydroxide was added to fuel oil. On the other hand, additions of dolomite to the combustion chamber were not effective in lowering the dewpoint.

One of the more-recent extensive evaluations of additives for the control of acid deposition was conducted in England in two boilers, as reported by Alexander and associates(2). Both stations used residual fuel oil containing between 2.9 and 4.6% sulfur. The effectiveness of the additives was measured as follows:

- (1) By analyzing the flue gas with
 - (a) Dewpoint meters
 - (b) Deposition probes
 - (c) Corrosion probes
- (2) By noting changes in boiler operations
- (3) By examining the boiler surfaces following each trial of 2-week duration.

The additives evaluated were:

- (1) Magnesium carbonate, 200 mesh
- (2) Proprietary additive, approximately equal proportion of magnesium carbonate and dolomite to which 3% zinc oxide was added
- (3) Metallic zinc, 6 to 8 microns
- (4) Pulverized-coal ash
- (5) Dual burning of oil and pulverized coal in the ratio 9:1. The dual-firing experiment was included to provide more information on the effects of the combustion of solid-fuel particles in an oil flame, combined with the action from chemically inert ash particles.

The additives were injected into the combustion chamber by means of compressed air with the following results:

It was found that the amount of sulfuric acid in the flue gas at the air preheater inlet and outlet was greatly reduced by the addition of magnesium carbonate, by the proprietary additive, and by the zinc dust. Since the proprietary additive caused the greatest fouling of the air preheater, and since zinc dust fouled the burner-air ports, the magnesium carbonate was considered the optimum material. Severe fouling, combined with deposition of sulfuric acid, resulted from dual firing and from injection of pulverized-coal ash.

Following the study, it was recommended that:

- (1) All oil-fired boilers should be operated with the minimum practicable amount of excess air.
- (2) Further trials with magnesium carbonate and zinc are warranted.
- (3) Improvements on methods for adding powdered additives to the boiler are needed.*

Other Methods for Control

Inhibition of Metal Surfaces by Passive Films. The steel-finishing industry uses special film-forming inhibitors in the acid to control the attack on the steel while removing mill scale and rust by pickling. This method has recently been applied to the corrosion problem in air preheaters, in economizers, and in other such relatively cool areas as the metal stacks.

In 1954, Kear(99) reported a reduction in corrosion rate at temperatures below 240 F when certain coal-tar bases were sprayed into the flue-gas stream at areas near 500 F. In 1958, Jarvis(93), in large-scale trials in a boiler, indicated some success when using a commercial coal-tar base sold under the tradename "Teramin". This material is a mixture of heterocyclic tertiary amines which vaporizes and subsequently condenses with the sulfuric acid at the cooler zones. Two years later, Davies and Alexander(48) summarized results showing how this additive was used on a laboratory scale and in a variety of large boilers, including marine installations. They reported a reduction in corrosion by as much as 80% when 0.03% of the amine (by weight of the fuel) was added to the flue gas. The amine treatment also appears to facilitate the removal of carbon and deposits from the metal surfaces when they are water washed.

Disadvantages of the treatments, in addition to the main one of cost, are the difficulties in obtaining uniform injection and distribution to the areas to be protected. Also reported are objectionable odors if leaks are present in the boiler or if too much of the amine is exhausted in the stack.

Less-encouraging results for these materials were presented by Wilkinson and Clark(403) from trials at the Marchwood Generating Station in England. They agreed that the inhibiting action reduced corrosion somewhat, but found objectionable amounts of deposits on much of the low-temperature surfaces.

*Recently the Central Electricity Generating Board has been adding small amounts of metallic magnesium continuously in a boiler at Marchwood Station in England. Not enough experience has been gained as yet to determine its effectiveness, but early results appear promising.

It would appear that, at the present time, the use of pickling inhibitors to reduce air preheater corrosion holds some promise, but further developments are required to justify widespread adoption.

Use of Insulated Chimney to Prevent Condensate Attack. Steel stacks or chimneys for boiler exhaust are made self-supporting and also are stayed with guy wires to allow lighter-weight construction. Wind velocity, height of the stack, and the difference between the flue gas and ambient temperature all affect the natural draft. For larger boilers, forced draft is commonly used.

The introduction of residual fuel oil for the firing of boilers has resulted in complaints in some areas. Acid smuts emitted from the chimney have resulted in damage to property, clothing, and materials in the neighborhood of the power plants. Even with good burner control, smuts are emitted when condensation takes place in a steel stack. The smuts are found to be spongy flakes of iron sulfate plus carbonaceous matter.

It is believed that acid agglomerates are formed on steel in contact with flue gas. Condensed sulfuric acid attacks the steel, and the iron sulfate flakes are re-entrained in the gas. Experiments have shown that maintaining the flue gas in the stack above the acid dew point will eliminate the problem. Blum and co-authors⁽¹⁵⁾ have tried installing an aluminum heat shield around the stack, allowing a 0.25-inch air space. This effectively maintains the interior metal wall of the stack above the condensation temperature of the flue gas during the firing period of the boiler. It practically eliminated the problem of smut emission under the conditions of their experiment.

The boiler used by Blum, et al. is fired on a cyclic basis. During the part of the cycle when the burner is full on the inlet flue-gas temperature was 650 F and the exit temperature was 540 F. During the off period, for the burner the inlet temperature was 320 F and the exit temperature was 290 F. Since the original experiment, a number of stacks have been insulated. It is reported that the method is widely applicable. In Britain, for example, one can purchase a prefabricated stack with an aluminum heat shield, or one can contract to have an existing stack insulated by aluminum.

Oil-Ash Corrosion

In most cases, the correction of a problem in one section of the boiler will affect the remainder of the system. A study of the entire system must be made. For example, Sulzer⁽¹⁹⁷⁾ indicated that formation of ash deposits and corrosion caused by oil ash are inseparably connected; that is, if the formation of deposits can be prevented, corrosion is also obviated. However, this view is not unanimously accepted, since other difficulties have arisen in some boilers. The major effort in the development of an oil-additive procedure has been concerned with (1) raising the melting point of the ash to eliminate sticky corrosive particles or (2) changing the characteristics of the deposit so that it could be easily removed if it deposited onto the metal surfaces. For many years, there has been a tremendous amount of effort expended on these two approaches to the problem.

The investigations reported in the literature fall into several categories:

- (1) Fundamental paper studies and experiments designed to provide information on melting properties of oil-ash additive mixtures, and development of phase or equilibrium diagrams of the systems

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- (2) Empirical evaluations of proposed additives in laboratory crucible tests, or in experimental rigs simulating boiler and turbine conditions
- (3) Tests of additives in full-scale operating boiler plants.

The use of additives to prevent high-temperature deposition is based on the theory that raising the melting point of the oil ash will avoid formation of sticky adherent particles. Consequently, additive materials are selected to form compounds with the oil-ash components having melting points higher than those of the untreated oil ash. For example, magnesium vanadate melts at 1535 F, which is 300 to 400 F higher than that of the various sodium vanadates that can form in the boiler. In this report, reference has already been made to much of the work that has been done on melting characteristics of mixtures and on phase diagrams. (See Chapter 3, "Oil-Ash Phase Diagrams".)

The fuel-oil additives fall into two classes, depending on whether or not they are soluble in the residual oil. The insoluble materials are usually solids which are either introduced into the oil or blown into the boiler at some point. Those put in the oil may be used as water solutions emulsified in the fuel, or they may be solids slurried into the oil. The oil-soluble materials are usually in liquid form to facilitate ease of mixing with the residual fuel oil.

Oil-Insoluble Additives

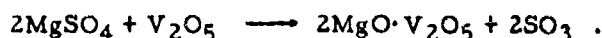
Principles Involved. A great deal of the experimental work in the additive field has been done with solids. Evans⁽⁵³⁾ was among the first to suggest an additive whose function would be to react chemically with the harmful ash components, forming compounds that would be solid at the operating temperature of the boiler components. Calcium oxide was shown to accomplish this in a crucible test when added in sufficient concentration to form $3\text{CaO} \cdot \text{V}_2\text{O}_5$. Evans pointed out, however, that a low-melting-point eutectic could form at a lower concentration of CaO, which would make the ash more harmful by lowering, rather than raising, the melting point.

Monkman and Grant⁽¹³³⁾ diluted synthetic ash with oxides of several metals and determined approximate melting points. They reported that MgO, CaO, and NiO increased the melting point considerably, whereas Al_2O_3 , SiO_2 , and ZnO had no effect whatsoever. Lucas, Weddle, and Preece⁽¹¹⁹⁾ used a Seger cone technique to determine the liquidus temperature of a number of vanadium pentoxide-metal oxide systems. MgO and NiO mixes gave the most rapid increases in melting point, while Al_2O_3 caused no increase until about 50% by weight had been added. These early studies were quite empirical, and Pfeil⁽¹⁴⁷⁾ suggested that the approach to these problems should be to get basic information on chemical equilibria which can be set up between the constituents of the ash and the products of oxidation of the alloy, with particular reference to melting ranges.

Magnesium and Calcium Compounds. Magnesium and calcium compounds have been selected as suitable additives by an overwhelming majority of the workers on the problem of high-temperature corrosion. The results in the laboratory and in practice apparently justify the selection. It is pointed out by Niles and Sanders⁽¹³⁸⁾, however, that there is still much to be learned. Factors that need further study are (1) the effect

of SO_3 and SO_2 on deposits and on complexes formed with additives and (2) the influence of the minor metallic elements that are present in fuel oil.

Niles and Sanders prepared pure compounds from V_2O_5 and MgO and obtained some information about the effect of SO_3 in the combustion system. Magnesium orthovanadate, $3\text{MgO} \cdot \text{V}_2\text{O}_5$, was formed from MgO and V_2O_5 , and it was shown that this was formed regardless of the mole ratio of MgO to V_2O_5 . However, when the ratio was less than 3 to 1, the reaction product included V_2O_5 , and when it was greater than 3 to 1, an excess of MgO was present. Similarly, mixtures of MgSO_4 and V_2O_5 were reacted. In this case the equilibrium mixture is the pyrovanadate:



Whether MgO or MgSO_4 is the reactant in a commercial system will depend on the partial pressure of SO_3 in the combustion gases. Units operating at atmospheric pressure may or may not have sufficient SO_3 partial pressure to form MgSO_4 , depending on the operating metal temperature. The importance of this basic chemistry was indicated in crucible corrosion tests at 1500 F, using the magnesium compounds described. The pure magnesium pyrovanadate was shown to be 100 times as corrosive as the pure, magnesium orthovanadate. This paper of Niles and Sanders represented an important contribution to the basic chemistry of the systems. However, it was pointed out in the discussion of the paper that the reactions described are not likely to go to completion in boilers because of the short residence time in the gas stream, and also because the low concentration of the reactants in the gas stream would prevent intimate contact between particles.

Young, Hershey, and Hussey⁽²²⁵⁾ developed a refined microfusion apparatus to determine accurately the fusion temperatures of ash mixtures. Four stages of melting were noted and proposed as standards for evaluating fuel-oil ashes: (1) sintering, (2) first bubbles, (3) initial melting, and (4) complete melting. Their preliminary results indicated, from melting-point data, that magnesium and calcium were possible additives. Corrosion tests confirmed these results for MgO , but in the case of CaO , more corrosion was observed than that found for untreated oil. The reason for this was thought to be related to the extremely heavy deposit that accumulated on the test specimens.

Later, Young, and Hershey⁽²²⁴⁾ reported that the microfusion technique proved useful as a rapid and convenient means for evaluating fuel additives, but they felt that phase diagrams for binary mixtures of ash constituents and proposed additives are really needed to select the concentration ranges which should result in solid ash products. Such diagrams, for the most part, were not available. From thermodynamic considerations, they calculated theoretical melting-point curves and dissociation constants for various oxides and sulfates. Their results indicated that the oxides of aluminum, calcium, magnesium, and silicon should be most effective in raising the oil-ash melting point. In addition, when the dissociation of sulfates, which would invariably be formed with the sulfur in the oil, was taken into account, an order of preference was established: aluminum, magnesium, calcium. Figure 40 shows composites of the curves for several oxides and sulfates and for vanadium pentoxide and sodium sulfate. The intersections of the V_2O_5 and Na_2SO_4 curves with those for the additive compounds represent the theoretical eutectic points.

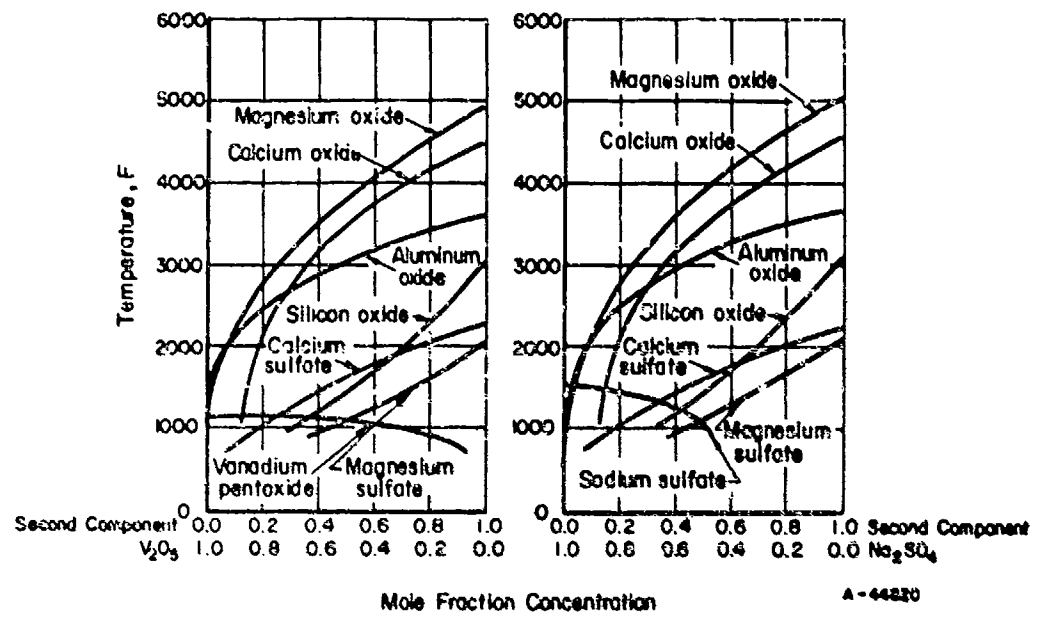


FIGURE 40. CALCULATED FREEZING-POINT DIAGRAMS WITH VANADIUM PENTOXIDE AND SODIUM SULFATE⁽²²⁴⁾

The excessive deposition that sometimes occurs with magnesium additions may be attributed to the use of an improper amount of the additive. Niles and Sanders⁽¹³⁸⁾ found that magnesium pyrovanadate, $2\text{MgO} \cdot \text{V}_2\text{O}_5$, occurred in deposits when the amount of magnesium added corresponded to the stoichiometric quantity needed to produce this compound with the vanadium available in the fuel. This pyrovanadate has a melting point of 1240 F and is capable of forming bonded deposits wherever metal temperatures reach this level. If metal temperatures are below 1240 F, however, a 2-to-1 ratio of MgO to V_2O_5 can be effective in changing deposits from molten globs to fluffy, easily removed particles, as has been the experience of the Public Service Electric and Gas Company pany⁽¹⁶¹⁾. When the magnesium-vanadium ratio was dropped to 1.4 to 1, tube wastage began, and if it was less than 1.4 to 1 the tube banks plugged. Generally speaking, the best results seem to have been obtained by using a 3-to-1 ratio of magnesium to vanadium.

Cunningham and Brasunas⁽⁴⁵⁾ referred briefly to the use of certain desirable additives and reported the results of one experiment with magnesium oxide as an additive. X-ray diffraction studies showed that a new crystalline substance was formed when MgO was added to the Na_2SO_4 - V_2O_5 mixture. No attempts were made to identify the new phase, although the mixture contained 21.8% by weight of MgO (53.5 mole %). This corresponded to $6\text{MgO} \cdot 4\text{V}_2\text{O}_5 \cdot \text{Na}_2\text{SO}_4$. Further it was shown that although the 4-to-1 ratio for $\text{V}_2\text{O}_5/\text{Na}_2\text{SO}_4$ is in a region of high oxygen solubility, the addition of 21.8% of MgO resulted in oxygen solubility decreasing almost to the vanishing point. Therefore, it appears that the beneficial effect of additives may be not only to raise the melting point of the ash but also to reduce absorption of oxygen. The latter effect should be investigated further.

The results of laboratory studies involving additions of metal oxides to a typical oil ash are shown in Figure 41. In this case MgO and CaO proved to be a great deal more effective in raising the melting point of the ash than either Al_2O_3 or SiO_2 .⁽¹³³⁾ The apparent contradiction of these results with the calculations of Young and Hershey probably stems from the fact that their calculations required the assumptions that ideal solutions result and that no intermediate compounds are formed.

In general, it may be concluded that metal oxides in very fine particle size are most effective as solid additives to oil-fired systems. Whether the metal should be aluminum, magnesium, silicon, or calcium appears to depend on the particular system in question. Variations in performance observed by investigators in this field are probably due to differences in conditions that prevail at the installations. An inorganic compound with basic properties, such as magnesium oxide or dolomite, holds most promise because it can fulfill the double function of reducing deposits caused by sodium and vanadium, and at the same time neutralize the SO_3 in the flue gases.

Oil-Soluble Additives

Unless the additive is well dispersed with the residual fuel oil at some stage in the combustion process, it may not be effective. Attention has been given to the possibility of choosing additives which will dissolve in the fuel oil to obtain increased effectiveness. A suitable additive in solution automatically will have intimate contact with each oil droplet formed in the burner. Under these conditions, it is more likely that the desired high-melting ash compounds will form in the course of combustion.

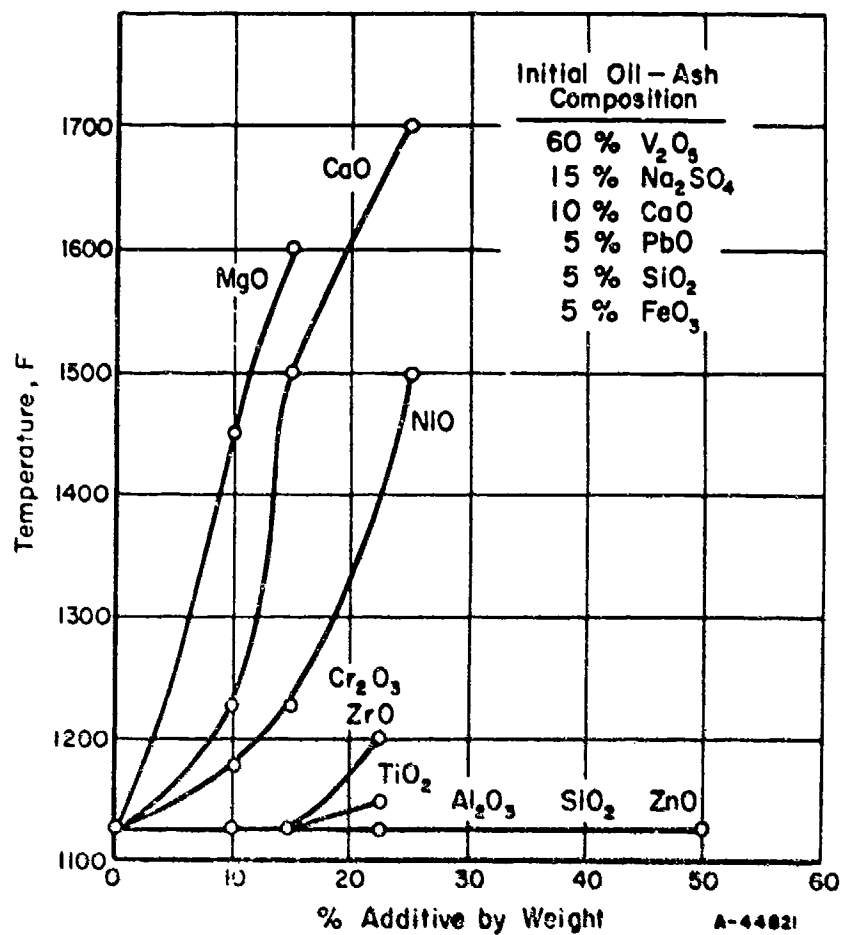


FIGURE 41. EFFECT OF INCREASING WEIGHTS OF VARIOUS OXIDES ON THE MELTING POINT OF A TYPICAL CRUDE OIL ASH⁽¹³³⁾

Metal Organics. Extensive experiments with oil-soluble additives were performed in a small-scale burner by Amero, et al. (4). Their results correlated well with similar tests in a full-scale, 10-inch combustor. The naphthenate salts of various metals were chosen because they are soluble in oil. Manganese, strontium, and rare-earth naphthenates performed better than calcium naphthenate, magnesium naphthenate, and an organic aluminum compound from the viewpoint of deposits. There seemed to be no correlation between the amount of deposit and the amount of corrosion. However, those compounds which gave the least deposits were not particularly effective as corrosion inhibitors. The most effective material for combined deposit and corrosion inhibition was manganese naphthenate, followed closely by rare-earth and magnesium naphthenates. It is significant that oil-soluble compounds of the elements tested were not necessarily more effective than insoluble compounds, although they were more expensive, per unit of active ingredient, because of the larger equivalent weight of the organometallic compound.

In a similar study conducted at the U. S. Naval Engineering Experiment Station (18C), 34 metal naphthenates were tested, using a high-vanadium fuel at temperatures from 1500 to 1700 F. The lanthanum, antimony, and iron naphthenates were best in reducing deposition and corrosion. Others which performed well were the derivatives of calcium, sodium, manganese, cerium, and neodymium. Barium naphthenate has also been shown to be an effective deposit inhibitor. (197)

Occasionally, it has been observed that a combination of an oil-soluble and a solid additive is more effective than either used alone. Of a series of tests with magnesium naphthenate, a mixture with kaolin reduced turbine-capacity losses to 3% (in 100 hours) as compared with 22% with the magnesium naphthenate alone and 27% for the kaolin alone. (163) It is particularly interesting to note the results of X-ray examination of deposits in these three cases:

- (1) Magnesium naphthenate - Deposits contained MgO , $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $3\text{MgO} \cdot \text{V}_2\text{O}_5$, and an unidentifiable material.
- (2) Kaolin - Deposits were mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), $2\text{NiO} \cdot \text{V}_2\text{O}_5$, and an unidentifiable material.
- (3) Magnesium naphthenate + kaolin - (a) With a small amount of kaolin deposits were only $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and unidentifiable material.
(b) With a large amount of kaolin the deposits consisted of $3\text{MgO} \cdot \text{V}_2\text{O}_5$ and a water-soluble material with approximate composition of $14\text{MgO} \cdot 11\text{Al}_2\text{O}_3 \cdot 22\text{SiO}_2 \cdot 8\text{V}_2\text{O}_5$.

Under the conditions of these tests, magnesium, either alone or with a little kaolin, formed sulfate rather than vanadate and deposited in large amounts. Additional kaolin was needed in the mixture to form the complex vanadium material which apparently was sufficiently high melting to be carried through the system with a minimum of deposition.

Proprietary oil-soluble materials have given indications of promise as deposit inhibitors also. A calcium additive reduced the sulfur and the vanadium content of superheater deposits significantly, when used in boilers at the West Lynn plant of the General Electric Company (168). Moderate deposition occurred in an evaluation of oil-soluble magnesium additives at the U. S. Naval Engineering Experiment Station. (179) An

aluminum-containing soluble inhibitor has been shown to raise the ash-fusion temperature of a high-sodium fuel from 1720 F to somewhere in excess of 2250 F (Al:Na = 0.75) and that of a high-vanadium fuel from 1225 F to a temperature greater than 2400 F (Al:V = 2:1.92)(139).

Mixed Formulations. The use of ethyl silicate or mixed ethyl polysilicates in an aromatic solvent has been claimed to maintain the efficiency of a gas turbine at 98% for many hours. (145) A mixture of MgO and sodium naphthenate reportedly is effective in reducing deposits in residual oils containing appreciable amounts of sulfur and vanadium. Mixtures of magnesium tallate and K_2CO_3 or talc and Na_2CO_3 were effective as well. (171) Case histories quoted in advertising for some proprietary additives point to the usefulness of various metal acetylacetonates in combatting deposits and corrosion.

Economic Factors. In spite of the success of oil-soluble additives, their cost militates against widespread use, even though they can be introduced into the system more easily than solid additives. On the other hand, water-soluble salts that can be emulsified in the oil have the same advantage of ease of introduction and are less expensive. Probably the truly oil-soluble additives will be restricted to rather specialized applications, where the expense can be justified.

Pilot Boiler Tests

The theoretical interpretation of the additive problem has been well substantiated by experimental programs.

Investigation of additives in pilot scale furnaces were made by McIlroy, Holler, and Lee(131), Rendle, Wilsdon, and Whittingham(167), and Phillips and Wagoner(149). In McIlroy's experiments, coils of stainless steel tubing were positioned at different heights above the combustion chamber in a vertical test rig, and the metal temperature was adjusted by blowing compressed air through the coils. Temperatures from 750 to 1350 F were maintained. Oil containing the various additives was burned, and the nature of the deposits was observed. Oxides of aluminum, magnesium, and calcium, in that order, gave best results, that is, readily removable powdery deposits.

A similar technique was used by Rendle and associates(167) in a pilot-scale boiler rig operating up to 1300 F. Two tube banks were placed at designated distances from the combustion chamber in a horizontal furnace, and the metal temperatures were adjusted by blowing air through the tubes. Low- and high-vanadium fuels were burned. In the additive studies, Swedish dolomite with an average particle size of 100 microns and Norwegian dolomite with an average particle size of 15 microns were fed into the flame from a vibrating tray. It was found that injection of dolomite equal to 0.04% of ash weight reduced the corrosion resulting from vanadium. However, there was an increase in the pressure drop across the fire-side of the tube banks. This was taken as a measure of fouling. With the Swedish dolomite, heavy fouling occurred after about 150 hours of operation. The Norwegian dolomite (with a higher magnesium content) also caused heavy fouling, but the deposits were softer and less adherent. Analyses of the deposits were not available.

Phillips and Wagoner also used a horizontal pilot-scale furnace, with three tube banks of five tubes each placed in three gas-temperature zones: 2500 F, 2100 F, and 1700 F, respectively. The tubes were cooled with steam to obtain approximately the same tube temperature in all three zones. Diesel oil with added compounds of sodium, vanadium and sulfur was burned to provide the oil-ash constituents. In the additive tests, MgO , $\text{Mg}(\text{OH})_2$, and $\text{CaCO}_3 \cdot \text{MgCO}_3$ as dry powders, were blown into the gas stream by compressed air. Significant reduction in corrosion was reported. The alloys under test suffered less corrosion at a metal temperature of 1200 F than at 1100 F without the additive. A ratio of magnesium to vanadium of at least 3 to 1 was required. It was emphasized that data obtained in other experiments under the isothermal conditions applicable to gas-turbine operation could not be applied to boiler operation, where a considerable difference exists between the gas and metal temperature.

Other laboratory and test-rig screening tests on possible additives have been reported^(4,54,73). The test conditions were more applicable to gas turbines than to steam boilers. All of the results are not discussed in detail here, but several interesting points are worthy of mention. For example, it was observed that (a) the order of effectiveness of additives is different on iron-base alloys than on nickel-base alloys and (b) the order may change with temperature. Also, oil-soluble compounds of elements are not necessarily more effective than aqueous solutions or insoluble powders. In Amero's work⁽⁴⁾, many of the additives substantially reduced corrosion. Micronized talc, KMnO_4 , and MgO were effective in small-burner tests at estimated materials cost of 1, 11, and 0.8 cent/barrel of fuel, respectively. Reduction in corrosion is not directly proportional to the concentration of the additive. The first increment apparently reduced corrosion more than did subsequent additions.

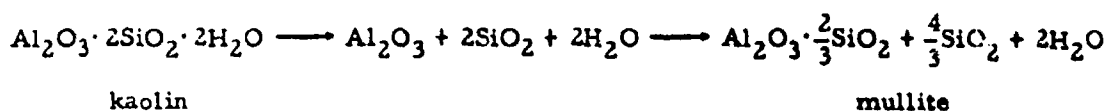
This review indicates that selection of an additive is not determined solely by its corrosion-inhibiting effects. Some of the other requirements include low cost, commercial availability, and effectiveness over a range of temperatures and on different alloy compositions. The effect on formation of deposits and their properties must not be overlooked. A factor that has not been discussed here, but which would undoubtedly be very important in practice, is the design of feeding mechanisms for the additives.

Control of Gas-Turbine Deposits

A considerable portion of the published papers and reports dealing with additives is directed to the problem as it pertains to gas-turbine applications. This is because operating temperatures are higher than in boilers, accentuating the molten-ash problem, and because relatively small quantities of deposits on turbine blades result in a significant drop in efficiency. In discussing developments that may apply to steam boilers, brief reference is made to these gas-turbine results because the inherent causes and cures are the same as for boilers.

Buckland⁽²⁴⁾, reporting on tests of the effect of additives on deposits in full-scale gas turbines, conducted at the Rutland and Graham Stations, found that increasing the aluminum content of the fuel with respect to its vanadium content decreased the deposition rate. However, deposits increased with increasing magnesium content of the additive. Nevertheless, in practice the use of magnesium compounds has been preferred for reasons of economy. Young and his associates⁽²²⁵⁾ have shown experimentally that MgO additions to residual fuels have reduced corrosion, both from Na_2SO_4 and V_2O_5 , and have made the deposits porous and friable.

Sulzer⁽¹⁹⁶⁾ has stated that promising results were obtained with a suspension of aluminum silicates in the residual oil used with a semiclosed-cycle 20,000-kw gas-turbine plant in Switzerland. The fuel contained 0.05% ash, consisting of 0.03% V_2O_5 and 0.01% Na_2O , with an additional 1.9% sulfur. With no additives in the fuel severe blade fouling occurred in the first three stages of the turbine after 50 hours of operation. The deposits consisted mainly of ash with dissolved corrosion products. With treated fuel, the turbine was still operating after 2200 hours, and no reduction in performance from fouling was detected. Fine deposits consisting of clear globules and needlelike crystals were visible on the backs of the blades of the final stages. Each of the globules resulted from the combustion of an oil droplet mixed with fuel additive. These particles consisted of about 90% silicates and contained 60 to 80% of the ash of the oil. Their melting point was about 2500 F, which was high enough to prevent adhesion in the turbine. The aluminum silicate is believed to dehydrate and eventually convert to mullite:



The use of aluminum silicate as an additive has been patented. (201)

Hydrated calcium silicate⁽¹⁷⁰⁾ and magnesium silicate or a mixture of magnesium and silicon compounds⁽¹¹⁶⁾ have been found sufficiently effective in specific cases to have been patented also. A mixture of calcium acetate and basic calcium sulfonate in a light oil has recently been patented⁽¹⁴⁰⁾ as an additive to minimize deposits from burning residual fuels.

A few other solids such as talc, kieselguhr, and diatomaceous earth have shown effectiveness as additives in gas turbines⁽¹⁹⁷⁾, while the use of crushed walnut shells (300 to 700 microns) as a deposit preventive has been patented⁽¹¹⁰⁾. Retardation of deposits in this case has been ascribed to mechanical rather than chemical effects.

A fuel oil, given a desalting treatment and containing a water-soluble, emulsifiable additive, was fed to a gas turbine. Its successful operation has been reported by Buckland^(23,26). Early turbine operation with a calcium additive experienced slight corrosion with a great deal of deposition. Since a water solution of magnesium sulfate has been used as an additive, deposition and corrosion have been almost eliminated. However, desalting by washing and centrifuging to bring the sodium and calcium content of the oil below 10 ppm is a necessary preliminary step. The magnesium-to-vanadium ratio is maintained at 3 or greater, while the sodium-to-vanadium ratio is kept below 0.3 for good results.

A number of reports have been written on the work carried on at the National Gas Turbine Establishment in England. Inorganic oxides were mixed with V_2O_5 and heated to about 1500 F. The mixtures that did not liquify were tested (usually at 1300 to 1500 F) in contact with some of the alloys used in gas turbines. Some of the tests were made in air and others in air containing 0.1% SO_3 . Additional tests were made in mixtures of proposed additives and ashes from Admiralty reference fuels.

In all of these tests only magnesia and zinc oxide were considered satisfactory additives to suppress corrosion. Magnesia was reported to be slightly better at temperatures over 1500 F, while zinc oxide was better below 1500 F. When SO_3 was present in the test atmosphere, calcium vanadate was converted to calcium sulfate. In another

investigation oil-soluble metal naphthenates were added to a reference fuel and the behavior examined in a test rig. The zinc compound proved to be the best additive in this experiment, reducing corrosion to one-tenth the original value. Magnesium and calcium compounds were next in order of effectiveness. Aluminum and iron compounds reduced corrosion by about one-half but caused excessive deposits. Another series of reports, also applying to gas turbines, described the investigations of The Shell Petroleum Company, Ltd. Again, magnesium and zinc compounds were reported to be the most effective in reducing corrosion when added in sufficient quantity to form the orthovanadates. An undesirable effect of magnesium was its tendency to slag on the silica-alumina refractories in combustion chambers. Magnesium additive was said to have only a marginal influence on ash deposition. Tests on a Ruston and Hornsby 3CT gas turbine showed that a mixture of kaolin and magnesium had a beneficial effect. Magnesium sulfate showed promise because corrosion was reduced and the deposits that formed were loose and readily removed.

Agreement among investigators is not complete as to the relative efficacy of magnesium additives. In the study of the oil-fired gas turbine aboard the tanker "Auris" (owned by Shell Petroleum, Ltd.), magnesium salt additions caused excessive slagging of refractories⁽¹¹⁰⁾. Kaolin, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, and ethyl silicate were the only satisfactory additives reported to have any promise. Ethyl silicate is oil soluble but expensive, whereas the insoluble 3 to 4-micron particles of kaolin tended to settle in the oil. The protective action of the silicate additives was thought to result from enveloping of the ash particles in glasslike spheres that did not adhere to the metal. However, the mechanism is not fully understood.

Another report on some very early work applicable to gas turbines was given by Stauffer⁽¹⁹⁴⁾. Alloy specimens were heated in contact with mixtures of ash and various additives at temperatures ranging from 1380 to 1560 F. Only cerium sulfate and calcium oxide produced significant decrease in corrosion. Darling⁽⁴⁷⁾ noted that fouling in a gas turbine operating at a maximum temperature of 1050 F was decreased to almost zero by changing the atomization to form oil droplets with minimum diameters of 77 microns. The oil droplets are not burned completely, and the ash particles leave the combustion chamber in a hard, dry form encased in carbon. No additive was used.

Treatment of Surfaces With Aqueous Slurries

Greenert⁽⁷²⁾ reviewed the work that has been conducted at the U. S. Naval Engineering Experiment Station (EES) and elsewhere. Today's most urgent need, he concludes, is simple and practical remedial measures to enable current equipment to operate with present contaminated fuel. Basic solutions to the problem, such as the use of fuel additives, or the substitution of more highly corrosion-resistant materials are neither applicable nor feasible in naval equipment. Therefore, an investigation of the use of simple washes and similar coatings, to be applied directly to contaminated boiler surfaces, was undertaken in the laboratory at Annapolis.

The technique used for evaluating corrosion behavior in this, and other EES investigations is briefly as follows.

- (1) Metallic specimens are precontaminated by immersion in molten synthetic ash at 1600 F for 2 hours. Two mixtures that have been used are (a) 70% V_2O_5 + 30% Na_2SO_4 or (b) 79% V_2O_5 + 21% NaVO_3 .

- (2) The specimens are then painted with a thick water slurry of various compounds being tested.
- (3) After drying, the relative corrosion resistance is determined by heating at 1600 F in oxygen at atmospheric pressure and measuring the quantity of oxygen consumed by the corrosion reaction. Time of test is usually 3 hours, and the results are compared with those obtained on untreated and uncontaminated surfaces, using change in weight as the criterion of corrosion.

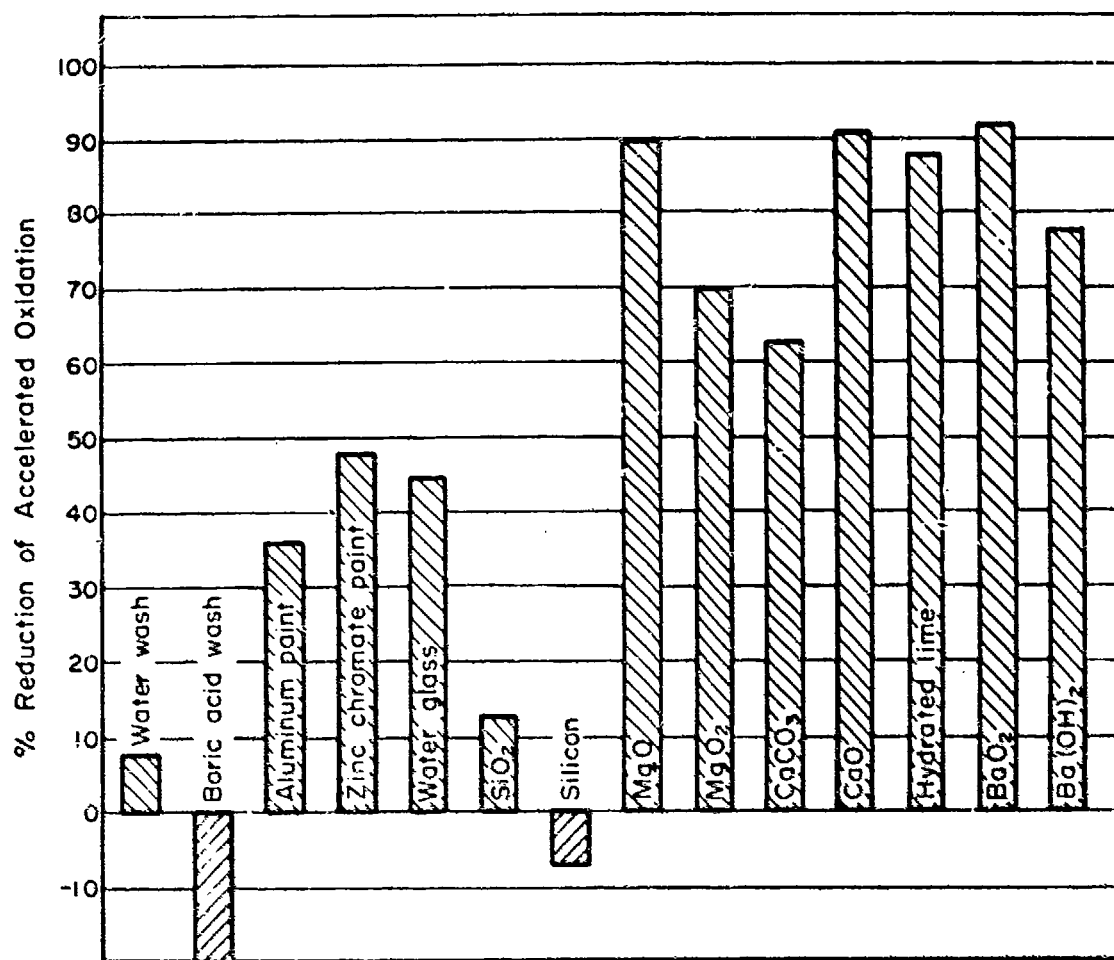
The effectiveness of the various remedial treatments is shown in Figure 42 taken from a report by Greenert and Richards⁽⁷³⁾. The bar chart shows that slurries of compounds of calcium, magnesium, and barium reduced corrosion by as much as 90%. Inexpensive hydrated lime was shown to be as effective as chemically pure calcium oxide. The beneficial effect is shown to persist over longer periods in Figure 43⁽⁷⁴⁾. It was also observed that treatment with the calcium and magnesium slurries made the vanadium ash deposits more water soluble.

Additional experiments were conducted⁽⁷²⁾ to develop practical treatments. Two treatments were developed that are intended primarily for boilers. The first one, suitable for use while steaming, or in a standby status, involves only periodic application of a water slurry of hydrated lime to sensitive boiler parts. The slurry may be applied through soot blowers or by a lance through boiler ports. The amount of slurry and frequency of application would depend on the vanadium content of the fuel and the amount of fuel fired. Visual observation of slag deposition would help to determine this. The second treatment is primarily intended to condition the slag for easy removal prior to shutdown for cleaning or overhaul. This involves an application of lime or calcium and magnesium oxide, as in the first treatment, and a period of heavy firing just before shutdown. This makes the slag more water soluble and easier to remove. No change in standard washing procedures would be required.

Economic considerations necessarily play a large role in deciding what materials are practical for use as additives. McIlroy and Lee⁽¹³¹⁾ found alumina to be the best additive for steam-generating units, with magnesium and calcium oxides promising. However, dolomite ($\text{MgCO}_3 \cdot \text{CaCO}_3$) was eventually put into use rather than any of these three because it was more desirable from operating and economic standpoints. The use of dolomitic lime was also found practical by Campbell⁽³¹⁾, with the result that ash deposits became powdery and easily removable. Corrosion in the cooler parts of the system was also materially reduced.

It is interesting to note that a slurry-spraying procedure has been reported to be operating successfully at boiler plants of the Florida Power and Light Company. The procedure was described by Keck⁽¹⁰²⁾ in 1959. In the initial investigation, coating the metal surfaces with a fine spray of calcium oxide-water slurry, prevented the adherence of slag deposits. Furthermore, a similar spray application to a heavily slagged boiler caused layers of slag to dislodge from the surface and drop to the furnace floor. The spray is applied through soot blowers; a discussion of the equipment is given in the paper.

Additional operating experiences with the process are given in a later paper by Keck⁽¹⁰¹⁾. Discussion of the development of the optimum slurry formula, processing schedules, and operating experience is given. At the Fort Myers boiler, the slurry is



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FIGURE 42. EFFECTIVENESS OF REMEDIAL TREATMENTS IN ARRESTING ACCELERATED OXIDATION OF LABORATORY-CONTAMINATED SPECIMENS⁽⁷³⁾

The alkaline earth compounds were applied as thick water slurries.

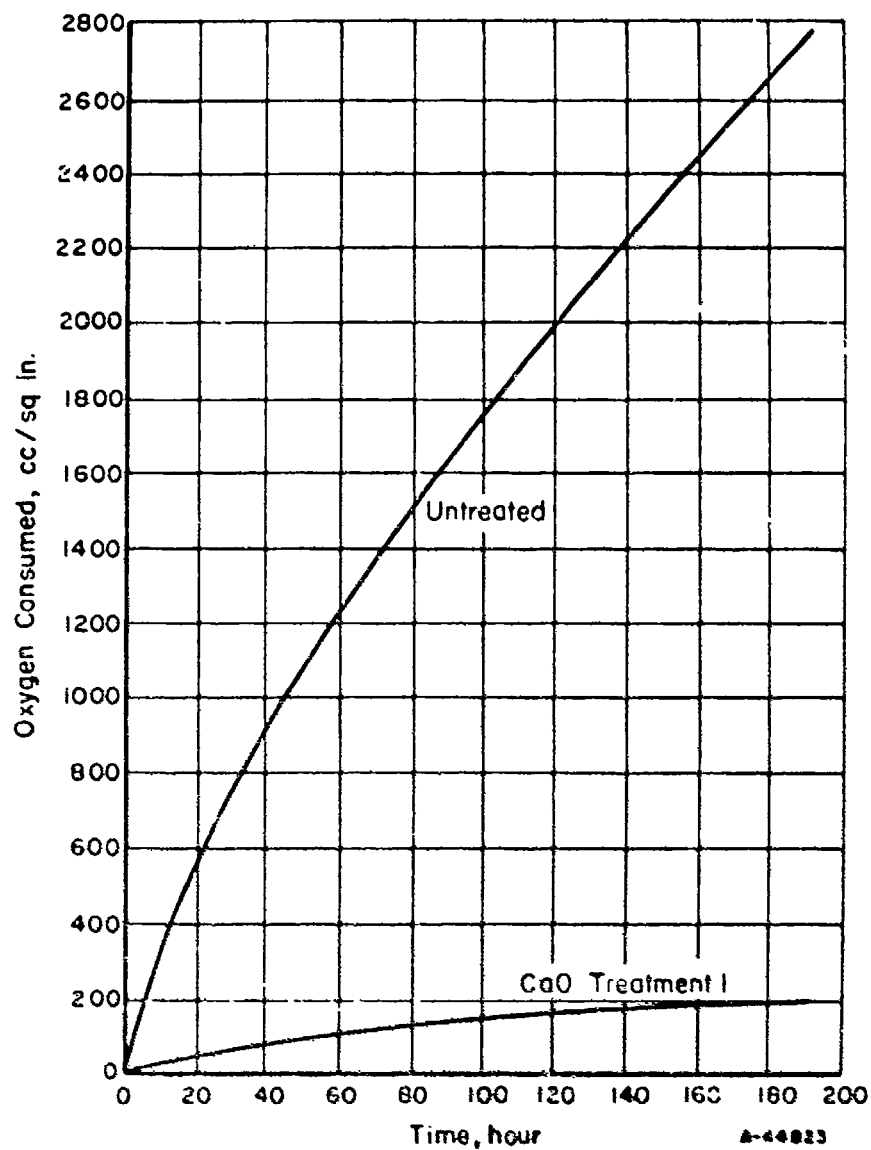


FIGURE 43. OXYGEN CONSUMPTION OF LABORATORY-CONTAMINATED SPECIMENS SHOWING EFFECT OF CaO REMEDIAL TREATMENT DURING LONG-TERM OXIDATION PERIOD⁽⁷⁴⁾

Test temperature, 1600 F; specimen material, 25Cr-20Ni steel.

composed of 0.25 pound of ground calcined magnesite mixed with treated water to form 1 gallon of slurry. The magnesite is ground so that 95% passes through an ASTM No. 100 sieve. The magnesite has a magnesium oxide-to-calcium oxide ratio of 20 to 1.

All surfaces exposed to gas temperatures exceeding 1000 F were washed daily with the slurry, and surfaces exposed to gas temperatures below 1000 F were sprayed weekly. This procedure made it possible to maintain surfaces relatively free of deposits and corrosion. Superheater and reheater tubes were examined during an unscheduled shutdown after 39 months of operation, during which fuel averaging 1.88% sulfur and 400 to 500 ppm of V_2O_5 was used. It was found that all samples were within the thickness tolerances specified for new tubes. The process was also described by Cantieri and Chappell⁽³³⁾. Corrosion is not discussed sufficiently in the above papers on slurry spraying to enable one to visualize the extent of corrosion quantitatively. Cantieri reported that superheater hangers do not receive the degree of protection from slurry spray to prevent deterioration in the course of time because of their very high metal temperatures.

Other Boiler Experiments

Heavy buildup of deposits with additives may in some cases be attributable to inefficient soot-blowing facilities. Greenwood⁽⁷¹⁾ carried out duplicate tests on two similar marine boilers, one having retractable steam blowers and the other with air puff blowers. When MgO was added at the rate of 0.1 per cent of fuel weight to residual oil having 300 ppm of vanadium the boiler with steam blowers was still 95% clean after 3-1/2 months of operation. The boiler having air puff soot blowers was 90% plugged after 5 months of operation. The condition of the latter boiler was worse than one in which no additive had been used. Consequently, the efficiency of an additive may depend on the conditions under which it is employed. The additive may be reacting with ash constituents to raise their melting point, but some other factor may cancel this beneficial effect.

Table 18 lists a summary of experiences using dolomite injected (a) as a slurry or (b) as a dry powder. The advantages in each case must be weighed against the disadvantages.

FUEL PRETREATMENTS AT THE BOILER PLANT

As problems involving corrosion and deposits developed in boiler and gas-turbine units fired with residual oils, one of the first steps taken was to investigate possible ways to reduce the concentration of ash-forming constituents to a lower and perhaps more-tolerable level. This interest persists, particularly with regard to reduction of the substances found to be primarily responsible for the troubles encountered, namely vanadium and alkali metal compounds. Residual oils are by-products of refinery processes designed primarily to produce the highest possible yields of gasoline and the high-value-distillate hydrocarbon fuels. Fuel-oil prices are scheduled to be competitive with other low-cost fuels, especially coal. The cost of any additional processing at the refinery to improve the quality of residual fuel oils must be allocated either to an increased price for the residual product or be included in the charges for the high-value-distillate fuels. Neither procedure can usually be justified economically. As long as

TABLE 18. SUMMARY OF EXPERIENCES WITH DOLOMITE ADDED TO BOILER FURNACES AS SLURRIES AND POWDERS^(a)

Country	Company or Authority	Power Station	Dosage Rate	Method of Injection Into Furnace	Advantages	Disadvantages
United States of America	Florida Power Corporation	Inglis	$\frac{\text{Dolomite}}{\text{Oil ash}} = \frac{1}{1}$	As a slurry in oil	Reduced slag formation and superheater blockages; reduced corrosive quality of flue gases; lowered dew-point from 270 to 180 F	Blockages in oil supply lines and strainers; burner-nozzle wear
United States of America	Public Service Electric and Gas Company	Kearny	$\frac{\text{Dolomite}}{\text{Oil ash}} = \frac{2}{1}$	As a slurry in oil	Reduced bonded deposit formation on superheater surfaces	Pump wear; blockage in convection superheater
United States of America	Public Service Electric and Gas Company	Sewaren	$\frac{\text{Dolomite}}{\text{Oil ash}} = \frac{1}{1}$	As a slurry in oil	No definite conclusions	Slagging in combustion chamber and on superheater tubes
United States of America	Consolidated Edison Co. of New York	Not stated	$\frac{\text{Dolomite}}{\text{Oil ash}} = \frac{1}{1}$	As a slurry in oil	Rate of blockage in superheater probably reduced	Not very successful
Brazil	Sao Paulo Light and Power Co., Ltd.	Piratinunga	$\frac{\text{Dolomite}}{\text{Oil ash}} = \frac{1}{1}^{(a)}$	Injected into flame of each burner in form of dry powder	Superheater deposits made friable	Slagging in combustion chamber
France	Electricité de France	Nantes-Cheviré	2.0 lb/1,000 lb oil	Injected as dry powder through two opposing coal burners	Superheater deposits made dry and powdery	Rapid fouling in superheaters, even with more frequent soot blowing
France	Electricité de France	Dieppedalle	2 to 3 lb/1,000 lb oil	As a dry powder into flame or into top of combustion chamber	None	Slag formation on brickwork around burners; rapid superheater fouling
Great Britain	Central Electricity Generating Board	Southport	6 lb/1,000 lb oil	As a dry powder through common windbox to four burners	Reduced dewpoint of flue gases from 300 to 240 F	Caused blockage in superheater

(a) Later added at a rate based on amount of deposit forming constituents in oil ash.

much of the residual fuel produced can be sold "as is" for steam-power generation, further processing ordinarily cannot be justified by the refiner on economic grounds.

Nevertheless, it is to the advantage of the consumer to carry out some processing of residual fuel when specialized applications such as the gas turbine are involved. As a result, some experimental work has been done to improve the quality of residual oils for special applications.

Water Washing

Processes involving water washing and centrifuging have been used with considerable success in preparing residual fuel for use in diesel engines, gas turbines, and marine plants. Centrifuging alone is useful in removing water from the fuel. If the associated water contains chlorides of sodium, magnesium, and calcium, these salts will be removed. If an emulsion is present, removal of the water entails some loss of oil. When microcrystalline salts are present, a preliminary washing with water will provide removal, again with the formation of undesirable emulsions unless an effective emulsion-breaking compound is added to the fuel oil before washing. The oil-soluble organometallic substances are not removed by centrifuging.

Buckland and Sanders⁽²⁶⁾, of the General Electric Company, have described a combination water washing and centrifuging process for modifying the ash content of residual fuel oils. The process consists of mixing the oil intimately with either fresh water or a water solution of a suitable salt, and then centrifuging the mixture. Before the mixing process, the oil is heated and an emulsion breaker is added to aid in the separation of the oil and water phases in the centrifuge and in the sludge tank. The centrifuge used was of the continuous, self-cleaning concentrator type.

Vanadium was not removed by the centrifuging process. Benefits of the washing-centrifuging process included: (1) reduction of the sodium content of the oil to 10 ppm or less; (2) adjustment of the ratio of the weight of sodium in the ash to vanadium in the ash to a value of 0.3 or less, to avoid corrosion, and (3) a convenient method of converting vanadium to the high-melting $3\text{MgO} \cdot \text{V}_2\text{O}_5$ compound by maintaining a 3-to-1 ratio of the weight of magnesium to the weight of vanadium in the ash. The particular limiting ratios mentioned are suggested specifications found useful in earlier studies of corrosion and deposits in gas turbines burning heavy fuel oils. Costs of the treatment were estimated to be 14 cents per barrel, including the heat, most of which would be required in any event. The authors believe that these costs could be reduced to 5 cents per barrel or less, at which stage the process might become attractive for use in utility plants.

Downing⁽⁵⁰⁾ and co-workers also have studied the treatment of residual fuel for use in marine diesel engines. Their treatment consists of heating the oil to 208 F, adding a demulsifying agent and mixing, washing with fresh water, and finally centrifuging. They report that 95% of the sodium present is removed by the combined water wash-centrifuging method, compared with 65% removed by centrifuging alone. Costs were estimated to be in the range of 5 to 10 cents per barrel.

The relative ineffectiveness of employing centrifuging for the removal of vanadium compounds from residual oil is illustrated by tests reported by Kottcamp and Crockett⁽¹⁰⁷⁾. Table 19 lists data obtained by centrifuging three No. 6 fuel oils.

Although treatment by centrifuging reduced the total ash content in the oil, it had no effect in reducing the vanadium content. Indeed, since the total quantity of ash was reduced without effect on the vanadium present, the percentage of vanadium in the ash, computed as V_2O_5 , was increased. The authors point out that if specifications for fuel oil limit the vanadium content by specifying maximum limits for V_2O_5 in the ash, centrifuging may have undesirable results.

TABLE 19. EFFECT OF CENTRIFUGING ON THE VANADIUM CONTENT OF NO. 6 FUEL OIL⁽¹⁰⁷⁾

Constituent	Oil A		Oil B		Oil C	
	Before	After	Before	After	Before	After
Ash, per cent by weight of oil	0.057	0.036	0.055	0.048	0.035	0.011
Vanadium as V_2O_5 , per cent of total ash	7.9	13.4	56.5	65.0	11.1	27.5
Vanadium, ppm of oil	26	27	174	175	22	17

Studies conducted at the Naval Boiler and Turbine Laboratory⁽⁵⁹⁾ showed that the sodium concentration in a number of Navy special fuel-oil samples was reduced to 5 ppm or less by water washing. Solutions of monobasic or dibasic ammonium phosphate were recommended for washing, in order to combat vanadium corrosion without introducing other metals.

Filtration

Inorganic materials such as scale, sand, dirt, and some of the crystalline salts present can be removed by filtration. Removal of oil-soluble compounds, including the organometallic complexes containing vanadium, is not accomplished by simple filtration.

Shields⁽¹⁸⁴⁾ has reported studies involving the filtration of No. 6 fuel oil using a rotary vacuum filter and a precoat base of diatomaceous earth and calcined clay filter aids. Results obtained with one No. 6 fuel oil are shown in Table 20.

The sodium content of the oil was greatly reduced. Substantial reductions were achieved in calcium, aluminum, iron, lead, magnesium, and total ash. The vanadium content was little affected. Tests with other No. 6 fuel oils gave similar results. The author indicates that the process using a continuous rotary filter, with use of precoat, is economically feasible to provide fuel for gas-turbines. A similar process, utilizing filter aids and an ordinary filter press, was developed by Sinclair Oil.⁽¹⁶⁴⁾ Reductions in mineral content of the same order of magnitude as shown in Table 20 were obtained.

Another method of removing the water from the fuel oil is to employ electrocoalescence. The agitated fuel oil is passed through an electrostatic field provided by electrodes maintained at about 5,000 volts potential difference. This field tends to coalesce the water and allow ready separation.

TABLE 20. RESULTS OF FILTERING A NO. 6 FUEL OIL AS SHOWN BY ASH ANALYSES⁽¹⁸⁴⁾

Element	Before Filtration, ppm in oil	After Filtration, ppm in oil
Na	217	2
Ca	250	48
Ni	20	14
Al	23	4.1
Fe	47	20.5
Pb	13.6	2
Cr	2.1	2
Mg	18	5.8
V	38	31.8
Cu	8	2
Zn	16	16
Ag	1	1
Mn	2	2
Ti	2	2
Sn	2	2
Total ash	1200	260
Sediment, per cent	0.0860	0.0097

Ion-Exchange Methods

Some interest has developed in recent years concerning the use of ion-exchange methods for demineralizing fuel oils, particularly for removal of sodium. Essentially, an ion-exchange process involves preheating the oil to perhaps 250 F and passing the oil through a bed of cation-exchange resin. The resins are of the hydrogen or ammonium type, and the process results in the removal of sodium, magnesium, and calcium. Work in this field has been done by the Brooklyn Polytechnic Institute⁽⁷⁵⁾ for the Office of Naval Research and by several oil companies.

The work at Brooklyn Polytech included tests of a large number of ion-exchange resins in attempts to remove vanadium. Wide ranges of experimental conditions were studied, but the attempts were unsuccessful. However, it was found that up to about 90% of the sodium in oil-sea water emulsions containing up to 1000 ppm of sodium could be removed by use of an ammonium ion-exchange resin. The effects of factors such as temperature, sodium concentration, demulsifying agents, space velocities, oil viscosity, and type of resin were studied. The economic factors related to practical use of the process were treated briefly, but from the data given, it is not possible to make direct comparisons with the costs of water washing or other methods.

Although some oil companies have indicated an interest in the possibilities of removing sodium from fuel oils by ion-exchange methods, economic data or details of any practical applications are not available. One company, in 1954, made preliminary cost

estimates involving a comparison of an ion-exchange process and a water wash-centrifuge method. The comparison showed operating and investment costs totalling 10.5 cents per barrel for the ion-exchange process (ammonium resin) compared with 12.8 cents per barrel for the water washing-centrifuging method. However, lack of data regarding the ability of the process to remove sodium to a level of less than 10 ppm, resin stability, and applicability of the process to specific fuel oils resulted in lack of interest in the process. It is possible, however, that use of newer resins, permitting higher oil preheat temperatures, lower viscosities, and higher space velocities, might furnish a basis for a worthwhile extension of the study.

Chemical Treatment

The removal of vanadium from residual oils has been effected chiefly by hydrogenation of the oil, followed either by filtration or by solvent extraction. The treatment with hydrogen at elevated temperature and pressure converts the vanadium porphyrins either into insoluble forms that can be removed by filtration or into smaller fragments that are soluble in organic solvents. A patent for such a process has been issued to Bieber and Hartzband⁽¹²⁾ of Esso Research and Engineering. The combination of high-pressure hydrogen treatment and solvent extraction that they used was claimed to have removed 96.6% of the nickel and 98% of the vanadium in a Venezuelan crude, with 90% yield of oil. Extraction alone removed only 10% of the vanadium, while hydrogenation alone removed 58%. Hess and associates⁽⁸⁶⁾ of Texaco, Inc., have also received a patent for hydrogen pressure treatment, followed by filtration. They claimed "essentially complete removal of vanadium".

A series of patents have been issued to F. W. B. Porter and R. P. Northcott, assigned to the British Petroleum Company, concerning the removal of vanadium and sodium from petroleum products^(154, 155, 156, 157). The method involved passing the oil through beds of material such as bauxite in the presence of hydrogen at pressures ranging from 500 to 1500 psig and at temperatures of 750 to 800 F. Space velocities were maintained in the range of 0.5 to 2.0 volumes per volume per hour. The method was developed for use with petroleum stock to be treated by a catalytic hydrogenation process for the removal of organically combined sulfur. The object was to remove vanadium and sodium which might otherwise deposit on the cobalt-molybdenum oxide catalyst and lower its activity. The inventors claim that about 70% of the vanadium, in a Kuwait crude oil containing 22 ppm, and 90 to 95% of the sodium could be removed. The removal of the vanadium is believed to be promoted by the hydrogenation, whereas removal of the sodium by the bauxite is primarily a physical process which is not improved by the hydrogen treatment.

The removal of vanadium by treatment with iodine is covered in a patent issued to Kavanagh and Chesluk⁽⁹⁷⁾ of the Texas Company. The vanadium complex in the oil is converted to an insoluble compound which can then be removed by filtration. In laboratory experiments with a Mara crude, the vanadium level was reduced from 200 ppm to 17 ppm and the nickel from 15 to 1 ppm by this process.

A number of older patents have claimed hydrogen treatment at different pressures, space velocities, and temperatures as effective means for removing vanadium from residual oils with efficiencies from 70 to 90%.

Solvent Precipitation

It is possible to separate most of the ash-forming constituents from fuel oil by treatment with selective solvents. The addition of certain solvents to residual fuel oils precipitates the colloidal asphaltenes of types and in amounts varying with the type of solvent, temperature, ratio of solvent to fuel, and other conditions of precipitation. Surface-tension considerations determine whether the asphaltenes are precipitated or brought into solution in the solvent. Since the vanadium porphyrin complexes present in the oil are of relatively high molecular weight, it would be expected that they would be precipitated in substantial amounts with the asphaltenes.

Sacks⁽¹⁷⁷⁾ and others have studied the effect of solvents on heavy fuel oils and have found that n-pentane, for example, removes from 83 to 95% of the vanadium regardless of the source of the fuel or the original vanadium content. A large proportion of the iron and nickel compounds was also precipitated. Other effective solvents were found to be petroleum ether and ethyl acetate. Naphtha had no precipitating effect on the vanadium; it appeared to remove asphaltenes of molecular size higher than that of the vanadium compounds present.

Garner et al. (66) found that 97% of the vanadium, 99% of the nickel, and 86% of the iron were removed from a Middle East residual oil when the asphalt was precipitated by propane treatment.

However, methods of solvent treatment of this type are expensive and result in substantial losses of oil. Thus, they cannot be considered economically feasible under ordinary circumstances.

CONCLUSIONS AND RECOMMENDATIONS

In many areas of the world, residual fuel oil is attractively priced and readily available. Steam-raising stations under control of the Bureau of Yards and Docks along coastal areas are using residual fuel oil in increasing amounts.

Unfortunately, the quality of the fuel oil being offered by many of the refiners is deteriorating. As a result of the higher ash content and the sulfur present, the corrosion and deposit problems in the boiler have become more troublesome. Where the boiler is of good design and the operator follows good housekeeping practices, experience has shown that in many cases the corrosion and deposit problem can be kept under reasonable control.

This topical report described in detail the many problems encountered in boilers. These difficulties can be classed as either low- or high-temperature problems. The low-temperature problems, in the air preheater and stack, for example, are attributed to the presence of sulfuric acid in the flue gases. For these problems it is suggested that combustion of the oil with a minimum of excess air be studied as the primary means of minimizing corrosion and deposits. With properly designed burners and controls, it should be possible to reduce greatly the SO_3 content of flue gases. A twofold effect would occur: (1) the dewpoint would be lowered to where dry conditions prevail and condensation of sulfuric acid in the air preheater and economizer would be prevented and (2) the amount of SO_3 available for the formation of corrosive compounds from the $\text{Na}_2\text{O}-\text{SO}_3-\text{V}_2\text{O}_5$ system would be minimized. This would be helpful also in alleviating the high-temperature problems. It is recognized that to operate a boiler on minimum excess air will require special equipment, elaborate controls, and operator training.

In very small-sized boiler units, where operation with low excess air may not be practical, raising the exit-gas temperature sufficiently to ensure that the sulfuric acid dewpoint is never reached would eliminate the low temperature corrosion. This result would be at the cost of some efficiency in operation but could still be the most economical corrective measure available. For situations in which low-temperature corrosion is limited to the stacks, insulation to maintain adequate wall temperatures is recommended.

High-temperature problems, occurring at locations where the metal surface temperatures are about 900 F or higher, appear to be more complex. Oxidation of the metal surfaces, formation of ash compounds that are plastic or molten at the temperature of the metal surfaces, reaction between the metal and the molten ash, and absorption of oxygen through molten ash layers have all been reported to take part in the reactions leading to corrosion and deposits.

An obvious solution to the problem is to reduce the steam-temperature requirements so as to maintain a maximum superheater-tube surface temperature below 900 F. However, where this is not possible, the use of additives should be considered. Compounds of magnesium and calcium have shown the most promise, their function being to raise the melting point of the ash above the maximum metal temperature and to form friable and readily removable deposits. The use of such compounds in the form of dry powders has been beset by problems related to feeding and proportioning equipment and to questions about where the powders should be injected into the boilers.

The reports on additives are sometimes conflicting. Additives may change the character of the ash, affect the rate of deposition, neutralize sulfuric acid in the low temperature zones, and affect local reactions such as oxidation by catalysts.

In boilers large enough to utilize soot blowers, applying a slurry of magnesium and calcium compounds to the tubes should be examined. In smaller boilers, the introduction of slurries through lances, or by spraying, should also be considered.

In medium-sized boilers having high-temperature problems, a nonproprietary oil-soluble chemical compound, such as magnesium naphthenate, could probably be used to advantage. Oil-soluble additives in general are too costly, but there may be some circumstances in which the economics would justify the use of an oil-soluble additive.

These recommendations are summarized in Table 21.

TABLE 21. METHODS OF CORROSION CONTROL RECOMMENDED FOR INVESTIGATION

Boiler Size	Methods of Control	
	High-Temperature Corrosion	Low-Temperature Corrosion
Small	Not applicable	Raise exit-gas temperature
Medium	Low excess air + oil-soluble additive or slurry-type additive	Low excess air
Large	Low excess air + slurry application	Low excess air

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B A T T E L L E M E M O R I A L I N S T I T U T E

APPENDIX A

PARTIAL LIST OF PATENTS ON ADDITIVES AND TREATMENTS
FOR REDUCING CORROSION AND DEPOSITS
CAUSED BY RESIDUAL FUEL OIL

BATTELLE MEMORIAL INSTITUTE

APPENDIX A

PARTIAL LIST OF PATENTS ON ADDITIVES AND TREATMENTS
FOR REDUCING CORROSION AND DEPOSITS
CAUSED BY RESIDUAL FUEL OIL

German Patent 128,616 (1900)
British Patent 166,285 (1921)
U. S. Patent 1,657,753 (1928)

All are concerned with the use of V_2O_5 to catalyze the oxidation of SO_2 to SO_3 .

British Patent 689,579 (1950)

Magnesium or zinc oxide, barium carbonate, or other metallic oxide which will combine chemically with V_2O_5 , is injected into the apparatus to reduce corrosion of heat-resisting steel.

Swiss Patent 281,764 (1952)

Addition of inorganic chlorides such as $NaCl$, $CaCl_2$ or $(NH_4)_2-SnCl_6$ to the fuel to partially inhibit formation of combustion products that attack high-temperature alloys.

Swiss Patent 281,765 (1952)

Addition of 5 g of Al_2O_3 /kg of fuel oil counteracts harmful effect of 0.2% V_2O_5 in the oil. Other additives suggested are zirconium oxide; diatomaceous earth; SiC ; CaC_2 ; $BaCO_3$; powdered iron, aluminum, silicon or ferrosilicon; and aluminum acetate.

U. S. Patent 2,687,985 (1954)

Removal of vanadium and sodium from petroleum by hydrogenation.

British Patent 743,472 (1956)

Addition of compounds that will react with the V_2O_5 to form a vanadium compound. Selected from the group consisting of iron, aluminum, oxides of these metals, and compounds of these metals yielding the oxides at combustion temperatures.

German Patent 946,020 (1956)

Surface-active Al_2O_3 or kaolin is added to the oil.

Swiss Patent 314,443 (1956)

Aluminum silicate can be used as an additive for gas-turbine fuels to prevent deposition and corrosion.

U. S. Patent 2,744,853 (1956)

Removal of vanadium from petroleum by reaction with iodine.

U. S. Patent 2,758,060 (1956)

Removal of vanadium and sodium from crude oil by hydrogenation in the presence of bauxite.

U. S. Patent 2,764,525 (1956)

Removal of vanadium and sodium from petroleum using iron oxide and alumina.

U. S. Patent 2,766,183 (1956)

Removal of vanadium and sodium from petroleum using Fuller's earth.

British Patent 771,597 (1957)

Magnesium or aluminum in the form of ribbon, wire, or rod, is introduced in the air stream of the turbine.

British Patent 772,296 (1957)

Method comprises both conducting the combustion in a reducing manner and adding to the fuel or introducing into the combustion space, or mixing with the combustion products, an aluminum silicate to lower the vapor pressure of harmful substances.

U. S. Patent 2,781,005 (1957)

Additive is selected from the group consisting of magnesium and zinc oxides, or magnesium and zinc compounds yielding the oxide on combustion. Introduced oxide to V_2O_5 of at least 3 to 1.

U. S. Patent 2,793,945 (1957)

Addition of hydrocarbon-soluble phosphorus-containing organic composition to the fuel oil.

British Patent 799,954 (1958)

Oil-soluble compounds of iron, tin, lead, or zirconium made from crude tall oil, dissolved directly in the fuel oil to inhibit corrosion. Amount added is 0.5 to 10 times the amount necessary to form the orthovanadate with vanadium in the oil.

German Patent 1,041,621 (1958)

Magnesium silicate is recommended as an additive to heavy oils to prevent deposition and corrosion.

U. S. Patent 2,843,200 (1958)

Hydrated calcium silicate is claimed to be a useful additive to residual oils to prevent deposition and corrosion.

U. S. Patent 2,846,358 (1958)

Use of catalytic hydrogenation combined with solvent extraction removes nickel and vanadium from crude oil.

U. S. Patent 2,857,256 (1958)

Addition of an oxide of arsenic to the fuel, to obtain a mole ratio of As/V of 2 to 10/1. Corrosiveness of the ash is almost completely eliminated, even at 1200 F or above.

German Patent 1,050,484 (1959)

A gel concentrate of an inorganic material such as fine granular SiO_2 , asbestos, or MgCO_3 is added to the oil at 14 F. The gel is made from aluminum stearate.

U. S. Patent 2,910,434 (1959)

Hydrogenation of petroleum or residual oil using heat and pressure converts vanadium to solid which can be removed by filtration.

British Patent 842,821 (1960)

Ethyl silicate or mixed ethyl polysilicates in an aromatic solvent will reduce deposition in gas turbines.

British Patent 846,174 (1960)

Stable dispersions of inorganic aluminum compounds in mineral oil added to the fuel oil to inhibit corrosion by vanadium or sodium compounds. Patent describes method of preparing the dispersion.

U. S. Patent 2,966,029 (1960)

Add enough sea water, or corresponding salts, to obtain a ratio of 1.5 to 4.0 atoms of sodium per atom of vanadium in the fuel.

U. S. Patent 2,949,008 (1960)

Mixtures of MgO and sodium naphthenate or K_2CO_3 and magnesium tallate or talc and Na_2CO_3 are effective in reducing deposits and corrosion from high-vanadium fuel oils.

U. S. Patent 2,968,148 (1961)

Addition of mixture containing 0.12% by wt ZnO and 0.2% Na_2CO_3 to a fuel containing 203 ppm vanadium and 11 ppm sodium to give a Zn/V mol ratio of 4/1 reduced corrosion of Type 310 stainless steel from 1430 to 9 mg/sq in. Deposits reduced from 1150 to 80 mg/sq in. Test conducted at 1450 F.

U. S. Patent 3,002,825 (1961)

A mixture of calcium acetate and basic calcium sulfonate in a light oil is used as an additive for residual oils.