

UNCLASSIFIED

| |
|--|
| |
| |
| |
| AD NUMBER |
| AD827053 |
| NEW LIMITATION CHANGE |
| TO Approved for public release, distribution unlimited |
| FROM Distribution authorized to U.S. Gov't. agencies only; Administrative/Operational Use; FEB 1968. Other requests shall be referred to Naval Ship Engineering Center, Attn: NAVSEC 6101F, Washington, DC 20360. |
| AUTHORITY |
| Naval Ship Engineering Center ltr dtd 3 Aug 1971 |

THIS PAGE IS UNCLASSIFIED

AD82053 Z

**FORMATION OF ALKALI IRON SULFATES
AND OTHER COMPOUNDS CAUSING CORROSION
IN BOILERS AND GAS TURBINES**

THIRD SUMMARY REPORT

July 1, 1967 – December 31, 1967

Contract No. N00024-68-C-5153

Each transmittal of this document outside
the agencies of the U. S. Government must
have prior approval of Naval Ship Engi-
neering Center, Washington, D. C. 20360
Attention: NAVSEC 5101F

AMERICAN SOCIETY OF MECHANICAL ENGINEERS
Research Committee On Corrosion And
Deposits From Combustion Gases

Prepared by
BATTELLE MEMORIAL INSTITUTE
Columbus Laboratories

DDC
RECEIVED
FEB 19 1968
RECEIVED
C

THIRD SUMMARY REPORT

on

FORMATION OF ALKALI IRON SULFATES
AND OTHER COMPOUNDS CAUSING CORROSION
IN BOILERS AND GAS TURBINES

to the

AMERICAN SOCIETY OF MECHANICAL ENGINEERS
RESEARCH COMMITTEE ON CORROSION AND
DEPOSITS FROM COMBUSTION GASES

July 1, 1967 - December 31, 1967

BATTELLE MEMORIAL INSTITUTE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

Battelle is not engaged in research for advertising, sales promotion, or publicity purposes, and this report may not be reproduced in full or in part for such purposes.

| | |
|--|-----------------------|
| APPROVED BY | |
| WHITE SECTION <input type="checkbox"/> | |
| DIFF SECTION <input checked="" type="checkbox"/> | |
| UNANNOUNCED <input type="checkbox"/> | |
| JUSTIFICATION | |
| BY | |
| DISTRIBUTION/AVAILABILITY CODES | |
| DIST. | AVAIL. and/or SPECIAL |
| 3 | |

FOREWORD

As with earlier Summary Reports in this series, this one is divided into two parts. Part one, marked GENERAL REVIEW, highlights the work of the last six months and recounts only the most important developments. Part two, marked TECHNICAL DETAILS, goes into the way in which the research was done, includes detailed accounts of experiments and descriptions of apparatus, and lists and analyzes the data obtained. A broad view of the project can be obtained by reading only the first part, but those seeking specific information will find it in the second part of the report.



The American Society of Mechanical Engineers

United Engineering Center / 345 E. 47th St., New York, N.Y. 10017 / 212 PL 2-6800

February 15, 1968

ASME Research - Corrosion & Deposits from Combustion Gases

Enclosed is a copy of the Third Summary Report of the study of "Formation of Alkali Iron Sulfates and Other Compounds Causing Corrosion in Boilers and Gas Turbines." This report covers work performed at Battelle from July 1, 1967 to December 31, 1967. It is sent to you in recognition of your support of the Committee's work.

During this period, experiments using radioactive sulfur have revealed the much greater reactivity of SO_3 , relative to SO_2 , with surfaces such as are present in a combustion gas stream. Detailed examinations have been made of numerous deposits removed from boilers and gas turbines, to identify the compounds present. Work was done to determine if an electrochemical cell could be used as a rapid indication of corrosive conditions; it was concluded that this would require more time to develop than could be justified for this project. Further experiments were made in a small oil-burning furnace to investigate reactions between flue gas constituents and compounds found in deposits associated with corrosive conditions.

The work will be continued as outlined in the report until June 30, 1968, when it will have to be terminated because of financial limitations. Another report will be sent to you soon after that date. Any comments or suggestions that you may have concerning the Committee's work will be welcome.

Very truly yours,

George C. Wiedersum, Chairman
ASME Research Committee on
Corrosion & Deposits from Combustion Gases

Encl.

BLANK PAGE

TABLE OF CONTENTS

| | <u>Page</u> |
|--|-------------|
| GENERAL REVIEW | 1 |
| Research Accomplishments Over the Past Six Months | 2 |
| Surface Investigations | 2 |
| Fuel-Burning Furnace Studies | 3 |
| Mechanism of Corrosion | 4 |
| The Next Steps | 5 |
| Published Papers | 5 |
| SURFACE INVESTIGATIONS | 7 |
| Sulfur-35 Studies | 7 |
| Effect of Temperature | 7 |
| Reactivity of K_2SO_4 | 8 |
| Reactivity of Fe_3O_4 | 9 |
| Effect of Lower SO_3 Concentration | 9 |
| Optical Microscopy Study of Deposits | 10 |
| Optical Microscopy Study of Intermediates | 12 |
| Future Work | 12 |
| FURNACE STUDIES | 13 |
| Electrochemical Cell | 13 |
| SO_3 Concentrations Beneath Deposits | 16 |
| Examination of Deposits | 17 |
| Future Work | 24 |
| MECHANISM OF CORROSION | 25 |
| Reduction of SO_3 Formation and Corrosion in Boiler Flue Gases by Control of Excess Air | 25 |
| Experiences in Europe | 26 |
| Experiences in This Country | 29 |
| Summary | 30 |
| LIST OF REFERENCES | 33 |

LIST OF FIGURES

| | |
|--|----|
| Figure 1. Reactivity of SO_2 and SO_3 with a Mixture of Fe_2O_3 and Na_2SO_4 as a Function of Temperature | 7 |
| Figure 2. Corrosion Rates of Stainless Steel Observed by Nelson and Cain | 8 |
| Figure 3. Reactivity of SO_2 and SO_3 with Various Surfaces | 9 |
| Figure 4. Test Using Iron:Platinum Cell Containing Sodium Carbonate | 13 |
| Figure 5. Test Using Iron:Platinum Cells Containing Alkali Sulfate and Alkali Sulfate-Ferric Oxide Mixtures | 14 |
| Figure 6. System for Determining Effect of Deposits on Formation of Corrosive Conditions in Fuel-Fired Furnace | 16 |
| Figure 7. Deposit Specimen From T-11 Ferritic Reheater Tube of Joppa Station | 19 |
| Figure 8. Section Through Joppa Specimen at 15X | 20 |
| Figure 9. Section Through Joppa Specimen at 100X | 20 |

LIST OF FIGURES (Cont'd)

| | <u>Page</u> |
|---|-------------|
| Figure 10. Potassium Distribution | 21 |
| Figure 11. Sodium Distribution | 21 |
| Figure 12. Iron Distribution | 21 |
| Figure 13. Sulfur Distribution | 22 |
| Figure 14. Silicon Distribution | 22 |
| Figure 15. Aluminium Distribution | 22 |
| Figure 16.. Profiles Obtained on Microprobe Traverses Through Joppa Specimen | 23 |

LIST OF TABLES

| | |
|---|----|
| Table 1. Relative Reactivity of SO ₂ and SO ₃ Toward Na ₂ SO ₄ -Fe ₂ O ₃ Mixture at Different Temperatures | 8 |
| Table 2. SO ₃ Concentrations Beneath Deposits | 17 |
| Table 3. Effect of Excess Oxygen on SO ₃ Formation for Coal and Oil | 26 |
| Table 4. Summary of Results of Operation with Low Excess Air | 31 |

Third Summary Report

on

FORMATION OF ALKALI IRON SULFATES
AND OTHER COMPOUNDS CAUSING CORROSION
IN BOILERS AND GAS TURBINES

Further work with S^{35} has confirmed the much higher reactivity of SO_3 compared with SO_2 in reactions with surfaces. The relative reactivity depends in part on the nature of the surface and the temperature, but with mixtures of Na_2SO_4 and Fe_2O_3 at 1200 F, only 30 ppm SO_3 was 50 times more reactive than 50,000 ppm SO_2 . Hence, although SO_2 participates in part to cause corrosion, its activity is insignificant compared with SO_3 . Further work with the electrochemical cell showed the utility of this method of indicating corrosion reactions, but the system is judged to be too complex for quantitative results. Recent review of the use of low excess air in oil-fired boiler furnaces shows an increase in the popularity of this method of controlling external corrosion.

GENERAL REVIEW

by

William T. Reid

When this investigation began in 1962, the experimental program was based largely on the formation of SO_3 in boiler-furnace atmospheres. It stressed the formation of SO_3 in flames, and later it investigated the catalytic oxidation of SO_2 to SO_3 as a contributor to high-temperature corrosion. More recently, the experimental program has included determination of such factors as the gradient in SO_3 over various types of surfaces in a slowly flowing gas stream. Again and again in this study, SO_3 has been emphasized as a dominant factor in the formation of deposits that lead either to rapid loss of metal beneath them, or to the formation of deposits that are closely involved in corrosion reactions. This emphasis on SO_3 has continued throughout the experimental program.

Data collected this past six months show without question that SO_3 is indeed a major contributor to corrosion through the formation of alkali trisulfates.

Whether formed within the flame or produced catalytically by oxidation of SO_2 , it is the SO_3 in flue gases or formed within deposits that reacts most readily to cause metal wastage. Although this basic conclusion has been postulated for many years, it is supported now by actual measurements giving a quantitative viewpoint - not speculation.

Such conclusions have been substantiated quantitatively by using radioactive S^{35} as a tracer. Incorporating a small amount of S^{35}O_3 in normal SO_3 , and then checking the products of reaction for radioactivity gives an accurate measure of the extent to which the SO_3 reacts in a system also containing nonradioactive SO_2 . In the same way, by tagging SO_2 with small amounts of S^{36}O_2 , the participation of SO_2 can be measured in comparison with nonradioactive SO_3 in the same gas mixture. This tool, then, provides a ready measurement of the relative chemical activity both of SO_2 and of SO_3 in simulated flue gas atmospheres. As noted in the Second Summary Report, describing the preliminary stages of the S^{35} work, only 25 microcuries of the radioactive sulfur oxide is used in an experiment. Nevertheless, even though this is only a ten-billionth of the nonradioactive sulfur oxides in the sample, it is ample to be counted radioactively with a precision within 2 to 3 percent. This small quantity of S^{35} gives a precise indication of how the remainder of the sulfur is reacting because the chemical behavior of the radioactive sulfur is exactly the same as that of the four stable sulfur isotopes.

This is a particularly powerful research tool. Radioactive S^{35} can be used safely only in a properly controlled laboratory, but its usefulness as a tracer of reactions involving sulfur provides a unique method of investigating sulfur chemistry. Radioactive sulfur warrants further attention by those investigating other aspects of sulfur-induced corrosion.

RESEARCH ACCOMPLISHMENTS OVER THE PAST SIX MONTHS

Surface Investigations

Initial results of reactions on surfaces showed that SO_3 is much more reactive than SO_2 . Those earlier tests, described in the Second Summary Report, were made at high SO_2 levels and at a fixed temperature. More recently, the whole temperature range from 1000 F to 1300 F has been investigated, and enough work has been done at an SO_2 concentration of 2500 ppm to show that the Battelle data apply to the SO_2 levels commonly found in boiler furnaces as well as to the high concentrations of SO_2 used in the initial laboratory experimentation.

With SO_2 at 58,000 ppm and SO_3 at only 30 ppm, the reaction of SO_2 with a surface containing Na_2SO_4 and Fe_2O_3 in a 3-to-1 mole ratio is shown to decrease between 1000 F and 1150 F and to increase between 1150 F and 1300 F. This 3-to-1 mole ratio is the stoichiometric ratio to form sodium iron trisulfate, $\text{Na}_3\text{Fe}(\text{SO}_4)_3$. On the other hand, the reactivity of SO_3 is little affected by temperature up to 1100 F, increases abruptly to a maximum at 1200 F, and then decreases again at 1250 F to about the same value as at 1000 F.

In this gas mixture, 30 ppm of SO_3 is 50 times more reactive than 58,000 ppm of SO_2 alone at 1200 F, and 10 to 15 times more reactive at temperatures just above and below 1200 F. The abrupt rise in SO_3 reactivity at 1200 F explains why a decrease of only 50 F in the temperature of a superheater element can affect corrosion so markedly. Hence, decreasing steam temperature from 1050 F to 1000 F, which would lead to a corresponding decrease of about 50 F in metal temperature, should markedly reduce corrosion rates if the metal temperature were 1200 F initially. On the other hand, if the metal temperature were 1250 F and then decreased to 1200 F, corrosion would be more severe. These measurements confirm the concept of the well-known "bell-shaped" curve, providing quantitative data to support the importance of relatively small changes in metal temperature.

At the lower concentration of 2500 ppm SO_2 , approximating the SO_2 level in furnace atmospheres, the reactivity of 30 ppm SO_3 compared with SO_2 is much greater than when the SO_2 is 58,000 ppm. Experimentally, at 1100 F, 30 ppm SO_3 was 360 times more reactive than 2500 ppm SO_2 . This series of tests is not completed, but it is probable that the peak SO_3/SO_2 reactivity ratio again will occur at 1200 F.

As a guide to pointing out when corrosion is likely, microscopic measurement of the index of refraction developed in this study on deposits from laboratory furnaces has been most useful in identifying the presence of trisulfates in many samples of deposits from boiler furnaces. This technique shows that most deposits collected in areas where corrosion is suspected or is known to occur contain small crystallites of trisulfates. Four samples collected in 1943-1945 from wall tubes showing wastage and a superheater in which corrosion was just beginning to be a problem all contain optically identified trisulfates, when in most of the cases the amount of trisulfate was much too small to be detected by X-ray diffraction. Of four other deposits obtained recently through the Corrosion and Deposits Committee, three definitely showed the presence of trisulfates, often in discrete layers. Samples of deposits from a gas turbine where the operating temperature was 1350 F did not contain trisulfates.

Additional work also has been done on the relative importance of K_2SO_4 and Na_2SO_4 in conjunction with Fe_2O_3 in reacting with SO_2 and SO_3 . Experiments at 1100 F show that K_2SO_4 is about twice as reactive as Na_2SO_4 . American coals, on the average, contain equal amounts of potassium and sodium on a molar basis, making it impractical to seek coals having a low potassium content. To add to the problem, potassium compounds have a higher vapor pressure than sodium compounds, thereby tending during combustion to vaporize more potassium than sodium from the mineral matter in coal. This in turn, leads to greater amounts of potassium in deposits.

Fuel-Burning Furnace Studies

Further tests with electrochemical cells to detect precisely when corrosion begins to occur as conditions are varied in the fuel-burning furnace were inconclusive because of the complex nature of the reactions that affect cell voltage and current flow. An electrical cell can be a useful device for indicating the occurrence and rate of corrosion, but great care must be exercised when

interpreting results. Apparently insignificant factors, such as the cracking of a few-micron-thick oxide layer on a metal surface, can affect voltage of the cell sufficiently to mask the major effects being studied. Hence, small temperature changes and slight differences in gas composition, coupled with random localized corrosion presumably even around grain boundaries, may produce voltages that serve mainly to obscure the main corrosion reaction. Electrochemical systems for detecting corrosion offer a great deal of promise, but the development of a reliable cell will involve more work than can be justified here. In the last experiments at Battelle, trisulfates could not always be identified in surface layers when the voltage of the cell indicated that corrosion was occurring. In part, this might have shown that the electrochemical cell is a much more sensitive indicator of corrosion than the presence of even optically identified trisulfates, but an inability to correlate these two methods led to terminating the electrochemical experiments.

The exact way in which deposits lead to corrosion on superheater elements has not yet been defined. One explanation is that the trisulfates are formed within the deposit from alkalis and iron oxides present in the deposit reacting with SO_3 produced catalytically within the deposit from SO_2 in the surrounding flue gas. Another is that the thermal gradient in the deposit favors the migration of alkalis to the cooler metal surface where the trisulfates then form. Still another is that the deposits simply shield a surface to provide a nearly stagnant layer of gas between the metal surface and the deposit so that ample time is available for formation of SO_3 and the eventual production of trisulfates. Actually, all of these effects may occur, even simultaneously. Some attempts have been made in this program to learn more precisely which of these actions is most significant, but the experiments have not been conclusive. Recent tests to answer some of these questions have been made with a newly designed specimen holder in which flue gas from the fuel-burning furnace can be drawn through a deposit and sampled at the specimen surface. Not enough data are available to draw any firm conclusions, but the apparatus appears capable of showing distinct differences in the SO_3 formed, and the tendency of the deposits to form trisulfates.

Mechanism of Corrosion

Operating boiler furnaces with low excess air as a means of eliminating corrosion in oil-fired equipment has advanced rapidly, particularly in Europe. For the present, at least, it is considered as a panacea for most of the ills involving sulfur and vanadium, if not by itself, at least in combination with an additive such as MgO . The requirement of low excess air, preferably not exceeding 1.5 percent, remains if the most effective results are to be obtained. Different opinions are being expressed on the need for highly precise control of fuel and air to each burner. Some operators demand individual burner control, others will settle for overall furnace controls. Combustion problems with pulverized coal at low excess air are obviously more difficult than with oil.

Along other lines, present plans for injecting massive doses of limestone or dolomite into boiler furnaces to capture sulfur oxides to reduce air

pollution can be expected to reduce corrosion although it may accentuate fouling. Operators may be required to install equipment for adding 500 tons of limestone daily to a 500-megawatt unit by air-pollution ordinances. In that case, the corrosion problem can be expected to disappear.

THE NEXT STEPS

Several steps need to be completed prior to the termination of this project in June, 1968. Some additional work with S^{35} will extend the data on the relative reactivity of SO_3 and SO_2 at the 2500-ppm level of SO_2 . Further steps also will be taken to identify the intermediate compound apparently formed just before the trisulfates appear. It is expected that knowing the composition of this material will help in deducing exactly how the trisulfates are formed.

The effect of deposits will be investigated in a series of tests in the fuel-burning furnace using the apparatus described in this report. This test series will include both single- and double-layer deposits to show as rigorously as possible how changes in the composition and physical structure of deposits affect SO_3 formation on a simulated tube surface and the production of trisulfates. Formation of SO_3 will be checked by gas analyses, and the presence of trisulfates by the index-of-refraction technique.

PUBLISHED PAPERS

This program has encouraged the publication of research papers to disseminate information as widely as possible. The following listing of papers presented or published in 1967 shows how that objective has been met:

Presented at Winter Annual Meeting of ASME, November 27-December 1, 1966:

"Basic Problems in the Formation of Sulfates in Boiler Furnaces", by William T. Reid. Trans. ASME, J. Eng. Power, vol. 89, Series A, no. 2, April, 1967, pp. 283-287.

"High-Temperature Corrosion Studies in an Oil-Fired Laboratory Combustor", by Richard E. Barrett. Trans. ASME, J. Eng. Power, vol. 89, Series A, no. 2, April, 1967, pp. 288-296. (Barrett received the Henry Hess Award of ASME for this paper.)

"Interactions in Sulphur Oxide-Iron Oxide Systems", by A. Levy and E. L. Merryman. Trans. ASME, J. Eng. Power, vol. 89, Series A, no. 2, April, 1967, pp. 297-303.

Distributed to the Committee, April 24, 1967:

"A Microprocedure for the Analysis of SO_2 and SO_3 ", by E. L. Merryman, A. Levy, and William T. Reid.

Papers presented in 1967 and not yet published:

"Present Status of Knowledge of High-Temperature Corrosion from Vanadium and Sulfur in Combustion Gases", by William T. Reid, P. D. Miller, and H. H. Krause. Presented at 32d Midyear Meeting of the Division of Refining of API, May 16, 1967.

"Corrosion and Deposits from Combustion Gases - A Review", by George C. Wiedersum. Presented at Joint Power Generation Conference, September 24-28, 1967.

"Sulfur Oxide Reactions: Radioactive Sulfur and Microprobe Studies of Corrosion and Deposits", by H. H. Krause, A. Levy, and William T. Reid. Presented at Winter Annual Meeting of ASME, November 12-17, 1967.

"Mechanisms of Formation of Sulfur Oxides in Combustion", by A. Levy, E. L. Merryman, and William T. Reid. Presented at 60th Annual Meeting of AIChE, November 26-30, 1967.

SURFACE INVESTIGATIONS

by

H. H. Krause

SULFUR-35 STUDIES

The experimental apparatus and procedures used in the S^{36} work this year were the same as used previously; they were described in the first two Summary Reports.

The current effort has emphasized the effect of temperature on the relative reactivity of SO_2 and SO_3 with a mixture of Fe_2O_3 and Na_2SO_4 . Previous experiments were all at 1100 F, so a series of runs was made in which the temperature range 1000 F to 1300 F was studied. In addition, the effect of substituting K_2SO_4 for Na_2SO_4 was examined, the data on Fe_3O_4 were completed, and experiments were made at an SO_2 concentration of 2500 ppm rather than at the higher levels used previously.

Effect of Temperature

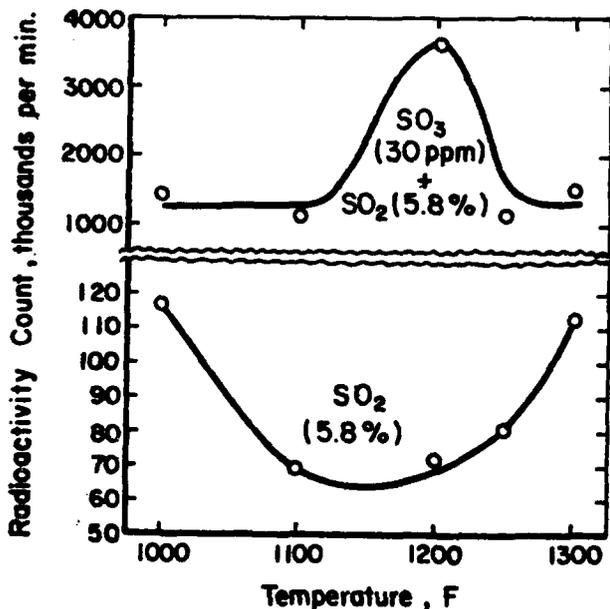


FIGURE 1. REACTIVITY OF SO_2 AND SO_3 WITH A MIXTURE OF Fe_2O_3 AND Na_2SO_4 AS A FUNCTION OF TEMPERATURE

The $S^{36}O_2$ and $S^{36}O_3$ were used to study the reactivity of the sulfur oxides with the standard. Na_2SO_4 - Fe_2O_3 mixture (3 to 1 mole ratio) at temperatures from 1000 F to 1300 F. The gas mixture used was the same as in previous experiments: 74.8 percent N_2 , 19.4 percent O_2 , 5.8 percent SO_2 , and when SO_3 was used, 30 ppm.

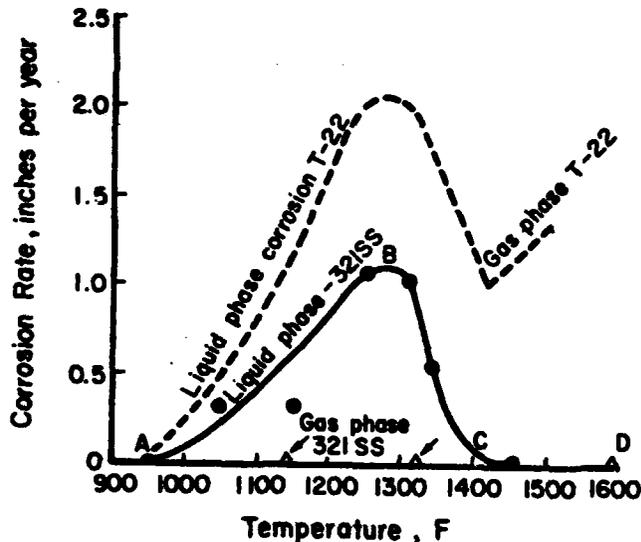
The results of these experiments are shown in Figure 1. At all temperatures the reactivity of SO_3 is much greater than that of SO_2 . Table 1 gives the reactivity ratios of SO_3/SO_2 at the various temperatures based on the observed radioactivity count.

The preponderant SO_3 reactivity at 1200 F, which results in a sharp peak in the reactivity curve, recalls the "ball-shaped curves" observed for corrosion of

TABLE 1. RELATIVE REACTIVITY OF SO₃ AND SO₂ TOWARD Na₂SO₄-Fe₂O₃* MIXTURE AT DIFFERENT TEMPERATURES

| Temperature, F | 30 ppm SO ₃ | 30 ppm SO ₃ | 1 mole SO ₃ |
|-------------------|--|--|--|
| | 58,000 ppm SO ₂ (Experimental) | 2500 ppm SO ₂ (Calculated) | 1 mole SO ₂ (Calculated) |
| 1000 | 12.6 | 293 | 24,400 |
| 1100 | 16.8 | 390 | 32,500 |
| 1200 | 50.2 | 1170 | 97,000 |
| 1250 | 14.6 | 340 | 28,200 |
| 1300 | 13.5 | 314 | 26,100 |

* 3 to 1 mole ratio



steels in flue gas mixtures by Nelson and Cain.(1,2) Figure 2 showing their results is included here for comparison. Maxima in the corrosion curves obtained by Nelson and Cain occurred at almost 1300 F, whereas the peak SO₃ reactivity in the experiments reported here was found at 1200 F. The fact that the SO₂ reactivity goes through a minimum in about the same temperature range that the SO₃ reactivity is a maximum, shows that the corrosion observed must be caused primarily by SO₃. The drop in reactivity above 1200 F can probably be explained by the decomposition of the trisulfate above this temperature.

FIGURE 2. CORROSION RATES OF STAINLESS STEEL OBSERVED BY NELSON AND CAIN(1)

Reactivity of K₂SO₄

The effect of substituting K₂SO₄ for Na₂SO₄ in the 3-to-1-mole-ratio sulfate-Fe₂O₃ mixture was investigated at 1100 F. Experiments were performed using the same gas mixtures as before. Figure 3 shows the results. Both SO₂ and SO₃ are more reactive with K₂SO₄ in the mixture than with Na₂SO₄ present. However, the increase with SO₃ is greater than with SO₂. Relative values at 1100 F based on the radioactivity count are:

$$\frac{\text{SO}_2 \text{ on } \text{K}_2\text{SO}_4 + \text{Fe}_2\text{O}_3}{\text{SO}_2 \text{ on } \text{Na}_2\text{SO}_4 + \text{Fe}_2\text{O}_3} = 1.7$$

$$\frac{\text{SO}_3 \text{ on } \text{K}_2\text{SO}_4 + \text{Fe}_2\text{O}_3}{\text{SO}_3 \text{ on } \text{Na}_2\text{SO}_4 + \text{Fe}_2\text{O}_3} = 2.2$$

$$\text{SO}_3/\text{SO}_2 \text{ ratio for } \text{K}_2\text{SO}_4 + \text{Fe}_2\text{O}_3 = 21.3$$

$$\text{SO}_3/\text{SO}_2 \text{ ratio for } \text{Na}_2\text{SO}_4 + \text{Fe}_2\text{O}_3 = 16.8$$

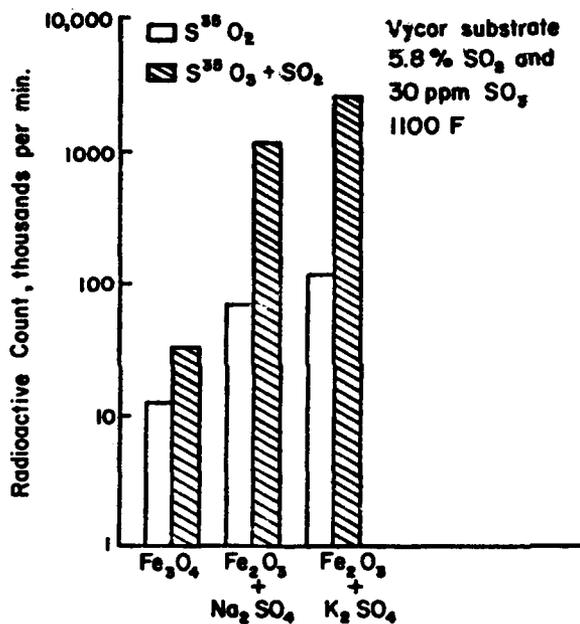


FIGURE 3. REACTIVITY OF SO₂ AND SO₃ WITH VARIOUS SURFACES

SO₂ + O₂ and of SO₃ is greater than that previously recorded with Fe₂O₃. Considering that Fe₃O₄ is always formed before Fe₂O₃ in an oxidizing iron system, intermediates to the trisulfates can probably start to form by reaction of Fe₃O₄ even before the surface of the iron is converted to Fe₂O₃, confirming work done earlier on this study using direct chemical methods.

It is a known fact that mixtures of K₂SO₄ and Na₂SO₄ form trisulfates at lower temperatures than does either pure component. Hence the greater reactivity of K₂SO₄ with sulfur oxides shown by these experiments demonstrates why K₂SO₄ is a major factor in high-temperature corrosion.

Reactivity of Fe₃O₄

To complete the data gathered previously at 1100 F, the reactivity of SO₃ with an Fe₃O₄ surface has been determined with radioactive sulfur at that temperature. The usual gas mixture was employed; the results are shown in Figure 3. The SO₃/SO₂ reactivity ratio is 2.6, which is consistent with the observation that all materials studied in this program to date have been more reactive with SO₃ than with SO₂. What is more significant is that the reactivity toward Fe₃O₄ both of

Effect of Lower SO₂ Concentration

Most of the early experiments at Battelle with S³⁵ were carried out using 5.8 percent SO₂ in the gas mixture because that concentration occurred in the flame studies and in the measurements of SO₃ concentration gradients over a

surface. This is a much higher SO_2 level than occurs in flue gas. Consequently, experiments made recently have been carried out with only 2500 ppm SO_2 to simulate boiler furnace conditions. The SO_3 concentration of 30 ppm used in these experiments also is about that formed in a flame when sulfur-containing fuels are burned, so it has always been at a realistic level in this work. Experiments in this series of tests were carried out at 1100 F with a gas mixture consisting of 78.9 percent N_2 , 20.8 percent O_2 , and 0.25 percent SO_2 . When SO_3 was used, 30 ppm were added.

Data from these runs are still considered tentative, because the results of an oxygen exchange experiment at 2500 ppm S^{35}O_2 are not yet available. For the present, the oxygen exchange correction of 10 percent found for 5.8 percent SO_2 is being used, although a smaller percentage correction is anticipated for an SO_2 concentration of 2500 ppm. With a mixture of Na_2SO_4 and Fe_2O_3 (3 to 1 mole ratio) on a Vycor substrate, reaction with 30 ppm SO_3 was 360 times greater than with 2500 ppm SO_2 . Previous results at 30 ppm SO_3 and 5.8 percent SO_2 gave a value of 16.8 for this SO_3/SO_2 reactivity ratio. Based on a linear extrapolation to the higher percentage of SO_3 in the mixture (30/2500 as compared to 30/58,000), the SO_3/SO_2 reactivity ratio would be 390. Hence the reactivity ratio of 360 obtained experimentally at 2500 ppm SO_2 in this system is in reasonable agreement with the extrapolated value.

Comparison of the relative reactivities of SO_2 and SO_3 with Fe_2O_3 at the two concentrations of SO_2 also was attempted, but the data obtained were inconclusive. Flow rates in the two sets of experiments were different, and the different residence times make the validity of comparisons doubtful. The experiment will be repeated later at the same flow rate to permit a better comparison.

OPTICAL MICROSCOPY STUDY OF DEPOSITS

Samples of boiler deposits from a number of stations have now been examined for trisulfate content by the index-of-refraction technique developed on this program. Details of the technique were given in the Second Summary Report, June 30, 1967, pages 17-18.

Flaky deposits furnished by R. C. Corey of the Bureau of Mines came mostly from wall tubes and were collected originally in 1943-1945 from several sites where external corrosion may have been occurring. Two different samples from the rear wall of the same boiler at 12th Street Station in Richmond each contained a few crystals of the trisulfate. A white crystalline material in the deposit from Delray Station, in this case from a superheater tube, consisted of Na_2SO_4 mixed with a substantial amount of the trisulfate. A few small crystals of trisulfate could be detected in a sample from a screen tube at Springdale Station. No positive identification of trisulfate could be made in a wall-tube sample from Windsor Station, but the sample was collected 12 feet above the floor where corrosion was at least questionable. Corey points out that the sample from Delray came from a stoker-fired boiler where superheater corrosion was just beginning to be a problem.

A sample of deposit obtained recently from the Cromby Station of Philadelphia Electric Company showed no trisulfate on the inner surface of the deposit in contact with the tube. A sample taken 1/32 inch from the inner surface contained very small crystals of highly refractive material, typical of the trisulfate but too small for positive identification. Material taken 3/32 inch from the inner surface definitely contained well-formed trisulfate crystals. This distribution indicates formation of the trisulfate from the iron oxide in the fly ash.

A deposit obtained recently by R. E. Barrett of Battelle from a boiler at Joppa also was examined. In this case, trisulfate was identified on the side of the deposit in contact with the superheater tube, although to the unaided eye the material appeared black. The white layer, about 1/32 inch from the tube metal in this case, contained a great deal of large, well-formed trisulfate crystals. The index of refraction of these crystals is indicative of substantial amounts of potassium present in the trisulfate. The orange-red powdery portion of the deposit, about 1/8 inch from the tube did not contain any trisulfate. This deposit appears to have formed trisulfate from the iron oxide on the tube surface as well as from that in the fly ash.

In boiler deposits from the Niles Station of Ohio Edison, obtained from Babcock & Wilcox, three distinct layers could be distinguished visually: (1) a light-colored layer at the tube surface, (2) a grey layer above it, and (3) an uppermost reddish powdery layer. Microscopic examination of material from these layers did not reveal any trisulfates, although both Fe_2O_3 and some sodium and potassium sulfates were present. A great deal of an unidentified phase having an index of refraction of about 1.666 was found in all of the layers, compared with a maximum index of Na- or K-iron sulfate of 1.628.

A powdered sample of the white layer in a deposit from the Ridgeland Station of Commonwealth Edison, also obtained from Babcock & Wilcox, contained trisulfates.

Several samples were examined from a Westinghouse gas turbine in Panama. These deposits were built up during 5000 hours of service burning cut residual fuel oil with <5 ppm V and <5 ppm Na, reduced to 0.05 ppm by washing. The fuel contained 1.2 percent sulfur. Operating temperature was 1350 F. Observations of the deposits showed the following:

- (1) First row, rotary compressor - mostly Fe_2O_3 , plus two unidentifiable anisotropic phases, not trisulfate.
- (2) Inlet scroll - Fe_2O_3 , plus anisotropic phase having index of refraction close to that of $Na_3Fe(SO_4)_3$. Crystallites very small and difficult to resolve.
- (3) Fourth rotating turbine - Fe_2O_3 plus crystals too small to identify.
- (4) Nozzle swirl caps - opaque particles, possibly carbon or Fe_2O_3 , anisotropic phase with index of refraction very close to that of $Na_3Fe(SO_4)_3$ - resolution difficult.

UNCLASSIFIED

- (5) Yellow deposit, pressure side 5th stage lower stationary - Fe_2O_3 , minor amount of Na_2SO_4 , and numerous small needles not identifiable.
- (6) Fourth row stationary turbine, from pressure side and round leading edge - mostly Fe_2O_3 , some Na_2SO_4 , third phase unidentifiable needles as seen in sample (5).
- (7) Fourth stage stationary suction turbine - Fe_2O_3 , and two anisotropic phases which are not sodium sulfate or the trisulfate.
- (8) Scale from inside secondary section combustor #1 and #3 - Fe_2O_3 and anisotropic phase growing around it; second anisotropic phase not sodium sulfate or trisulfate.

Considering the operating temperature of 1350 F, it is not surprising that trisulfates were not found in these specimens.

Deposits on hand from other companies will be examined during the remainder of the program.

OPTICAL MICROSCOPY STUDY OF INTERMEDIATES

In the investigation of the chemical intermediates which lead to trisulfate formation, it was found that a material having an index of refraction between that of Na_2SO_4 and $\text{Na}_3\text{Fe}(\text{SO}_4)_3$ could be obtained by passing SO_2 and O_2 over an Fe_2O_3 - Na_2SO_4 mixture for about half an hour. Crystals of this intermediate compound are formed around the Fe_2O_3 particles, and when 30 ppm SO_3 is added to the gas stream, the crystals are soon transformed to the trisulfate. With SO_3 present in the gas stream from the beginning of the experiment, a large amount of trisulfate forms while none of the intermediate compound can be seen.

With a mixture of Na_2SO_4 and $\text{Fe}_2(\text{SO}_4)_3$ in a 1 to 1 mole ratio heated in a stream of SO_2 and O_2 for several hours, a large number of trisulfate crystals are formed around the $\text{Fe}_2(\text{SO}_4)_3$ particles at both 900 F and 1000 F. Unreacted starting material is still present, but no intermediate compounds can be detected under these conditions. Efforts will be continued to prepare larger amounts of the intermediate compound to determine its composition by chemical analysis or X-ray diffraction.

FUTURE WORK

A few concluding experiments with S^{38} are planned. These will explore further the reactivity ratios of SO_3/SO_2 at the 2500 ppm level of SO_2 . The effect of using $\gamma\text{-Fe}_2\text{O}_3$ (magnetic) instead of $\alpha\text{-Fe}_2\text{O}_3$, the ordinary form, will be studied to decide whether this possible intermediate stage in the oxidation of iron has any effect on the corrosion mechanism. Emphasis will be placed on isolation and identification of the intermediate compound formed apparently before the trisulfate appears.

FURNACE STUDIES

by

R. E. Barrett

As in the earlier part of this work, the fuel-burning-furnace studies are intended to facilitate application of the fundamental studies to large boilers and gas turbines. Additional work was done this period with the electrochemical cell and some attempts were made to measure SO_2 levels beneath deposits. Work with various forms of electrochemical cells showed high chemical activity occurring almost at once when a specimen was exposed to corroding conditions, but the electrochemical relationships are so complicated that a separate detailed investigation would be necessary to identify all the variables. Hence further work on electrochemical systems was considered impractical on this project and the cell work was stopped. A few other exploratory experiments on the role of deposits in the corrosion mechanism were made before the furnace studies were recessed temporarily.

ELECTROCHEMICAL CELL

Figure 4 shows the results of a test with an iron:platinum cell using sodium carbonate as the corrodent mixture. The cell configuration was identical to that shown in Figure 7 of the Second Summary Report. No. 2 fuel oil without

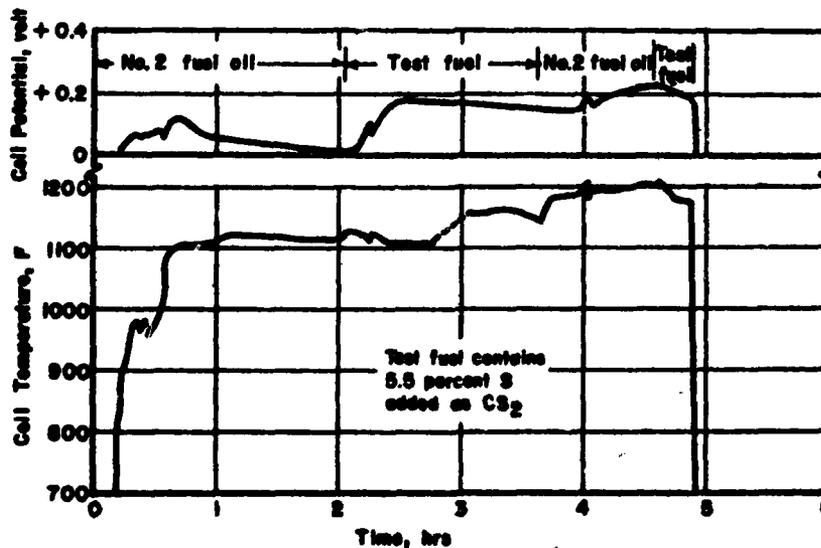


FIGURE 4. TEST USING IRON:PLATINUM CELL CONTAINING SODIUM CARBONATE

added sulfur was fired during the first two hours of this test; thereafter "test" fuel containing 5.5 percent sulfur added as carbon disulfide was burned intermittently with the low-sulfur No. 2 fuel. Measurement of the cell potential with no sulfur present either in the cell or in the flue gas gives an indication of the output that can be attributed to gas-phase oxidation of the iron. The low cell output of 0.1 volt measured during the first two hours of this test shows that the cell output of more than 0.8 volt measured in most previous tests is not the result of gas-phase oxidation and must have involved other mechanisms.

To decrease the time required to come to equilibrium, the cell design was modified slightly to reduce the mass of material required to bridge the gap between the iron and platinum electrodes. This was not expected to cause any significant change in cell operation or output. The new cell used a smaller boat than the previous cell and permitted two or more cells to be present in each test, thereby providing for a comparison of outputs of several cells containing different materials during a single test.

Figure 5 shows the results of a test with an alkali sulfate mixture (1 mole $\text{Na}_2\text{SO}_4 \cdot 1$ mole K_2SO_4) in one boat and an alkali sulfate-ferric oxide mixture (1.5 mole $\text{Na}_2\text{SO}_4 \cdot 1.5$ mole $\text{K}_2\text{SO}_4 \cdot 1$ mole Fe_2O_3) in a second boat. The cell potential for this test was similar to that observed in previous tests with the alkali sulfate mixture - an initial voltage peak was followed by a decay of cell potential. Some details of the test with the alkali sulfate-ferric oxide mixture

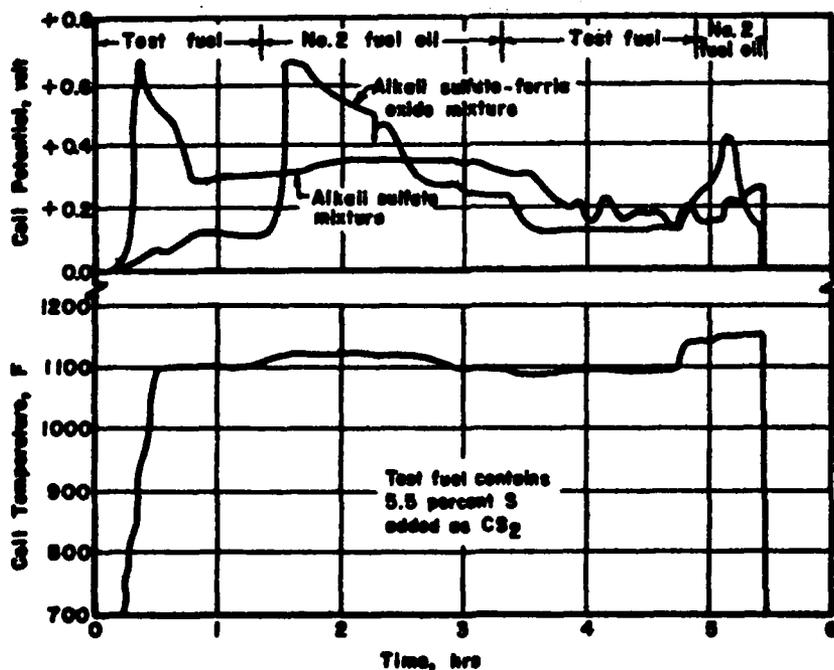


FIGURE 5. TEST USING IRON:PLATINUM CELLS CONTAINING ALKALI SULFATE AND ALKALI SULFATE-FERRIC OXIDE MIXTURES

in the boat have not been explained. One unexplained result is the increase in cell potential observed when switching from a high-sulfur to a low-sulfur fuel. These shifts of cell potential may be associated with unavoidable temperature changes which occur simultaneously with changes of fuel.

Optical microscopy techniques have now been used to examine the specimens from previous tests. Such examination indicated that trisulfates definitely were formed in one test, Figure 10, and possibly were formed in another, Figure 11 of the Second Summary Report. The average temperature of the test in which trisulfates definitely were produced was 975 F with the temperature never exceeding 995 F. Inability to identify trisulfates positively in tests at higher temperatures could result from the instability of trisulfates heated above 1000 F in atmospheres low in SO_2 .

Four samples were examined of the deposit from each test specimen, to insure that the presence or absence of trisulfates in deposits could not be attributed to a sampling error. In each case, trisulfates were present in all four samples from a particular specimen, or trisulfates were absent in all samples. Hence the positive identification of trisulfate can be taken as proof that this material was actually present, while its absence is nearly equally good evidence that the trisulfates were not present in amounts great enough to be significant.

It is not known why trisulfates were definitely formed in one test but not during others where the electrochemical cell indicated a similarly high rate of corrosion. More detailed studies of the electrochemistry of corrosion under these special test conditions no doubt would be useful, but such work was not considered to be within the scope of this investigation.

A paper describing a more detailed study of the electrochemistry of sulfate corrosion has been presented by Cutler, Fountain, Hart, and Holland.⁽³⁾ Some of their observations of voltage peaks and voltage decay agree closely with results obtained in this study. In general, these authors conclude that a corrosion potential can be measured on an inert metal against a fixed-reference electrode. They show that the potential at steel electrodes can be used to indicate the occurrence of corrosion while the current passing through this electrochemical cell is a measure of the rate of corrosion. These conclusions are essentially identical to those reached in the Battelle study. In explaining the initial high potential in an electrochemical corrosion test followed by a gradual decrease in voltage with time, as observed with most of the Battelle specimens, these authors interpret the effect as being caused by the gradual formation of an oxide film on the surface of the metal. The abrupt rise in cell voltage when the temperature is increased stepwise probably occurs because of changes in this oxide film, but the exact mechanism is still obscure.

This British work explains many of the factors involved in high-temperature corrosion, such as the electrode process that occurs at the edge of deposits, and the deviation from a parabolic corrosion rate caused by intermittent cracking of a protective oxide layer. Many of their conclusions must be considered speculative, however, until more experimentation is done either in boiler furnaces or under closely simulated furnace conditions. This is a fruitful field for research, but one that will require careful interpretation to make the results useful in the field.

SO₃ CONCENTRATIONS BENEATH DEPOSITS

Although it has been recognized for many years that external corrosion occurs only beneath deposits, the exact explanation of how deposits lead to corrosion is still obscure. Some work has been started recently to investigate some of the many possible factors.

Figure 6 is a sketch of a device constructed for determining the SO₃ concentration and the formation of trisulfates beneath deposits in the fuel-burning furnace. The container to hold the deposit being examined is constructed of stainless steel to minimize catalysis on its surfaces. An 18-gauge iron sheet is wrapped over a stainless steel tube through which the gas sample is drawn to provide an oxidizable surface to simulate tube scale. The material simulating a

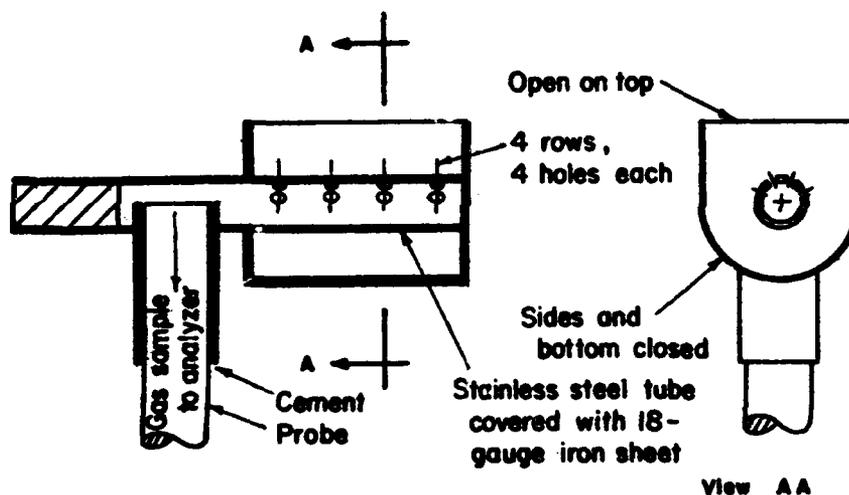


FIGURE 6. SYSTEM FOR DETERMINING EFFECT OF DEPOSITS ON FORMATION OF CORROSIVE CONDITIONS IN FUEL-FIRED FURNACE

deposit is applied over this iron surface in a layer about 0.5 inch thick. To prevent the furnace flue gas from blowing this material out of the holder, the top layer is dampened initially with acetone. During the test, flue gas is drawn through the deposit at a rate of about 0.07 cu ft per hr to simulate the limited gas movement expected under a normal deposit, giving a residence time of from 0.5 to 1.0 minute. Temperatures are measured by a thermocouple imbedded in the deposit holder. Actual deposit material temperatures may vary slightly from the measured temperatures.

Table 2 lists the measured SO₃ concentrations for two tests at 1000 F with the deposit holder filled: (1) with a mixture of Na₂SO₄, K₂SO₄, and Fe₂O₃, and (2) with Fe₂O₃. The SO₃ concentrations of the gas drawn through these "deposits" were 140 ppm to 435 ppm for Test 1, and 80 ppm to 245 ppm for Test 2, compared with the 30-ppm SO₃ concentration in the bulk flue gas entering the

TABLE 2. SO₃ CONCENTRATIONS BENEATH DEPOSITS

| Test | Deposit | Average Temperature, F | SO ₃ Measured Beneath Deposit, ppm | | Sulfur Oxides in Bulk Flue Gas | |
|------|---|------------------------|---|---------|--------------------------------|-------------------|
| | | | Average | Range | SO ₃ | SO ₂ * |
| 1 | Na ₂ SO ₄ , K ₂ SO ₄ , Fe ₂ O ₃ | 1000 | 268 | 140-435 | 30 | 3200 |
| 2 | Fe ₂ O ₃ | 1003 | 123 | 80-245 | 31 | 3200 |

* By calculation.

device. These tests demonstrate mainly that conditions in the system are suitable for forming SO₃ when the materials present are known to be catalytic.

Based on earlier work, Fe₂O₃ was expected to produce a much higher SO₃ concentration than the Na₂SO₄-K₂SO₄-Fe₂O₃ mixture. Catalytic studies in the fuel-burning furnace at 1175 F to 1190 F showed that Fe₂O₃ was at least 10 times as catalytic as this mixture. Also, profile studies at 1100 F reported in the First Summary Report showed that the SO₃ concentration above an Fe₂O₃-covered surface was 10 times the concentration above a surface covered with a mixture of Fe₂O₃ and Na₂SO₄. Possibly the lower temperature was responsible for the results observed in the recent test. Another possible explanation is that SO₃ being formed by the flue gas passing through the "deposit" was reacting rapidly with the deposit so that it would not be observed in the gas sample leaving the system.

Examination of the deposit from Test 1 showed that a 1/16-inch-thick layer of whitish material developed near the top of the deposit. Optical microscopy techniques definitely established the presence of trisulfates in the whitish layer. The material in the vicinity of the layer was somewhat chunky and under the microscope had a sintered appearance. Visual examination showed no indication of melting.

EXAMINATION OF DEPOSITS

Samples of undisturbed superheater tubes in corrosion areas were collected on September 16, 1967, in a visit to Joppa Station of Electric Energy, Inc. Mr. Jesse Jacob, Chief Chemist at the Joppa Station, was particularly helpful in assuring that useful specimens were obtained for laboratory analysis. Several samples of deposits were obtained intact on sections of superheater elements which show the layered structure typically associated with corrosion.

One of the deposits from Joppa from a ferritic reheater tube with a metal temperature estimated to be 1025 F was examined microscopically and with the electron-probe microanalyzer. The specimen, mounted in plastic, was polished under oil to prevent loss of water-soluble portions during preparation. This particular specimen, shown in Figure 7, included the blackish metal oxide layer, the entire white layer, and the reddish outer layer of ash.

TECHNICAL DETAILS

Figure 8 is a 15X photograph of a polished section through the specimen showing the three layers. Figure 9 is a 100X photomicrograph of the area within the box marked on Figure 8. It shows the heterogeneous nature of the deposit.

Figures 10 through 15 are microprobe photos of a 185-by-185-micron section of the white layer. These photos show the occurrence and distribution of the elements K, Na, Fe, S, Si, and Al. Estimated occurrence of these elements in the white layer is as follows:

- K - spots with up to about 5 percent.
- Na - significantly less than K, maybe 2 percent in spots.
- Fe - small quantities.
- S - much, spots with up to 35 percent.
- Si - much.
- Al - some.

Some similarities can be seen in the patterns for all elements except that of Si, which is essentially the negative of the other patterns. These figures show the heterogeneous nature of the distribution of elements in the white layer.

The S and Fe content of the darker layer are estimated to be as high as 35 and 50 percent, respectively. This probably reflects the presence of FeS in the tube-side layer.

Figure 16 summarizes microprobe traces made across the specimen and which included all three layers. These profiles also show the nearly random nature of the various layers.

Optical-microscopy examination of the same deposit specimen shows the presence of trisulfate on the side of the deposit in contact with the superheater tube, although to the unaided eye the material appeared black. The white layer, about 1/32 inch from the tube metal in this case, contained a great deal of large, well-formed trisulfate crystals. The index of refraction of these crystals was indicative of substantial amounts of potassium present in the trisulfate. The orange-red powdery portion of the deposit, about 1/8 inch from the tube, did not contain any trisulfate. In this deposit, it is evident that trisulfates formed both from the iron oxide on the tube surface and from that in the fly ash.

The main impression given by these examinations is the random way in which the deposit varies in composition from point to point. What may appear to be relatively uniform areas to the unaided eye turn out to be made up of a great many individual chemically different areas at moderately high magnification.



FIGURE 7. DEPOSIT SPECIMEN FROM T-11 FERRITIC REHEATER
TUBE OF JOPPA STATION



Tube Side

FIGURE 8. SECTION THROUGH JOPPA SPECIMEN AT 15X

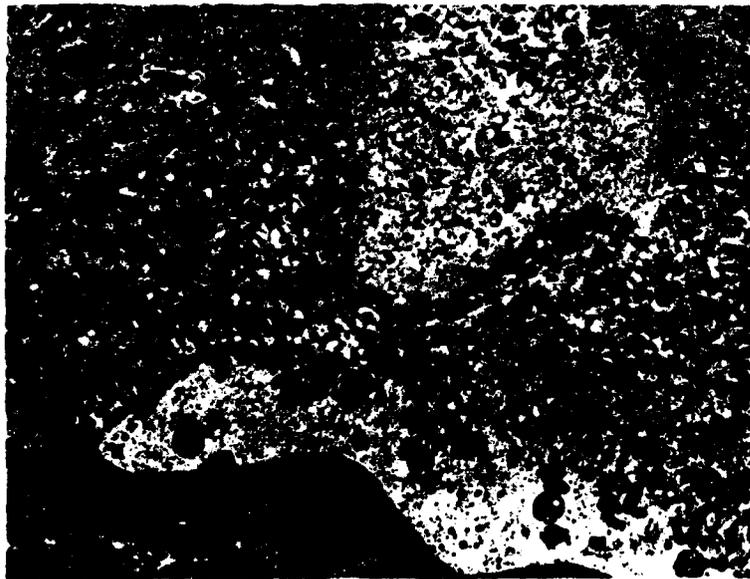


FIGURE 9. SECTION THROUGH JOPPA SPECIMEN AT 100X

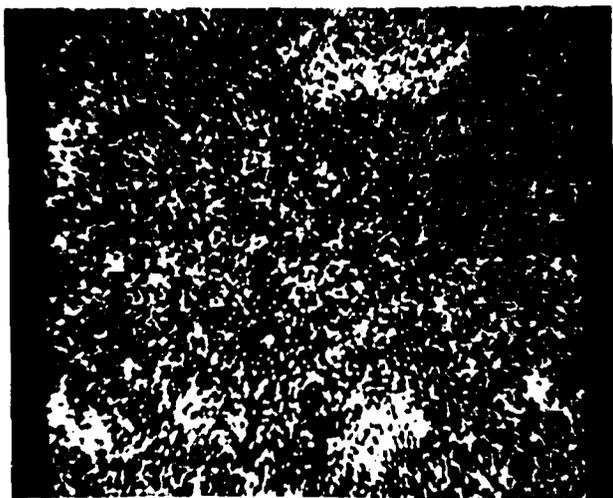


FIGURE 10. POTASSIUM DISTRIBUTION



FIGURE 11. SODIUM DISTRIBUTION



FIGURE 12. IRON DISTRIBUTION

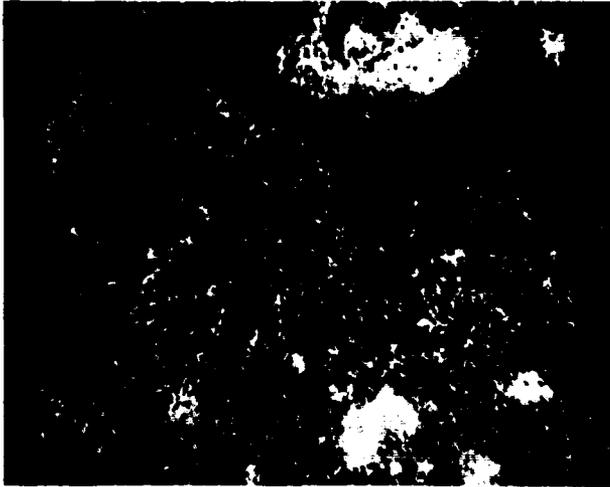


FIGURE 13. SULFUR DISTRIBUTION

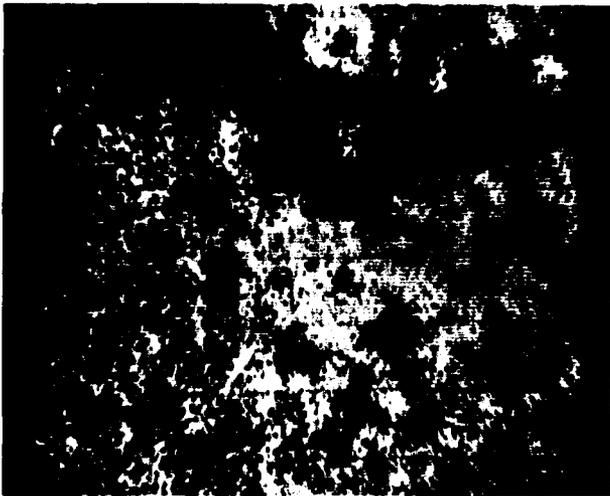


FIGURE 14. SILICON DISTRIBUTION

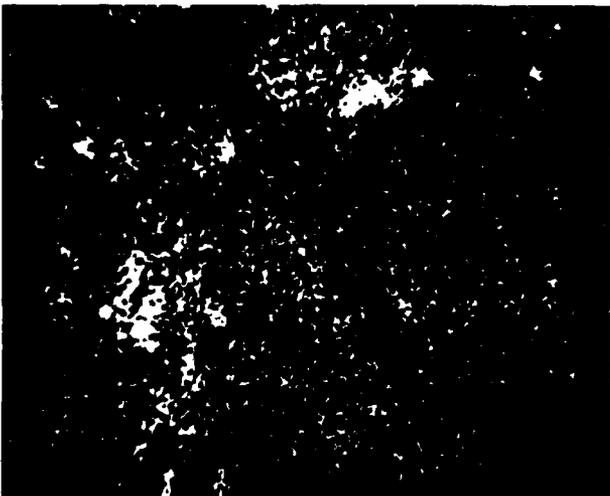
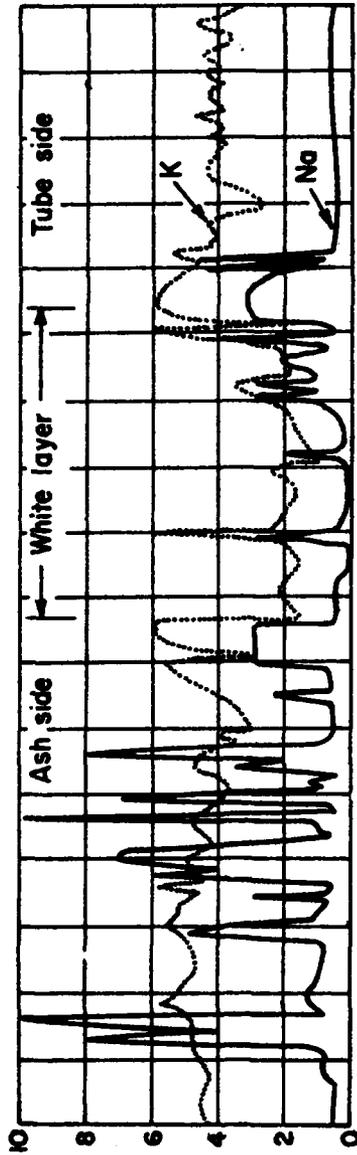
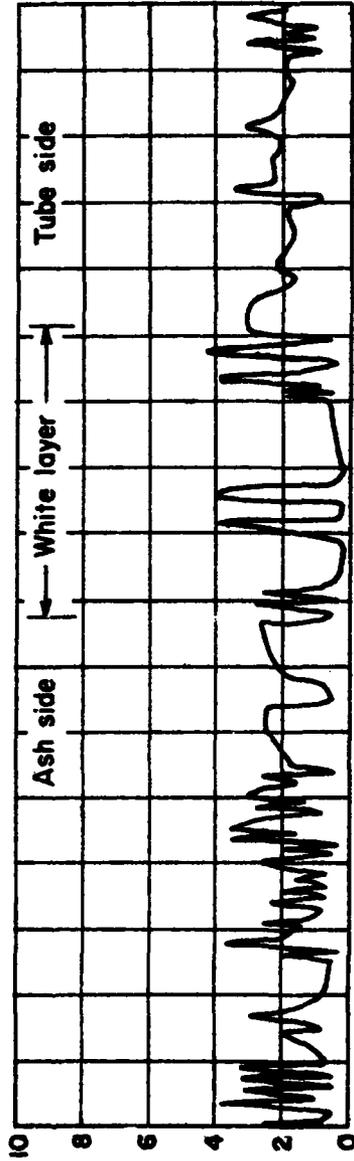


FIGURE 15. ALUMINUM DISTRIBUTION



a. Potassium and Sodium Profiles



b. Sulfur Profile

FIGURE 16. PROFILES OBTAINED ON MICROPROBE TRAVERSES THROUGH JOPPA SPECIMEN

Intensity units are relative and scale differs for each element.

STAFF REPORT

FUTURE WORK

During the next several months, the furnace studies will be concentrated on determining the effects of deposits on formation of trisulfates.

One technique for studying deposits will be to conduct tests utilizing the device shown in Figure 6 with a number of materials and material combinations such as:

Single Layer: Fe_2O_3
 $\text{Fe}_2\text{O}_3 + \text{Na}_2\text{SO}_4$
 $\text{Fe}_2\text{O}_3 + \text{K}_2\text{SO}_4$
 $\text{Fe}_2\text{O}_3 + \text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4$
 $\text{Fe}_2\text{O}_3 + \text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{CaCO}_3$
 $\text{Fe}_2\text{O}_3 + \text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{CaSO}_4$
 $\text{Fe}_2\text{O}_3 + \text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{MgSO}_4$
 $\text{Fe}_2\text{O}_3 + \text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{Kaolin}$

Two Layers: Fe_2O_3 over $\text{Fe}_2\text{O}_3 + \text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4$
 $\text{Fe}_2\text{O}_3 + \text{CaSO}_4$ over $\text{Fe}_2\text{O}_3 + \text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4$
 $\text{Fe}_2\text{O}_3 + \text{MgSO}_4$ over $\text{Fe}_2\text{O}_3 + \text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4$
 $\text{Fe}_2\text{O}_3 + \text{Kaolin}$ over $\text{Fe}_2\text{O}_3 + \text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4$
Fly ash over $\text{Fe}_2\text{O}_3 + \text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4$.

These layers of materials will simulate the layered structure found in deposits on tubes. A small quantity of flue gas will be drawn through these samples as in previous tests. Temperatures during these tests will be varied from 900 F to about 1100 F to cover the range where trisulfate formation seems most pronounced.

Another technique for investigating the effects of deposits would be to deposit a layer of material that has passed through the flame or been injected just downstream of the flame. Consideration would have to be given to the fact that rapid quenching of the flue gas by the cool furnace walls might not provide a good simulation of conditions in a boiler.

TABLE 3. EFFECT OF EXCESS OXYGEN ON SO₂ FORMATION FOR COAL AND OIL⁽⁴⁾

| Oxygen in Flue Gas, percent | SO ₂ Concentration, ppm by volume | | |
|-----------------------------|--|---------------|---------------|
| | 6.3 percent S | 7.3 percent S | 5.5 percent S |
| | Coal | Coal | Oil* |
| 0.25 | 5 | 3 | - |
| 0.50 | 10 | 5 | 13 |
| 1.00 | 20 | 11 | 17 |
| 1.50 | 28 | 16 | 23 |
| 2.00 | 35 | 22 | 28 |
| 2.50 | 41 | 28 | 32 |
| 3.00 | 46 | 33 | 37 |
| 3.50 | 50 | 38 | 40 |
| 4.00 | 52 | 43 | 42 |
| 4.50 | 53 | 48 | 43 |
| 5.00 | 54 | 53 | - |
| 5.50 | 53 | 56 | - |

* Sixth Summary Report to ASME Research Committee on Corrosion and Deposits from Combustion Gases, October 31, 1965, p. 43.

The use of high-temperature electrochemical probes in following corrosion from combustion with low excess air in oil-fired boilers has been described briefly by Pfeiffer.⁽⁶⁾ He also investigated the action of dolomite added to coal in conjunction with partial limiting of the oxygen level. Adding limestone or dolomite to boiler furnaces, either with the coal or with separate injection systems into the furnace, are now being proposed widely as an inexpensive way to decrease the emission of SO₂ from central-station plants. Such additives also would eliminate corrosion if, indeed, all the sulfur oxides in the flue gas were captured. Fouling certainly would become more troublesome.

Experiences in Europe

It will be recalled that the initial demonstration of the effectiveness of using combustion control to minimize acid-smut emission and cold-end corrosion was carried out in England at Bankside A power station over 10 years ago.^(7,8) The CEGB has continued the development of this technique and has adapted several stations to its use. Furthermore, the benefits were such that the new 500-mw plant at Fawley was designed to operate at excess oxygen levels not to exceed 1 percent and with the understanding that it probably would be operated at such lower levels.

One of the more practical developments to be reported recently by CEGB^(7,8) is concerned with details of burner design and installation procedures. Detailed examples are given of how the components are integrated into the system to produce improved operation. It is significant that discussions of this work brought out the fact that the final steam temperature at the boiler outlet was still limited to about 1000 F to minimize gas-side superheater corrosion.

Glaubit⁽⁹⁾ again has pointed out the elimination of corrosion in cold areas of boilers when operating with no more than 0.2 percent excess oxygen. Operating time in his units has now covered over 45,000 working hours. The boilers also remain free from high-temperature corrosion.

Pfeiffer⁽¹⁰⁾ described the construction and use of test electrodes for following high-temperature corrosion in an operating boiler. The types of readings obtained with his electrochemical system indicate whether the flue gas atmosphere is oxidizing-corrosive, reducing-corrosive, or harmless. Pfeiffer's system has been used as an aid in regulating combustion in oil-fired unit to obtain minimum corrosion using low excess air.

A brief summary of combustion procedures involving low excess air has been translated recently.⁽¹¹⁾ No new or original data were presented.

The effect of changes in excess air on boiler operation is also being studied in the Soviet Union.⁽¹²⁾ Results are reported on a study of the effect of the burner arrangement on heat absorption of the individual superheaters in three different boilers. No cleaning of the external superheater surface was required during 2400 hours of operation.

Another interesting study has been reported from Russia concerning corrosion in high-temperature areas of a boiler operating with low excess air.⁽¹³⁾ The unit burned oil containing 3 percent sulfur, with excess air at 2 to 3 percent. Corrosion specimens were exposed at temperatures ranging from 850 F to 1250 F, with corrosion rates varying from relatively low values at the lower temperature to about 30 mil/yr at 1200 F. It was concluded that limiting the air for combustion reduced low-temperature corrosion but was not effective in retarding high-temperature corrosion. The authors suggested additives for combating vanadium corrosion.

These same investigators⁽¹⁴⁾ concluded that the minimum allowable temperature of the regenerative air heaters should be 185 F for burning oil containing 2.5 to 3.0 percent sulfur and when operating the boiler at about 2 to 3 percent excess air.

Other Russian experience with low excess air (about 0.5 percent oxygen) as reported by Kharuzin⁽¹⁵⁾ indicates a reduction in corrosion by a factor of 5 and the formation of easily removed deposits.

Additives together with combustion with low excess air have been investigated recently in Italy.⁽¹⁶⁾ The effective use of a liquid organic-base additive is described, but the composition of the additive is not given. These tests show, interestingly enough, that the amount of SO₂ in the economizer was always higher than in the superheater, demonstrating the effect of catalysis on the superheater surfaces. This action cannot always be demonstrated in large boiler furnaces although, theoretically, it should occur.

Recent developments in France on combustion with low excess air have been presented in a two-part paper⁽¹⁷⁾ showing that in their case: (1) high-precision monitoring of combustion was essential, (2) the fuel oil had to be pre-heated, and (3) special combustion controls were required. Detailed descriptions of procedures followed in modifying the station and in controlling operations are given. A gas chromatograph was used to follow combustion changes. It was concluded that any reduction of excess air, when firing No. 2 fuel oil, reduces corrosion and fouling of the low-temperature heat exchangers. Optimum excess air values for these investigators are in the range of 2 to 3 percent at full load. As added insurance of trouble-free operation, 900 Pyrex glass tubes replaced steel tubing in part of the low-temperature air heater.

An interesting review of current thinking in CEGB regarding operation with low excess air, about high temperature oil-ash corrosion, and the effects of these variables on general operating economy has been presented by Jackson.⁽¹⁸⁾ He concluded that a marginal economic gain could be provided by extracting more heat from the flue gases, although further gains would be possible if the final steam temperature could be raised to 1050 F. Material limitations to provide this higher temperature have been under study at various laboratories under overall coordination by CEGB. Preliminary results suggest that only a 12Cr ferritic steel would be acceptable at current concentrations of excess oxygen (0.5 to 1.0 percent) provided mechanical and fabrication requirements can be met. It was shown further that the corrosion rate drops off at lower ranges of oxygen and that at 0.3 percent excess oxygen either Type 437 austenitic steel or 12Cr ferritic steel should have adequate corrosion resistance.

Crossley⁽¹⁹⁾ has prepared a more recent commentary on corrosion and fouling. He emphasizes the effectiveness of decreasing the formation of SO_3 by limiting the supply of oxygen.

A general review of combustion with low excess air has been presented by Brown.⁽²⁰⁾ He concludes that benefits in reducing low-temperature corrosion are well demonstrated. The effect of low-excess-air combustion on high-temperature deposition is not well defined, and more controlled experiments in this area of research are recommended.

One of the more extensive studies of combustion control carried out in the past few years was a cooperative program reported by Bunz, Niepenberg, and Rendle.⁽²¹⁾ Front-wall and corner-fired water-tube boilers were operated near stoichiometric combustion conditions (down to 0.05 percent excess oxygen). The study followed the relationship between the oxygen content of the flue gas and the following factors:

1. SO_3 concentration.
2. Acid dew point.
3. Rate of acid build-up.
4. Low-temperature corrosivity.
5. Solids burden.

The depth of the program is better understood from the fact that five types of oil, two types of boilers, and three steam loads were involved.

Results cannot be reported here in detail, but it should be mentioned that the first four factors listed above all grew larger as the excess oxygen was greater. At about 0.2 percent excess oxygen, the SO_3 was in the range 6 to 12 ppm. The solids burden, of course, decreased as the excess oxygen was increased. The sulfur content of the fuel oil (1.7 to 3.6 percent S) was found to be important, but the effect was small at low levels of excess oxygen.

The design of firing and control equipment so that a boiler can be operated at low excess air levels was outlined by Niepenberg.⁽²²⁾ No definite conclusions were drawn from the work still in progress, but it was stated that low-temperature corrosion was almost eliminated. Niepenberg believes that catalytic oxidation of SO_2 to SO_3 is negligible.

The same author discussed combustion control in somewhat more detail in another paper of the same title.⁽²³⁾ Control of excess air was related to flue gas analysis, using paramagnetic measurement for oxygen and infrared absorption for carbon dioxide. Controls involve: fuel oil flow, atomizing steam and oil pressure, fuel oil temperature and viscosity, air pressure behind air heater, and combustion air. It was concluded that measuring and control equipment is still in the development stage, and that continuing efforts are required to devise suitable systems. It should be pointed out that the procedure has been used in boiler plants of various sizes and no corrosion on the flue-gas side has been detected when excess air is sufficiently low.

Experiences in This Country

Low excess air has been employed in a few cases by oil-fired stations in this country, but the overwhelming acceptance accorded this scheme in Europe has not been duplicated in the United States as yet.

According to Childs⁽²⁴⁾, a station on the East Coast was designed specifically for this application, using 2.5 percent excess air. Startup of this installation was scheduled for 1967. In 1963, the Long Island Lighting Company began using low-excess-air combustion with about 2.0 percent excess air coupled with the addition of finely divided MgO as a means of reducing acid-smut problems.⁽²⁵⁾ One unique development has been the value of the recovered concentrated V_2O_5 product which has more than offset the cost of the added MgO .

A description of controls needed for low excess air was presented at the ninth annual Power Instrumentation Symposium of the Instrument Society of America.⁽²⁶⁾

There have been many arguments about how elaborate the controls must be for low excess air, depending somewhat on the design of the furnace. The following requirements have been specified for low-excess-air control of a tangentially fired boiler:

1. Burner air flow must be carefully balanced by adjustment of secondary air dampers.

TECHNICAL DATA

2. Accurate recording of flue gas oxygen and combustibles should be coupled with suitable alarms.
3. Accurate metering of total air and total fuel is required.
4. Fuel should be limited to available air.
5. Windbox-to-furnace differential must be maintained above an acceptable minimum.
6. Rapid response on furnace draft control is needed.
7. Stable pressure control over wide load requirements is important.

Methods for accomplishing the desired controls are described. It is reported that the boiler at Long Island Lighting Company is operating on automatic load control over a wide range. The excess air is adjusted automatically between 2 percent at full load to 4 percent at half load. The heat rate at this station has been improved 1 percent as a result of the operation with low excess air coupled with use of an additive.

An interesting technique was described by Bender⁽²⁷⁾ to provide low-excess-air operation of smaller, industrial or commercial boiler plants to minimize danger of corrosion and fouling. The procedure employs sonic or ultrasonic oscillations to achieve good combustion in acoustic burners.

A useful review paper on corrosion was presented in Canada two years ago, ⁽²⁸⁾ discussing the fire-side corrosion of utility and industrial boilers firing coal, residual fuel, or kraft black liquor. Evidence is presented showing that low-temperature corrosion from combustion of oil can be prevented by a combination of low excess air and alkaline earth additives.

Summary

These many investigations illustrate the continuing interest in low-excess-air operation. Those papers which discuss useful operating levels of oxygen and/or corrosion are listed in Table 4 along with the corresponding references which can be studied for details. A differentiation is shown as to whether the method was effective in reducing either high- or low-temperature corrosion. It can be seen that operating oxygen levels near 0.3 percent are favored, and that large stations have been burning residual fuel with low excess air. Note also that both high- and low-temperature corrosion have been alleviated in nearly all instances. Only one investigator reported that high-temperature corrosion is not reduced by operation with low excess air; all others indicate favorable results. A reduction in low-temperature corrosion by means of combustion control seems to be found in all cases where it has been evaluated.

TABLE 4. SUMMARY OF RESULTS OF OPERATION WITH LOW EXCESS AIR

| Reference | Fuel | Size of Operation | Optimum Operating Range, Oxygen, percent | Effective in Reducing Corrosion* | |
|-----------|------|-------------------|--|----------------------------------|-----------|
| | | | | High Temp. | Low Temp. |
| 4 | Coal | Pilot | 0.3-1.0 | - | Yes |
| 6 | Coal | Large | Not Given | Yes | - |
| 7 | Oil | Large | 0.3-0.8 | - | Yes |
| 8 | Oil | Large | 0.3-0.8 | - | Yes |
| 9 | Oil | Large | 0.25 | Yes | Yes |
| 10 | Oil | Large | 0.4-0.7 | Yes | - |
| 11 | Oil | Large | 0.5 | - | Yes |
| 12 | Oil | Large | 0.7 | Yes | - |
| 13 | Oil | Large | 0.3-0.5 | No | Yes |
| 14 | Oil | Large | 0.3-0.5 | - | Yes |
| 15 | Oil | Large | 0.5 | Yes | - |
| 16 | Oil | Large | 2.0 | - | Yes |
| 17 | Oil | Large | 0.3-0.5 | - | Yes |
| 18 | Oil | Large | 0.1-0.5 | Yes | - |
| 21 | Oil | Large | 0.2 | - | Yes |
| 22 | Oil | Large | 0.2-0.5 | - | Yes |
| 23 | Oil | Large | 0.25-0.5 | - | Yes |
| 24 | Oil | Large | 0.3 | - | Yes |
| 25 | Oil | Large | 0.1-0.3 | Yes | Yes |
| 26 | Oil | Large | 0.1-0.2 | - | - |
| 27 | Oil | Medium | 2.75 | - | - |
| 28 | Oil | Large | 0.5 | Yes | Yes |

* Blank space indicates no measurements made.

It appears certain that additional work can be expected in this field, particularly with respect to combustion of coal. With its high ash content, coal may behave satisfactorily at somewhat higher levels of excess air than is necessary with fuel oil, perhaps easing in part the problem of mixing involved with solid particles compared with liquid droplets. As the state of the art improves with low-excess-air operation of residual fuel oil, attention can be expected to be directed toward similarly good combustion of pulverized coal. Reduced corrosion in the high-temperature range where the complex sulfates are molten would be anticipated and this area of research needs study.

TECHNICAL DETAILS

LIST OF REFERENCES

- (1) Wharton Nelson and Carl Cain, Jr., "Corrosion of Superheaters and Reheaters of Pulverized-Coal-Fired Boilers", Trans. ASME, J. Eng. Power, vol. 82, Series A, no. 3, July, 1960, pp. 192-204.
- (2) Carl Cain, Jr. and Wharton Nelson, "Corrosion of Superheaters and Reheaters of Pulverized-Coal-Fired Boilers, II", Trans. ASME, J. Eng. Power, vol. 83, Series A, no. 4, Oct. 1961, pp. 468-474.
- (3) A.J.B. Cutler, M. J. Fountain, A. B. Hart, and N. H. Holland, "Electrode Processes in the Corrosion of Steel by Sulphate Deposits", ASME Paper No. 67-WA/CD-4, presented at ASME Winter Annual Meeting, Pittsburgh, Penna., Nov. 12-17, 1967.
- (4) G. K. Lee, F. D. Friedrich, and E. R. Mitchell, "Effect of Fuel Characteristics and Excess Combustion Air on Sulphuric Acid Formation in a Pulverized-Coal-Fired Boiler", J. Inst. Fuel, vol. 40, no. 320, Sept. 1967, pp. 397-405.
- (5) "Improving Boiler Combustion", The Engineer, vol. 224, no. 5815, July 7, 1967, pp. 12,13.
- (6) W. Pfeiffer, "Development of an Instrument for the Measurement of High-Temperature Corrosion", Mitt. V.G.B., vol. 86, Oct. 1963, pp. 300-309.
- (7) W.J.D. Brooks, L. Holmes, and D. B. Leason, "Power Station Oil Burner Systems for Low Excess Air Operation", J. Inst. Fuel, vol. 38, no. 292, May, 1965, pp. 218-237.
- (8) Discussion of Ref. (4), J. Inst. Fuel, vol. 39, no. 310, Nov. 1966, pp. 485-495.
- (9) F. Glaubitz, "Prevention of Corrosion in Oil-Fired Boilers by Burning the Oil with Extremely Low Excess Air", Werkstoffe und Korrosion, vol. 16, no. 12, Dec. 1965, pp. 1033-1039.
- (10) W. Pfeiffer, "Results of a Continuous Check on Materials for High-Temperature Corrosion by Measuring the Electromotive Force", Werkstoffe und Korrosion, vol. 16, no. 12, Dec. 1965, pp. 1013-1024.
- (11) P. de Lachaux, "Burning Sulfurous Fuels with Slight Excess Air", Fuel Efficiency, vol. 14, no. 1, Jan. 1966, pp. 14-17.
- (12) L. A. Goikhman, Yr. A. Migalin, and L. G. Madoyan, "A Performance Study of TM-84 Boiler Burning High Sulfur Oil", Thermal Engrg., vol. 13, no. 2, Feb. 1966, pp. 35-40.
- (13) R. A. Petrosyan and N. D. Sergeeva, "High-Temperature Corrosion Rate When Burning High-Sulfur-Content Oil with Low Excess Air", Thermal Engrg., vol. 13, no. 11, Nov. 1966, pp. 65-69.
- (14) R. A. Petrosyan and N. D. Sergeeva, "Corrosion of Sulfur-Bearing Fuel Oil With Small Excess Amounts of Air", Thermal Engrg., vol. 13, no. 5, May, 1966, pp. 53-56.

- (15) M. E. Karuzin and Iu. P. Eniakin, "Combustion of Sulfur-Bearing Fuel Oil With Small Excess Amounts of Air", *Elektricheshu Stantsu*, no. 10, Oct. 1965, pp. 20-23.
- (16) M. Bartoletti and B. Wichser, "Recent Experiences With Organic Additives to Prevent Corrosion and Fouling of High and Low-Temperature Surfaces in High-Pressure Steam Generators", *Combustion*, vol. 38, no. 11, May, 1967, pp. 29-32.
- (17) René Cardinal and Jean Glevarec, "Industrial Low Excess Air Operation of the Nantes-Chevire Power Station Unit No. 4", Part I - Combustion, vol. 37, no. 11, May, 1966, pp. 20-27; Part II - Combustion, vol. 37, no. 12, June, 1966, pp. 18-23.
- (18) P. J. Jackson, "Generating Station Efficiencies", Proc. of Conf. on Applications of Liquid Fuels, Torquay, England, 18-22 April 1966, Institute of Fuel.
- (19) H. E. Crossley, "External Fouling and Corrosion of Boiler Plant: A Commentary", presented at Symposium on the Science and Technology of Coal, Ottawa, Ontario, March 31, 1967.
- (20) T. D. Brown, "The Case for Stoichiometric Combustion", *Combustion*, vol. 37, no. 10, April, 1966, pp. 40-45.
- (21) P. Bunz, H. P. Niepenberg, and L. K. Rendle, "Influences of Fuel Oil Characteristics and Combustion Conditions on Flue Gas Properties in Water-Tube Boilers", *J. Inst. Fuel*, vol. 40, no. 320, Sept. 1967, pp. 406-416.
- (22) Horst P. Niepenberg, "Combustion Control of Oil-Firing Systems Operated at Low Excess-Air Levels", *J. Fuel and Heat Tech.*, vol. 14, no. 7, July, 1966, pp. 34-36.
- (23) Horst P. Niepenberg, "Combustion Control of Oil-Firing Systems Operated at Low Excess-Air Levels", Proc. of Conf. on Applications of Liquid Fuels, Torquay, England, 18-22 April 1966, Institute of Fuel.
- (24) Gary D. Childs, "Countermeasures Against Flue Gas Corrosion and Deposits", *TAPPI*, vol. 50, June, 1967, pp. 122A-125A.
- (25) L. M. Exley, A. E. Tamburrino, and A. J. O'Neal, "LILCO Trims Residual Oil Problems", *Power*, vol. 110, no. 4, April, 1966, pp. 69-73.
- (26) S. W. Lovejoy, J. F. Cox, and A. B. Geuder, "Combustion Controls for 2 Percent Excess Air Firing of Residual Fuel Oil", presented at Ninth Symposium, Instrument Society of America, May, 1966.
- (27) R. J. Bender, "Low Excess Air and Sonic Atomization Team Up", *Power*, vol. 110, no. 7, July, 1967, p. 71.
- (28) A. L. Plumley, J. Jonakin, and R. E. Vuia, "A Review Study of Fire-Side Corrosion in Utility and Industrial Boilers", presented at Corrosion Seminar, McMaster University and Engineering Institute of Canada, Hamilton, Ontario, May 19-20, 1966.