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

SECOND REPORT SUMMARY

January 1, 1967 – June 30, 1967

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

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Prepared by
BATTELLE MEMORIAL INSTITUTE
Columbus Laboratories

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SECOND 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

January 1, 1967 - June 30, 1967

BATTELLE MEMORIAL INSTITUTE
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505 King Avenue
Columbus, Ohio 43201

The American Society of Mechanical Engineers
United Engineering Center / 345 E. 47th St., New York, N.Y. 10017 / 212 PL 2-6800

August 2, 1967

ASME Research - Corrosion and Deposits from Combustion Gases

Enclosed is a copy of the Second 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 January 1, 1967 to June 30, 1967. It is sent to you in recognition of your support of the Committee's work.

The report is arranged so that the "General Review" section summarizes the progress made, and the plans for the future, so that the reader can quickly determine the status of the project. The "Technical Details" section presents the data and references used in drawing the conclusions that are presented.

The current project is being carried out on a year-to-year basis, and the first year ended on June 30, 1967. Early in 1967, the Committee determined that the work was proceeding satisfactorily enough to justify continuing it beyond that date. Almost all of the previous contributors responded favorably to a solicitation to support the additional work, and some new contributors were obtained. The Committee is appreciative of this continued support of its work. It is expected that another report will be issued in January, 1968.

We hope that you will find the results reported to be helpful in the development and application of means for alleviating the problems due to corrosion and deposits from combustion gases. Any comments or suggestions that you may have will be welcome.

Very truly yours,

George C Wiedersum

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

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Second Summary Report
on
FORMATION OF ALKALI IRON SULFATES AND OTHER COMPOUNDS CAUSING CORROSION IN BOILERS AND GAS TURBINES

The question of the relative importance of SO_3 and of $SO_2 + O_2$ in flue gas in forming the complex sulfates that lead to corrosion has been answered by recent work with radioactive sulfur as a tracer. These tests have shown that SO_3 even in low concentrations is much more reactive. Furthermore, additional measurements of the reaction of $SO_2 + O_2$ on catalytic surfaces confirm that ample SO_3 can be formed at the surface at a low gas velocity to account for the formation of the trisulfates. Such low gas velocities may exist on surfaces in boiler furnaces and gas turbines beneath layers of deposits. Trace amounts of trisulfates now can be detected by an optical technique, and also an electrochemical device has been developed that appears capable of indicating the onset of corrosion within a few minutes after establishing corrosive conditions.

GENERAL REVIEW

by

William T. Reid

In defining the exact conditions that cause corrosion of superheaters and reheaters, one of the most serious gaps in our knowledge has been the origin of the high levels of SO_3 that are necessary for the formation of trisulfates. Thermodynamic calculations and experimental work have agreed that $Na_3Fe(SO_4)_3$ and $K_3Fe(SO_4)_3$ can exist above 1000 F only when the SO_3 is much higher than the 35 ppm SO_3 or so usually present in the flue gas. Most investigators attribute the required SO_3 to "catalysis", but data on the formation of SO_3 on surfaces under furnace conditions have been lacking. One of the objectives of the present Battelle work is to provide such information.

Efforts over the past year and particularly over the past six months have been spent mainly in developing the basic knowledge of actions occurring on surfaces that lead to high SO_3 values and hence to metal wastage. Earlier work that investigated the reactions occurring in flames showed that low excess air was the only way found to limit the formation of SO_3 during combustion. Although practical with oil firing, low excess air at the required levels of less than 0.2 percent O_2 cannot be achieved at present when burning pulverized coal. Hence, this investigation has turned to reactions occurring on surfaces themselves as a guide to other methods of corrosion control.

Although it is still not possible to describe a corrosion mechanism that defines with numerical values the steps by which metal is lost from a boiler or gas-turbine surface, such a definition remains as the objective of the Battelle study. Knowing precisely the reactions that occur and the effect on them of varying such factors as chemical composition and physical effects including temperature and velocity, it will be possible to decide which factors can and must be controlled, and which can be ignored.

For example, metal wastage occurs only under deposits, and it has been known for many years that where such deposits do not form, corrosion does not occur. Various explanations have been suggested, but most of these are based on the deposit providing the chemical constituents - such as iron oxides, alkalies, or SO_3 - that can then react with the metal surface. An equally plausible explanation can be based on the physical environment provided by a deposit on a heat-receiving surface. Where deposits do not "wet" the metal surface, there is a gas film present between the metal and the deposit. Combustion gases can diffuse into this film through the deposit or may flow slowly over the metal through cracks in the deposit. The characteristics of this gas-metal interface, then, may be equally as important as the deposit itself in influencing corrosion.

To provide data on the possible importance of such factors, this study recently has considered the many reactions that can take place on surfaces. Velocity is important in establishing the SO_3 concentration in the gas layer over a catalytic surface exposed to $SO_2 + O_2$, but more data will be necessary to decide on the importance of velocity in establishing the pickup of SO_3 by that surface. Also, the presence of alkalies on an iron surface has a great effect on the rate at which SO_3 is picked up by that surface, again showing the importance of knowing the exact conditions that lead to chemical compounds causing loss of metal.

In the coming year, it is hoped that a logical quantitative description can be provided of the individual steps which culminate as metal wastage. Then possible corrective measures can be evaluated most successfully.

RESEARCH ACCOMPLISHMENTS
OVER THE PAST SIX MONTHS

Experimental work recently consisted mainly of surface investigations and of tests in the noncatalytic fuel-burning furnace. The surface studies have been concerned primarily with surface catalysis and with radioactive sulfur as a tracer to follow gas-surface reactions. Tests in the fuel-burning furnace have concentrated on means of quickly detecting the onset of corrosion after corrosive conditions are established.

Surface Investigations

The importance of the steep gradient in SO_3 concentration over a catalytic surface was pointed out in the First Summary Report, and measurements were given of the high SO_3 levels that can exist immediately over an active surface. This work has now been extended to include the effect of gas velocity. It shows that as the boundary layer is thinner, the maximum measured SO_3 concentrations are markedly less. The data show in fact that increasing the gas velocity by 10 times, from 1.2 feet per second to 12 feet per second, decreases the SO_3 level 0.005 inch above the catalytic surface from 1600 ppm SO_3 to 100 ppm SO_3. This minimum experimental distance of 0.005 inch, limited by roughness of the surface, is still great enough to prevent estimates of the SO_3 level in the molecular layer of gases immediately over the surface, but it does illustrate the effect of low gas velocity. Such data are expected to be particularly useful in assessing the influence of an overlying deposit, which of course would assure nearly zero velocity of flue gas over a corroding superheater element.

When alkalies are added to an otherwise catalytic surface of Fe_2O_3, there is no measureable increase in SO_3 in the boundary layer. For the present, it appears that SO_3 being formed by reaction of SO_2 and O_2 on the Fe_2O_3 surface is captured at once by the alkalies or by the alkali-Fe_2O_3 combination so that none escapes to the bulk gas stream. This will require further checking, but several experiments thus far have suggested this hypothesis. An interesting further point is that some sulfates with a higher SO_3 content than Na_2SO_4 can be formed when not more than 20 to 40 ppm SO_3 is present in the bulk gas stream. Although these sulfates may not lead directly to the trisulfates at this SO_3 level, such SO_3-rich substances may be a chemical intermediate important in the overall reactions.

Tests with radioactive S^{35}, used as a tracer to assess the relative importance of SO_2 and SO_3, have confirmed that alkalies present in Fe_2O_3 layers trap large quantities of SO_3 from gas. For example, with Fe_2O_3 alone, the amount of SO_3 captured by the surface under a given set of conditions was one-eighth of that with Na_2SO_4 added in a 3:1 mol ratio. Similarly, with SO_2 and O_2, the amount of sulfur picked up from the gas phase is 4 to 5 times more when Na_2SO_4 is present than when Fe_2O_3 alone is present.

Probably one of the most significant points here is the high reactivity of SO_3 in forming complex sulfates compared with SO_2 and O_2. Despite the demonstrated catalytic activity of Fe_2O_3, its reaction with SO_2 and O_2 was only about one fourth as much as with SO_3. When Na_2SO_4 was also present with the Fe_2O_3, the reactivity of the mixture of sulfate and oxide with SO_3 was at least 10 times that with SO_2 and O_2. When these data are reduced to the SO_2 and SO_3 levels of boiler furnaces, rather than the high SO_2 concentrations used in these laboratory measurements, the proportionate ratios show that SO_3 reactivity may be in the order of 200 times that of SO_2 and O_2. Such data continue to confirm the importance of SO_3 in the corrosion mechanism.

A useful laboratory tool was developed during the past six months to identify trace amounts of the alkali iron trisulfates in corrosion products. Based on a measurement of the index of refraction of $Na_3Fe(SO_4)_3$ and $K_3Fe(SO_4)_3$ and mixtures of these trisulfates, the system is capable of identifying even individual crystals of the compounds. Whereas X-ray diffraction methods of analysis require that at least 10 percent of the sample be the trisulfate for positive identification, this optical method is sensitive enough to show the presence of trace amounts of trisulfates. Thus it has detected trisulfates in a test sample held for only 3 hours in a flue gas atmosphere containing normal amounts of SO_3. As much as 100 hours exposure may be necessary to provide enough trisulfates for identification by X-ray diffraction methods. Use of this index-of-refraction method is expected to add considerably to following the reactions leading to the trisulfates.

Fuel-Burning Furnace Studies

It is not always feasible in laboratory tests to operate for hundreds of hours. Usually, steady-state conditions are attained fairly rapidly, often in a few hours, but the gradual growth of corrosion products can require 100 hours or more to provide enough material, such as $Na_3Fe(SO_4)_3$, to indicate by conventional tests that corrosive conditions have been established. The optical technique recently developed is a great aid in detecting trace amounts of the trisulfates once a test is over, but other procedures that can be applied while a test is in progress would be even more useful. Hence, to provide a guide for detecting the onset of corrosion, several versions of electrochemical cells were evaluated.

The first electrochemical cell used here was intended to show simply the development of a molten phase in the test apparatus exposed to furnace conditions; the latest one not only indicates when corrosion is occurring but apparently also gives a measure of the rate of corrosion. Complete interpretation of the data from these electrochemical cells is still open to question. Nevertheless, such techniques show a great deal of promise in following corrosion reactions as they take place. There is an obvious advantage in such a procedure over one that simply, even though more accurately, shows the extent of corrosion once a test is over.

The major purpose in developing these electrochemical cells was to provide a means of determining when corrosion occurs in the fuel-fired furnace where the flue-gas atmosphere closely duplicates that in full-size boiler furnaces. A successful cell is now available that indicates when a change in flue-gas composition or temperature affects corrosion activity. In one case, switching alternately from a sulfur-free fuel to a high-sulfur fuel resulted in a voltage output that lagged slightly behind the changes in fuel, but that nevertheless clearly indicated the alternate formation of complex sulfates and their apparent dissociation as the sulfur content changed.

All the data from the electrochemical cell cannot be interpreted so easily. One common factor appears in all recent work - as the temperature is increased stepwise, abruptly higher voltage outputs are obtained for periods of a few minutes, followed by a gradually decreasing voltage. The reason for this is not at all clear, but at least in one case, following the peak, the rate of falloff in voltage increased with temperature. This action is observed only above about 900 F, suggesting that it may be related to the instantaneous formation and possible later dissociation of complex sulfates. The same effect is not observed when sulfur oxides are not present in the flue gas. The effect is so striking and so consistent as to warrant further attention.

Voltage output and current flow through such electrochemical cells is a direct indication of corrosion, but the scheme is so sensitive that it is difficult to collect sufficient corrosion product to identify the complex sulfates chemically. Yet, in one case, in which a 5.5 percent sulfur fuel oil had been burned for slightly less than 3 hours, with the voltage curve showing the usual peak followed by a gradual decrease in output, examination of the specimen after the test by the index-of-refraction method positively identified the presence of the trisulfates. The corrosive mixture in this case (Figure 11) was Na_2SO_4 and K_2SO_4, and the test temperature was 975 F. A large amount of sulfide was also found on the specimen, suggesting that the trisulfates had been present.

Conclusions thus far from the tests with the electrochemical cells in the fuel-fired furnace are that:

1. Corrosion is occurring between about 900 F and 1200 F. The most rapid change in voltage occurs at the higher temperature.

2. Abrupt increases in temperature result in some transient corrosion reaction, not yet identified, which appears to be tied up with more rapid dissociation of some corrodent as the temperature increases.

3. Corrosion occurs in the fuel-burning furnace with flue gas of normal composition, even though not under deposits. This may be attributed to low gas velocity which probably does not exceed 3 feet per second.

4. The presence of sulfides on most specimens, and the positive identification of the trisulfate in one specimen, indicates that corrosion is occurring in the electrochemical cell as the cell output shows.

5. Long periods are not necessary for corrosion to begin. In essentially all cases, no induction period was observed and corrosion as indicated by voltage output began almost as soon as the proper conditions were established.

Mechanism of Corrosion

Corrosion by sulfidation is particularly evident at high temperature and is a frequent source of trouble in gas turbines. It is also a contributing factor on superheaters where FeS is an end product of the reaction of the trisulfates with tube metal. A further complicating factor is the low melting point of 1490 F for nickel sulfide, Ni_3S_2, and, more importantly for superheaters, the Ni_3S_2-Ni eutectic that melts at 1193 F. Hence even high-nickel alloys may fail catastrophically when sulfides are formed on their surface.

Except for the case of excessively low excess air, or where locally reducing conditions may be present as caused by unsatisfactory mixing of oil and air, the reducing action where sulfides are formed is a fundamental property of the metal alloy and overlying sulfate-containing deposits. Unless the fuel can be desulfurized, or the alkalies removed or complexed with an additive such as kaolin, the problem appears to be one mainly of developing alloys resistant to sulfidation, just as many of the current high-temperature alloys have been developed to be oxidation resistant.

THE NEXT STEPS

The intent at present is to follow this general plan:

1. Gradient in SO_3 over a catalytic surface. Using a microsampling probe, as in past work, does not allow analysis of the 0.005-inch-thick layer of gas immediately next to a catalytic surface. Other techniques will be sought for sampling the gas within this nearly stagnant zone, as by inserting the probe from the back of the specimen through a closely fitting drilled hole.

2. Analysis of boundary-layer data. An attempt has been made to use boundary-layer theory as a mathematical tool to analyze the gradient in SO_3 over a surface, but the results were inconclusive. Additional efforts along these lines will be made as more data are available.

3. Effect of SO_3 in bulk gas stream on formation of deposits. Additional data are needed on the pickup of SO_3 from the bulk gas stream, compared with SO_3 formed on a surface by catalysis. Presently available information needs to be supplemented by additional tests to settle the relative importance of $SO_2 + O_2$ and of initially available SO_3.

4. Radioactive S^{35}. Based on the excellent results obtained thus far with S^{35}, additional tests will be made to extend this type of investigation to include other temperatures than 1100 F. Lower temperatures to enhance the formation of complex sulfates, and higher temperatures to dissociate them appear worth investigating.

5. Levels of SO_3. Earlier work on the formation of sulfates on surfaces was done with high concentrations of SO_3 to match still earlier work and to ease the problem of identifying

products. The techniques being used appear now to be at the point where more realistic levels of SO_2 can be tried. Plans are to conduct later tests with no more than 2500 ppm SO_2 in the test apparatus.

6. <u>Identification of complex sulfates</u>. The index-of-refraction method has been gratifying as a means of positively identifying $Na_3Fe(SO_4)_3$, $K_3Fe(SO_4)_3$, and mixtures of these two trisulfates. The same basic technique will be applied next to identifying the chemical products formed as an intermediate to the trisulfates.

7. <u>Influence of forms of alkalies on formation of trisulfates</u>. Little attention has been paid by most investigators to the manner in which alkalies are deposited on surfaces such as superheaters and reheaters. Tests are planned for the fuel-burning furnace whereby alkalies volatilized in the flame are compared with alkalies physically laid down on test surfaces.

8. <u>Corrosion beneath deposits</u>. Experimental measurements need to be made of the role of deposits in causing corrosion. Earlier tests, where deposits were formed by compressing fly ash into slabs, gave little meaningful data. Other tests will be made now with the better detection schemes available to learn whether deposits are harmful because they provide a stagnant gas layer over the metal surface, or because they furnish the alkalies, the trisulfates, or the SO_3 that leads to wastage.

9. <u>Mechanism of corrosion</u>. Current reviews of the work of other investigators will be continued, and specific problem areas will be reviewed from time to time for the guidance of the Battelle team and as a part of these reports.

SURFACE INVESTIGATIONS

by

H. H. Krause and A. Levy

Under usual coal- and oil-burning conditions in full-scale boiler furnaces, the sulfur dioxide level leaving the combustion zone is 2000 to 3000 ppm and the SO_3 level is about 30 to 40 ppm. It has been shown that all of this SO_3 can be produced in the homogeneous combustion zone. However, it is also known that SO_3 can be produced catalytically when SO_2 and O_2 are in contact with ferric oxide or other catalytic surfaces. The purpose of these investigations has been to determine what occurs when the combustion gases are in contact with hot metallic surfaces such as superheaters and reheaters. More specifically, these surface investigations hope to explain what reactions occur between SO_2, SO_3, O_2, oxidized iron surfaces, and alkaline materials. An effort is being made to define the types of reactions and the mechanisms leading to the formation of the simple alkali sulfates and the complex alkali iron trisulfates. It is these sulfates that hold the answer to the corrosion and deposit problem. Hence special attention to them is warranted.

Two approaches have been used in this study of surfaces over the past six months: (1) measurement of the SO_3 concentration profiles above the surface of iron oxides, sulfates, and NaOH, and (2) S^{35} tracer studies to distinguish the reactions of SO_2 from those of SO_3.

SO_3 CONCENTRATION GRADIENTS

The study of surface reactions is considered important to this program because the concentration of SO_3 in the bulk gas stream is not high enough, nor can it become high enough in typical boiler flue gases, to explain the formation or stability of ferric sulfate or the complex alkali iron sulfates found on superheaters. As has been pointed out in earlier basic studies, both ferrous and ferric sulfates are unstable at 1200 F. Based on available thermodynamic data, ferrous sulfate is more stable than ferric sulfate, but even it requires theoretically that 90 ppm SO_3 be present in the surrounding atmosphere at 1200 F assuming it decomposes to form FeO. With ferric sulfate at this temperature, the calculated equilibrium SO_3 level is 20 percent. Experimental measurements made by Corey(1) and his co-workers show that sodium iron trisulfate [$Na_3Fe(SO_4)_3$] required 250 ppm SO_3 at 1100 F. At lower SO_3 levels, it will dissociate. Under some conditions, $FeSO_4$ may form with the SO_3 present normally in flue gas, but only a moderate increase in temperature would cause it to dissociate. Hence, to develop a logical mechanism for the formation of the intermediate and final products, it is necessary to explain why these normally unstable sulfates are found in corrosion areas.

It is quite conceivable that metastable sulfates exist under certain boiler conditions, especially if some of the products can be built up beneath a coating of fly ash. It is also recognized that SO_2 and SO_3 are strongly adsorbed gases, and it has been shown during the past year in laboratory experiments that SO_3 concentrations immediately next to the surface can be much higher than those in the bulk flue gas stream. Further measurements have been made of this SO_3 concentration above various surfaces, as an indication of the conditions that can exist leading to the formation of the relatively unstable sulfates.

Apparatus and Procedure

The experimental apparatus used in this study over the past six months is that described in Figure 1 of the First Summary Report. It provides a means of sampling the gas mixture at a carefully measured level above the surface to be investigated. The distance of the sampling probe from the surface being studied is measured by a cathetometer, with the probe maintained at a fixed position and the furnace adjusted upward or downward as required by a micrometer screw arrangement. The major changes made during this period were provisions for varying the gas velocity over a wide range.

Previous Experimental Results

Experimental results obtained during the first six months of the current program, as listed in the First Summary Report, showed that:

1. The highest SO_3 concentrations were found above surfaces of Fe_2O_3 and $FeSO_4$. These SO_3 concentrations varied from about 200 ppm 0.2 inch above the surface, to 1500 to 2000 ppm at a distance of 0.005 inch from the surface.

2. When the SO_2 concentration above a surface of Fe_2O_3 was varied between 1.5 and 6 percent, it was found that the SO_3 values at the point of closest approach to the surface were almost proportional to the square of the SO_2 concentration.

3. The SO_3 profile above a 50-weight-percent mixture of Fe_2O_3 and Fe_3O_4 was found to be similar to that above an oxidized iron surface, suggesting that the oxidized iron surface also consisted of Fe_2O_3 and Fe_3O_4 as might be expected. Under these conditions, Fe_3O_4 has negligible catalytic activity, providing only 100 ppm SO_3 compared with upward of 1500 ppm with Fe_2O_3.

4. The addition of NaOH or Na_2SO_4 to an Fe_2O_3 surface substantially reduced the SO_3 concentration above the surface. The SO_3 concentration at the point of closest approach (0.005 inch) decreased to 50 to 150 ppm, compared with 1500 to 2000 ppm with Fe_2O_3 alone.

5. Large differences were noted between the SO_3 concentrations found above V_2O_5 obtained from different sources.

Effect of Flow Velocity on SO_3 Gradients

Similar measurements have been made recently of the SO_3 levels above Fe_2O_3 at greater gas flow rates. The intent was to permit some sort of extrapolation to the velocities in boiler furnaces. As usual, the Fe_2O_3 was supported on an inert Vycor plate, the temperature was 1100 F, and the gas mixture consisted of 5.8 percent SO_2, 19.4 percent O_2, and 74.8 percent N_2. The flow rate was increased from the 40 cc per second previously used to 60 cc per second, thereby increasing linear velocity from 1.2 feet per second to 1.8 feet per second. In another experiment, the cross-sectional area of the system was reduced to provide a linear velocity of 12 feet per second at the same 40-cc-per-second flow rate.

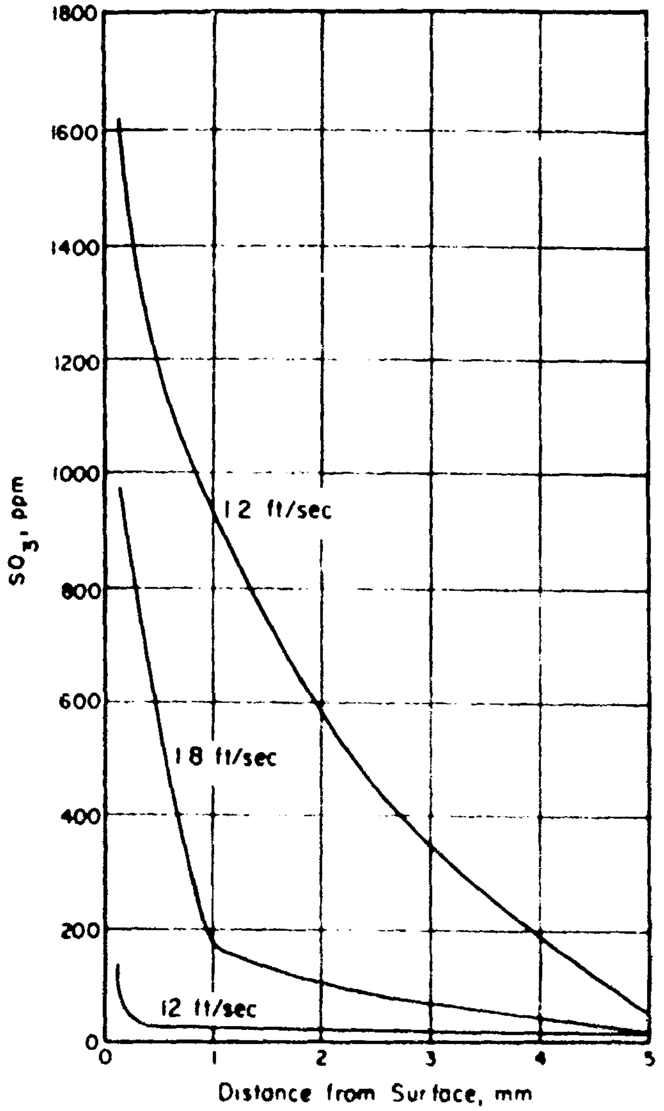


FIGURE 1. EFFECT OF FLOW VELOCITY ON SO_3 GRADIENT ABOVE Fe_2O_3

Figure 1 compares the SO_3 gradients measured under these relative velocity conditions of 1 to 1.5 to 10. The initial 50 percent increase in velocity resulted in approximately a 40 percent decrease in SO_3 concentration near the surface. Increasing the linear velocity by a factor of 10 resulted in about a 90 percent decrease in the SO_3 concentration 0.005 inch from the surface, the closest approach feasible with the microprobe under the present operating conditions. These results show that the microprobe is measuring concentrations in the boundary layer, which is greatly affected by the flow rate of the gas stream. Large differences in these SO_3 profiles found for various surfaces under relatively low-velocity conditions must be reflecting what is occurring in the part of the boundary layer in contact with the surface where the gas stream has little motion.

It should be recognized that physical limitations of collecting a gas sample through even the 30-micron-diameter (0.0012 inch) opening in the microprobe prevent getting a true picture of the SO_3 concentration within the deposit itself. The abrupt increase in SO_3 through the boundary layer even at the highest velocity suggests that the SO_3 within the surface will be much greater than in the bulk gas stream.

Effect of Sodium Salts on SO_3 Gradients Over Fe_2O_3

The SO_3 levels over surfaces of Fe_2O_3 mixed with either NaCl or Na_2SO_4 also were studied. In both cases, the NaCl and Na_2SO_4 were present in the mixtures in a 3:1 mol ratio with Fe_2O_3, as required to form $Na_3Fe(SO_4)_3$. Essentially no SO_3 gradient existed above the NaCl surface; 20 to 40 ppm SO_3 was found at all distances above the surface between 5 millimeters and 0.12 millimeter. Because 40 ppm SO_3 was found 5 and 2.5 millimeters from the surface, and 20 ppm SO_3 at lesser distances, depletion of the SO_3 apparently was occurring near the surface. A qualitative test showed that a large amount of sulfate had been formed. Some chloride remained.

In the case of Na_2SO_4, the SO_3 gradients were compared above two different specimens. The first was a freshly prepared surface; the second had been reacted with SO_2 and oxygen at 1100 F for 65 hours. The SO_3 profiles above these two surfaces were essentially the same, the SO_3 concentration reaching a level of about 150 ppm at the point of closest approach to the surface. Both samples were analyzed quantitatively and additional sulfate was found beyond that initially present as Na_2SO_4. The total amount of sulfate found in the second sample was actually greater than that required to convert the sample to $Na_3Fe(SO_4)_3$, but there is some question as to the reliability of the barium chloranilate method for sulfate analysis at the relatively high concentration found.

The results of these experiments in which Fe_2O_3 and a sodium salt are exposed to an SO_2-O_2 atmosphere indicate that the reaction to form complex sulfates can occur without any significant amount of SO_3 appearing in the bulk gas stream. As rapidly as any SO_3 forms, it must react to form complex sulfates of some sort.

In another experiment, the SO_3 concentration 0.010 inch above a surface of Fe_2O_3 plus Na_2SO_4 (75 mol percent) was measured as a function of time. Sampling was started as soon as the surface reached 1100 F, about 10 minutes. Three samples taken approximately 20 minutes apart gave the same result of 45 ppm for the SO_3 concentration. This result indicates that the reaction to form complex sulfates on a surface probably begins as soon as some sodium compound is available on an Fe_2O_3 surface.

SO_3 Concentration Gradients Above V_2O_5 Catalyst

Additional studies were made of the catalytic effects of V_2O_5 surfaces in the formation of SO_3. The commercial V_2O_5 catalyst which had been studied earlier was run again in the form of the original pellets in which the V_2O_5 is coated on Al_2O_3. Alundum cement was used to hold the spherical pellets in place on the Vycor plate. The SO_3 concentrations found above the whole pellets were significantly higher than those found over the crushed catalyst, and the value at the 0.005-inch distance from the surface was nearly equal to that obtained with Fe_2O_3. Figure 2 compares these values for the whole catalyst pellets with

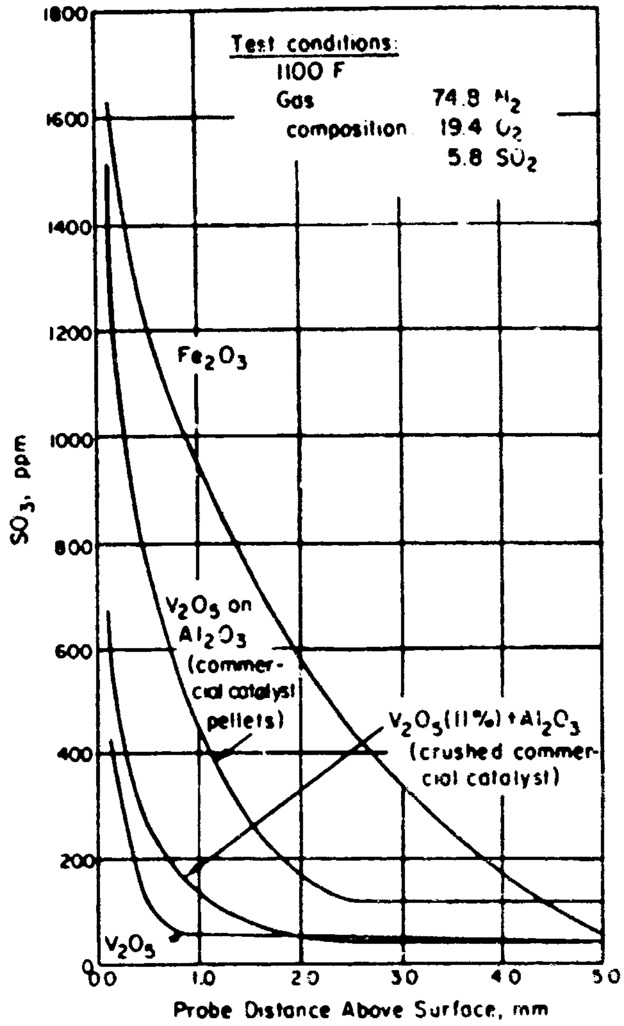


FIGURE 2. SO_3 GRADIENTS ABOVE V_2O_5 SURFACES

those measured previously for the crushed pellets and for an off-the-shelf sample of V_2O_5. Data are also included for a typical Fe_2O_3 surface. It was noted that the SO_3 concentration above V_2O_5 remains relatively low at distances greater than 1 millimeter from the surface, although this concentration depends largely on the flow conditions of the experiment. All SO_3 concentrations increase rapidly at distances less than 1 millimeter from the surface. These profiles show that some types of V_2O_5 can promote very high SO_3 at points quite close to the surface, and probably can lead to the formation of complex vanadyl sulfates which have been found in many highly corrosive deposits.

Wide variations in the effect of different V_2O_5 samples in converting SO_2 to SO_3 had been noted previously by Wickert.(2)

These SO_3 concentration profiles have shown that relatively large SO_3 concentrations can exist near catalytic surfaces, and that large differences exist among the catalytic effects of various materials. The presence of sodium salts with iron oxides has been demonstrated to be particularly effective in reducing the SO_3 concentration near the surface to that of the bulk gas stream, apparently by reaction with the SO_3 and O_2 to form complex alkali sulfates.

RADIOACTIVE TRACER STUDIES

Radioactive sulfur, S^{35}, is being used in a series of experiments to shed further light on the mechanism by which the alkali iron trisulfates and other corrosive materials can be formed in an environment containing SO_2, SO_3, and O_2.

As pointed out in the First Summary Report, this study continues the work of Fletcher and Gibson,$^{(3)}$ who used radioactive sulfur to investigate the formation of Na_2SO_4 by the action of SO_2 and SO_3 on NaCl. They demonstrated effectively that it was the SO_2 in the gas stream that played the larger part in the conversion of NaCl to Na_2SO_4. This formation of alkali sulfates in boiler systems is generally accepted to be fairly rapid and direct.$^{(4)}$

Of primary interest in furnace corrosion is the additional action of SO_2 and SO_3 with alkali sulfates and iron oxides to form the alkali iron trisulfates. The goal of this part of the program is to differentiate between the roles of SO_2 and SO_3 as they enter into the reaction by which alkali iron trisulfates are formed. By labeling the SO_2 or SO_3 with S^{35}, the participation of the SO_2 and the SO_3 in sulfation reactions can be identified, and ultimately it should be possible to determine the specific steps taking place in the overall reaction.

The low-energy beta radiation (0.167 mev) of S^{35} is particularly suitable for this type of research, as safety hazards are minimized. The half-life of this isotope (86.7 days) also is convenient because it provides a statistically significant radioactive count over reasonably short periods. The formation of appreciable quantities of alkali iron trisulfates requires many hours even under laboratory conditions. Consequently, the ability to follow the progress of sulfur through the reaction steps in relatively short experiments requires detection of very small amounts of material. The use of radioactive sulfur makes detection at these levels feasible.

Apparatus and Procedure

The reaction system used for the S^{35} tracer studies is the same as that shown in Figure 7 of the First Summary Report. Desired mixtures of N_2, O_2, SO_2 carrier gas, and radioactive $S^{35}O_2$ are provided from gas cylinders. In some experiments, SO_3 was added to the gas stream by heating sulfuric acid. The gas mixture used in these runs was the same as that in previous experiments - 5.8 percent SO_2, 19.4 percent O_2, and 74.8 percent N_2. One liter of gas from the cylinder containing radioactive $S^{35}O_2$ was used during each experiment. The radioactive $S^{35}O_2$ was obtained from the Matheson Company.

This amount of $S^{35}O_2$ provided 27 microcuries of S^{35} in the initial experiments, and by the time the last experiments were carried out the activity was down to about 9 microcuries. Because the duration of each experiment depended on the time to withdraw one liter of gas from the cylinder containing the S^{35}, each run required 35.5 minutes.

The substrates used in these experiments measured 1 inch by 4 inches and were either a Vycor plate or a piece of low-carbon steel. Various oxide and sulfate mixtures to be studied were deposited as a thin film on these substrates. The SO_3 in the gas stream after passing over the specimens was trapped out as sulfuric acid at 32 F; unreacted SO_2 was absorbed by hydrogen peroxide solution in several bubblers to prevent escape of any unreacted S^{35} from the system. These hydrogen peroxide bubblers converted the $S^{35}O_2$ into $H_2S^{35}O_4$ which in later experiments was then decomposed at 450 C to provide radioactive $S^{35}O_3$.

After each experiment, the specimen plates were washed with water, so that all soluble sulfate material would be dissolved. This solution was then diluted to a standard volume for radioactive counting. In the case of the steel substrate, any water-insoluble sulfur which remained in the surface also was checked by radioactive counting. The SO_3 trapped out by the ice bath was diluted to standard volume and a quantitative sulfate determination was made on it by the barium chloranilate method. This sample was also counted for radioactivity. The radioactivity absorbed in the hydrogen peroxide scrubbers was determined as well, to establish the total amount of S^{35} that had been used in each experiment. Radioactivity counting was done in a Packard Tricarb Model 314 AX, using a liquid scintillator system. Sample volume was 25 microliters, and the counting time was 100 minutes. Duplicate sample counts were made. Counting efficiency was determined by adding 25 microliters of a C^{14} standard. Precision of the radioactive counting was of the order of 2 to 3 percent.

Experimental Results

Figure 3 gives the results of the experiments with radioactive sulfur. The reactivity of the surfaces used with both $S^{35}O_2$ and $S^{35}O_3$ is shown in this figure in terms of the radioactive count detected in the surface. Inasmuch as the ratio of nonradioactive sulfur oxides to that of $S^{35}O_2$ was of the order of 10^{10}, the radioactivity detected in the surface represents only a very small fraction of the total amount of sulfur oxides that actually reacted with the surface. Never-the less, because S^{35} behaves chemically exactly like the four stable sulfur isotopes, even this small quantity gives a precise measure of how all the sulfur is reacting.

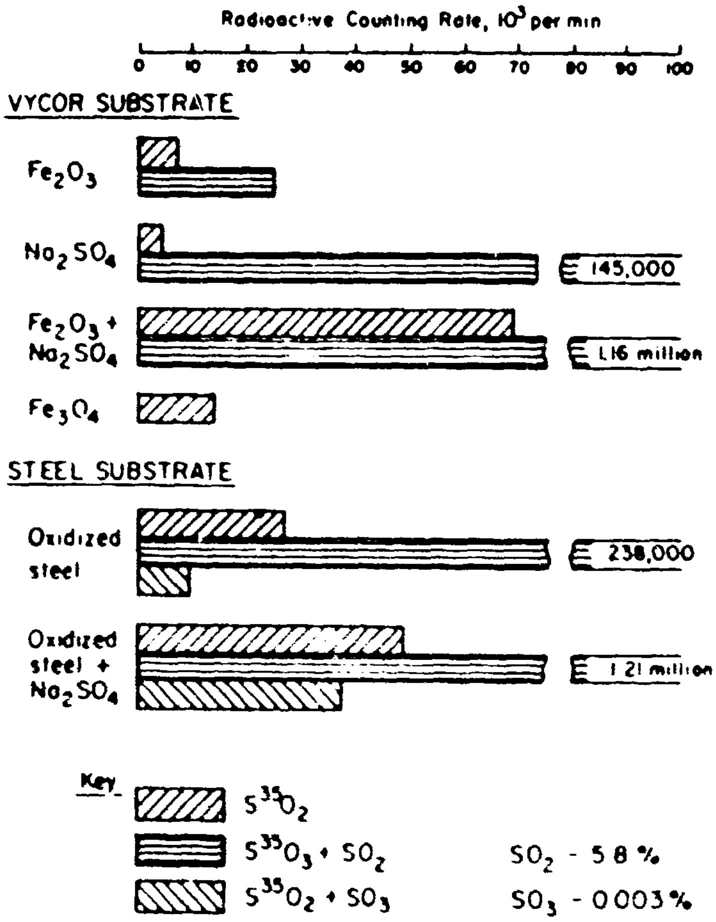


FIGURE 3. REACTIVITY OF SURFACES WITH S^{35} OXIDES

The data shown in the figure have been corrected for radioactive decay and for oxygen exchange. It was found under these experimental conditions that when the radioactive sulfur was in the SO_2, the combined oxygen exchange and oxidation reactions as represented below amounted to about 10 percent:

$$S^{35}O_2 + SO_3 \rightarrow S^{35}O_3 + SO_2$$

$$S^{35}O_2 + \tfrac{1}{2}O_2 \rightarrow S^{35}O_3 .$$

When the radioactive sulfur was in the form of $S^{35}O_3$, the reverse oxygen exchange amounted to only 2 percent:

$$S^{35}O_3 + SO_2 \rightarrow S^{35}O_2 + SO_3 .$$

For all of the surfaces studied, reactivity with SO_3 was significantly greater than that with SO_2. In the case of Fe_2O_3, the reactivity of SO_3 was about 4 times as great as that of SO_2. When Fe_3O_4 was exposed to $S^{35}O_2$ in the gas stream, approximately twice as much of the SO_2 reacted with the Fe_3O_4 as with Fe_2O_3 under the same experimental conditions. With a surface of Na_2SO_4, the reaction with SO_2 was almost as much as it was with Fe_2O_3. However, SO_3 was much more reactive with Na_2SO_4; approximately 6 times as much SO_3 reacted with Na_2SO_4 as with Fe_2O_3. A very large increase in reactivity with the surface was observed when a combination of Fe_2O_3 and Na_2SO_4 was used. In this case, with a 3:1 mol ratio of Na_2SO_4 to Fe_2O_3 on the surface, about a ten-fold increase occurred in reactivity with SO_2. With SO_3, the reaction with this combination of oxide and sulfate was almost 50 times as much as it was with the Fe_2O_3, and about 10 times as much as it was with Na_2SO_4 alone.

The oxidized steel surfaces were prepared by heating the low-carbon steel substrates in an atmosphere of moist oxygen at 1100 F for two hours. The oxidized steel was then cemented to a Vycor plate to limit the reactivity to the top surface. With these specimens, the reactivity of the oxidized steel with SO_2 was greater than that of Fe_2O_3 or Fe_3O_4. When sodium sulfate was coated on the oxidized steel the reactivity of the SO_2 doubled, but this increase was not as striking as that noted when sodium sulfate was added to the Fe_2O_3 on a Vycor surface. It was evident that SO_3 was tremendously more reactive with the oxidized steel surface than was SO_2, the increase being almost ten fold in this case. When Na_2SO_4 was coated on the oxidized steel, the reaction of SO_3 was approximately 5 times as great as that on the oxidized steel alone.

In another set of experiments, $S^{35}O_2$ was mixed with a gas mixture containing nonradioactive SO_3. These runs were made with the oxidized steel surface, and a decrease was noted in the amount of sulfur dioxide reacting with the surface. For the oxidized steel alone, only about one third as much of the SO_2 reacted as when no SO_3 was in the gas stream. In the case of the oxidized steel coated with sodium sulfate, there was about a 20 percent decrease in the amount of reactivity as compared to that for SO_2 alone. The results of these two experiments emphasize further the preferential reactivity of SO_3 over that of SO_2.

After all the water-soluble components were removed from the oxidized steel surfaces, it was found that some insoluble sulfur still remained in the surface, as detected by a small radioactivity count of the order of 100 to 150 counts per minute. This insoluble sulfur was found to be present in the form of sulfide, as was verified by the sodium azide test.(5) This formation of sulfide is the result of the oxidation of iron and FeO in the surface by the SO_2 and SO_3, and is indicative of the manner in which Fe_2O_3 continuously becomes available on the surface.

All these radioactivity experiments have shown the strong preferential reactivity of SO_3 for surfaces containing Fe_2O_3, Na_2SO_4, and particularly mixtures of these two compounds. The data shown in Figure 3 are the direct count of the radioactive S^{35}. If these data are converted to a molar basis, the reactivity of SO_3 compared with SO_2 becomes about 1900 times that shown in the figure where the SO_2 concentration in the gas stream amounted to 5.8 percent and the SO_3 concentration was only 30 ppm.

OPTICAL MICROSCOPY STUDIES

The need has long been recognized for a technique useful in detecting very small amounts of the alkali iron trisulfates. A procedure using an optical method has now been developed at Battelle whereby individual crystals of $Na_3Fe(SO_4)_3$ and $K_3Fe(SO_4)_3$ can be identified in a laboratory specimen.

Samples of pure $Na_3Fe(SO_4)_3$ and $K_3Fe(SO_4)_3$ and a mixture of the two were prepared in the laboratory for use as standards. These samples of the trisulfates were prepared by mixing the alkali sulfate with Fe_2O_3 in a 3:1 mol ratio and maintaining the mixture at 1100 F in an atmosphere of SO_3, SO_2, and oxygen for about 120 hours. The X-ray diffraction spectra of these products showed that good samples of the trisulfates had been formed, the mixture showing the lines of both compounds. Analysis of the mixture by flame photometry for sodium and potassium showed that the mixture consisted of 65 weight percent of the potassium salt and 35 weight percent of the sodium salt.

Determinations of refractive index were made on both of the pure samples and on the mixture, using standard index-of-refraction oils whose index of refraction is known to four significant figures. The refractive indices of the trisulfates were determined by a trial-and-error method of matching the index of refraction of one of the standard oils to that of the sample. When a proper match has been made, crystals of trisulfates in the sample in the correct orientation disappear from view and reappear as the stage of the microscope is rotated. Because these trisulfates form hexagonal crystals, two values of the index of refraction can be determined, one for each axis. The values measured for $Na_3Fe(SO_4)_3$ using this oil immersion technique were found to be 1.590 and 1.628; those for $K_3Fe(SO_4)_3$ were found to be 1.584 and 1.622.

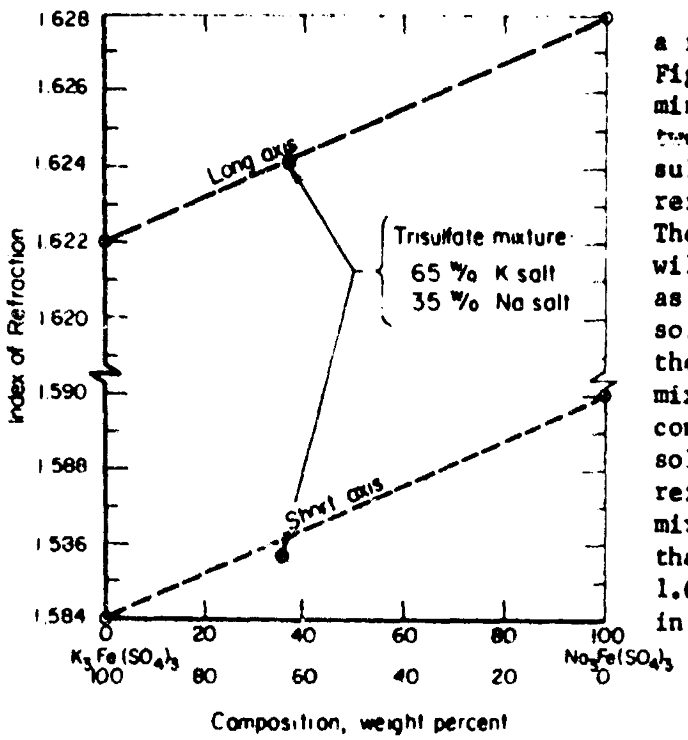


FIGURE 4. REFRACTIVE INDEX OF ALKALI IRON TRISULFATES

By plotting these values as a function of composition, as shown in Figure 4, it is also possible to determine the relative quantities of these two compounds in a mixture of the trisulfates by measuring the indices of refraction of the unknown material. The index of refraction of a mixture will change linearly with composition as long as the two materials form a solid solution. The X-ray spectra of the two trisulfates compared with a mixture of the two indicate that these compounds do indeed form such a solid solution. Hence, when the index-of-refraction values for the trisulfate mixture were determined, it was found that the value for the long axis was 1.624 which falls on the curve as shown in Figure 4, almost in exact agreement with the predicted value. However, the value for the index of refraction along the short axis fell slightly below the line joining the two points for pure potassium and sodium compounds, indicating that a refinement of the index of refraction values to 5 significant figures may be necessary in this case. The standard oils available change by steps of two units in the fourth significant figure, and by mixing these oils intermediate values can be obtained and the fifth significant figure can be approximated. However, for the purposes of identifying the trisulfate in a mixture of other materials, the values shown in Figure 4 have been found to be quite adequate.

This index-of-refraction technique has been applied to samples run in the fuel-burning furnace, and the presence of the trisulfate has been identified in some of the specimens at levels which would be much too low for detection by X-ray diffraction. Experiments were also carried out in which a mixture of Na_2SO_4 and Fe_2O_3 in a 3:1 mol ratio was subjected to a gas stream containing SO_2 and O_2 at 1100 F. Under these conditions, the presence of $Na_3Fe(SO_4)_3$ was verified after 65 hours exposure by this index-of-refraction method. The minimum time required to form the trisulfate under these conditions has not yet been determined, although an experiment of four hours' duration revealed that some crystals had been formed which were neither Na_2SO_4 nor $Na_3Fe(SO_4)_3$. Apparently they were a reaction intermediate, possibly one of the sodium iron disulfates which have been reported in the literature. With SO_3 in the gas stream in addition to SO_2 and O_2, very small crystals of the trisulfate were detected after only four hours of exposure at 1100 F.

This optical technique offers a powerful tool for tracing the course of the reaction and shedding light on the reaction mechanism, because it can detect such small amounts of the trisulfates while early reactions are still occurring.

FUTURE WORK

A further effort will be made to determine the SO_3 concentration nearer the surface than 0.005 inch, and, if possible, mathematical extrapolations will be made to calculate SO_3 levels in the stationary edge of the boundary layer. Some experiments will also be carried out with a known amount of SO_3 added to the gas stream to provide a more quantitative measure of the amount of SO_3 taken up by various mixtures of Fe_2O_3 with sodium salts.

Investigations with the radiotracer S^{35} will be continued, with emphasis on the effect of temperature. All previous experiments were carried out at 1100 F. Some data will be obtained at 1000 F and at 1200 F to determine whether or not there is any change in the relative reactivities of SO_2 and SO_3 with temperature. Additional experiments will be performed with SO_2 concentrations of the order of 2500 ppm, which are more realistic levels in terms of boiler operation.

An investigation also will be carried out to identify the intermediates to trisulfate formation which have been detected by optical microscopy. This study will require the preparation and characterization of some standard samples of such materials as sodium pyrosulfate, sodium ferric disulfate, and disodium ferrous disulfate. With standard samples of these materials available, values of their index of refraction can be determined, and from these values it will then be possible to identify whether or not these are indeed the intermediates to the trisulfates. Reactions of SO_2 and O_2 or SO_3 with these intermediates will then help to trace the course of the reactions leading to trisulfate formation.

FUEL-BURNING FURNACE STUDIES

by

R. E. Barrett

These fuel-burning furnace studies are intended to extend the fundamental studies of reactions occurring at surfaces, and to facilitate the application of such data to large boilers and gas turbines. Although alkali iron trisulfates appear to be responsible for most superheater corrosion, it is generally accepted that, at superheater temperatures, trisulfates can form only when the SO_3 concentration is many times that available in the bulk flue-gas stream of a boiler furnace. Other experimenters have produced trisulfates in laboratory-scale tests, but generally at SO_3 concentrations much greater than those encountered in industrial equipment. Fundamental studies of catalysis on surfaces have provided quantitative data showing that high concentrations of SO_3 can exist in localized areas around specimens, even when the SO_3 concentration in the bulk gas is not high. Therefore, the fuel-burning furnace has been used to investigate the formation of alkali iron trisulfates and corrosion caused by trisulfates when the SO_3 in the bulk flue-gas stream is relatively low - certainly no more than in full-scale boilers and gas turbines.

During this report period, the major effort with the fuel-burning furnace was directed at development and application of means of detecting corrosion when it first occurs. The procedures used are based on measurements of voltage and current in an electrochemical cell. Several versions were tried, the first being based on detecting the presence of the molten trisulfates by the change in electrical conductivity provided by a molten salt compared with a solid "electrolyte". The latest cell shows corrosion by the voltage generated and the current flow between the test iron electrode and a passive platinum electrode. Initial results have been encouraging, but the measurements, even though consistent, have proven difficult to interpret. The studies have not progressed far enough as yet to describe exactly what is occurring in the electrochemical cell, but results indicate a close relationship between the conditions established in the fuel-burning furnace and the output of the cell.

EQUIPMENT AND TECHNIQUES

The oil-fired fuel-burning furnace used for the furnace studies has been described in detail.(5,6) In general, it consists of a stainless steel combustion chamber with its walls at 500 F to prevent condensation of SO_3 and unwanted formation of SO_3 by catalysis which would occur on hotter walls. A pressure-atomizing nozzle, which has been substituted for an earlier air-atomizing nozzle, provides a short stable flame at 15 percent excess air. All tests reported here were made when burning either No. 2 fuel oil normally containing about 0.25 percent sulfur, or No. 2 fuel oil to which sufficient carbon disulfide was added to produce a 5.5 percent sulfur fuel. The SO_2 and SO_3 concentrations of the bulk flue gas are approximately 3200 ppm and 40 ppm, respectively, duplicating sulfur oxide levels in large-scale boiler furnaces.

Identification of Alkali Iron Trisulfates

Prior to development of the optical technique, positive identification of alkali iron trisulfates on specimen surfaces was a difficult problem. Except for refractive index, it was difficult to find any conveniently determined characteristic of the trisulfates which is not also characteristic of other compounds that might form during these tests, such as pryosulfate, ferric sulfate, and ferrous sulfate. Properties of alkali iron trisulfates considered helpful, but not positive, for identification are melting point, pH of an aqueous solution, pH prints, and evolution of SO_3 on heating.

Because some postulated corrosion mechanisms include formation of sulfides at the metal surface, occurrence of sulfides at the scale-metal interface may establish that trisulfates had been present during a test. The sodium azide test(5) has been used here to identify the presence of sulfides, but this test is not quantitative. It consists of applying a few drops of a mixture of sodium azide (NaN_3) and iodine to the interface while observing the specimen through a microscope. The reaction between sodium azide and iodine, which occurs only in the presence of sulfides, releases nitrogen gas which is readily observed through the microscope as bubbles in the solution. This is an exceedingly sensitive test for sulfide sulfur, but unfortunately it is not even a qualitative test for trisulfates because sulfides can form from other reactions than the reduction of the trisulfates by an iron surface. The azide test nonetheless is a useful tool for examining supposedly corroded surfaces.

Until the index-of-refraction method was developed, only X-ray diffraction gave a sure indication of the presence of trisulfates after a test. The concentration of trisulfates necessary for certain identification by X-ray diffraction is approximately 10 percent, too high except for test durations probably longer than 100 hours. Hence, although it gives a sure indication whether or not trisulfates were formed, X-ray diffraction is not a practical means of indicating the onset of corrosion except through prolonged tests.

Electrochemical Cell

The electrochemical cell was conceived originally as a detector of trisulfates by using melting point as the measured characteristic. The presence of a molten electrolyte between the two electrodes would provide a battery to generate a low, but measurable, voltage. This concept proved workable, but as a result of further tests, the electrochemical cell developed into a corrosion "meter" which can be used to indicate the instantaneous rate of corrosion. Because the rate of corrosion is much greater at temperatures of 1000 F to 1200 F with trisulfates present than when trisulfates are not present, the cell also acts as an indirect measure of the presence of trisulfates. However, if high corrosion rates are produced by reactions which do not include trisulfates, these reactions also would be indicated as a voltage and a current flow. The electrochemical cell can be most helpful in investigating the corrosion mechanism by measuring the corrosion directly, rather than by measuring corrosion indirectly by sensing the presence of compounds such as the trisulfates. The index-of-refraction method now meets that requirement.

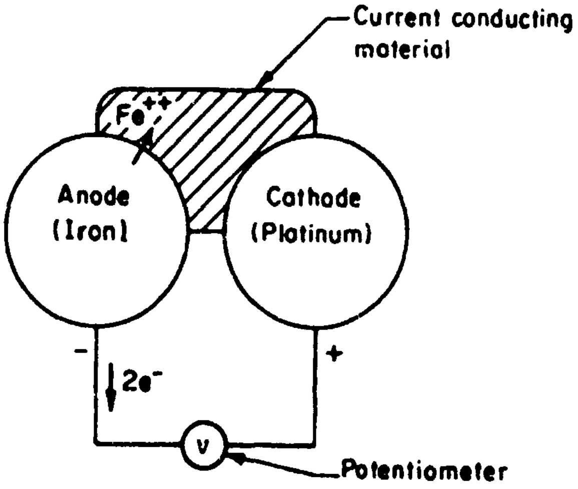


FIGURE 5. PRINCIPLE OF THE ELECTROCHEMICAL CELL

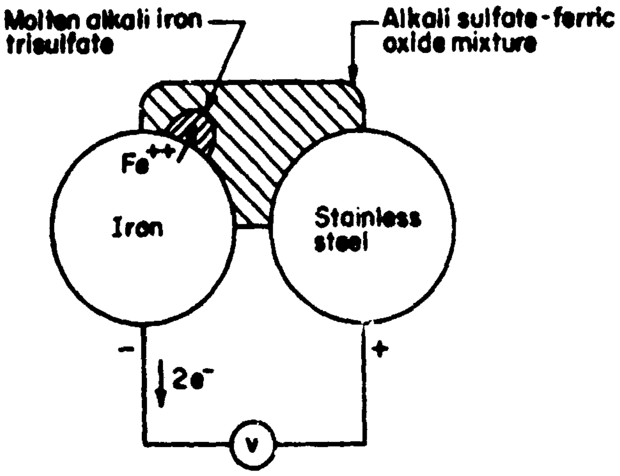
Figure 5 illustrates the principle of the electrochemical cell. The cell consists of two dissimilar metals separated by a small gap, with each metal connected to a high-resistance voltmeter by a wire of the same material. When a current-conducting salt (not necessarily molten) bridges the gap between the metals, it provides an electrolyte and the circuit is completed. If the anode corrodes, its neutral metal atoms become positively charged ions, which migrate into the electrolyte. The anode remains electrically neutral because electrons released in forming the positively charged metal ions flow from the anode by way of the attached wire. The conducting material also remains electrically neutral because the flow of positively charged ions going into solution is balanced by the flow of electrons from the cathode. This flow of electrons in the external circuit produces a measurable current which, passed through the high-resistance voltmeter, is indicated as cell voltage. Current flow in the circuit is proportional to corrosion, and by providing a meter resistance of 100,000 ohms by bridging the input terminals of a recording potentiometer, current flow is related to voltage by the equation:

$$\text{current} = \text{voltage} \times 10^{-5} ,$$

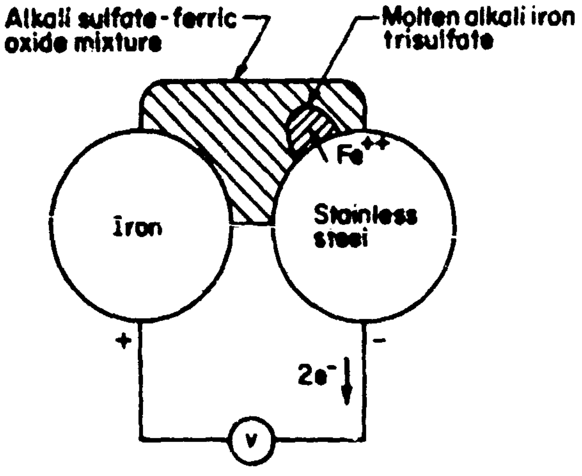
so that 0.8 volt in this circuit is equivalent to 8×10^{-6} amperes or 8 microamperes flowing through the cell.

Some difficulty was experienced in arriving at the proper choice of electrode materials. The two metals must be dissimilar, and the electrode that corrodes, the anode, should be typical of furnace materials. Low carbon steel was selected as the anode material in preference to corrosion-resistant high-alloy steels because the increased rate of corrosion would be more readily detected. The cathodes were made initially of stainless steel or nickel, but the iron:stainless steel and the iron:nickel cells produced positive and negative voltages randomly which were difficult to interpret.

The sign of the initial voltage apparently depends on which electrode the molten trisulfate first appears. If an alkali sulfate-ferric oxide mixture is placed on an iron:stainless steel cell and a molten nodule of trisulfate forms only on the iron surface, the iron electrode will corrode more rapidly than the stainless steel. Therefore, the iron will be at a negative potential (anodic) as iron dissolves into the electrolyte and electrons leave the iron through the wire as shown in Figure 6a.



a. Molten Nodule on Iron Only



b. Molten Nodule on Stainless Steel Only

FIGURE 6. VOLTAGES GENERATED BY AN IRON:STAINLESS STEEL ELECTROCHEMICAL CELL

If the molten-trisulfate nodule forms first on the stainless steel electrode, that spot on the stainless steel will corrode and it will become the negative electrode (anodic) as shown in Figure 6b. This causes the iron electrode to be positive (cathodic) as occurred in some tests. That such nodules of molten trisulfate can form is supported by indications of low pH by a print-out method on damp pH paper, which always show that the low-pH material forms in spots on the surface and not as a continuous film.

The answer to this problem was to use iron as the anode and a completely inert material for the cathode that would not corrode in the presence of molten alkali trisulfates. Platinum was selected as this material for the cathode. An iron:platinum cell could then be used to detect the presence of corrosion of the iron electrode without concern for the presence of molten trisulfates elsewhere in the system.

Two tests of cells with iron, stainless steel, and platinum electrodes in a common electrolyte confirmed the fact that both the iron and stainless steel could be at a negative voltage relative to the platinum, but at the same time, the iron could be at a voltage either positive or negative relative to the stainless steel. These tests confirmed that using metals which can corrode at furnace conditions for both electrodes produces inconclusive results.

Figure 7 shows the configuration of the iron:platinum cell used in all tests reported here, except for the test shown in Figure 8. The corrosive mixture is placed in the iron boat filling the gap between the boat and the platinum wire which is wound on an alumina tube. In the system shown, the mixture was about ¼-inch thick. Temperature of the boat is measured by an embedded thermocouple.

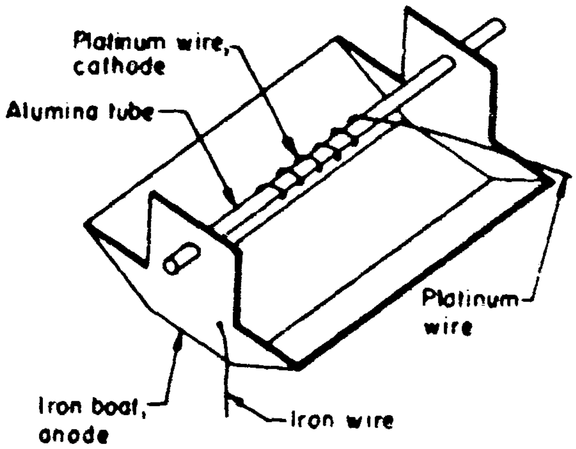


FIGURE 7. CONFIGURATION OF IRON:PLATINUM ELECTROCHEMICAL CELL

RESULTS OF STUDIES WITH ELECTROCHEMICAL CELL

Iron:Nickel Oxide Cell

An early test to check conductance as an indication of the presence of molten trisulfates used a cell made of two electrodes of 3/16-inch diameter rods of iron and oxidized nickel placed end to end. The rods were cemented on a porcelain rod with a gap of 0.005 to 0.010 inch between the two metals, and were set in the central position of the usual specimen holder shown in Figure 19 of the Seventh Summary Report (April 30, 1966). Other conventional 3/16-inch-diameter tubular steel specimens were placed in the remaining positions in the holder to duplicate a regular test.

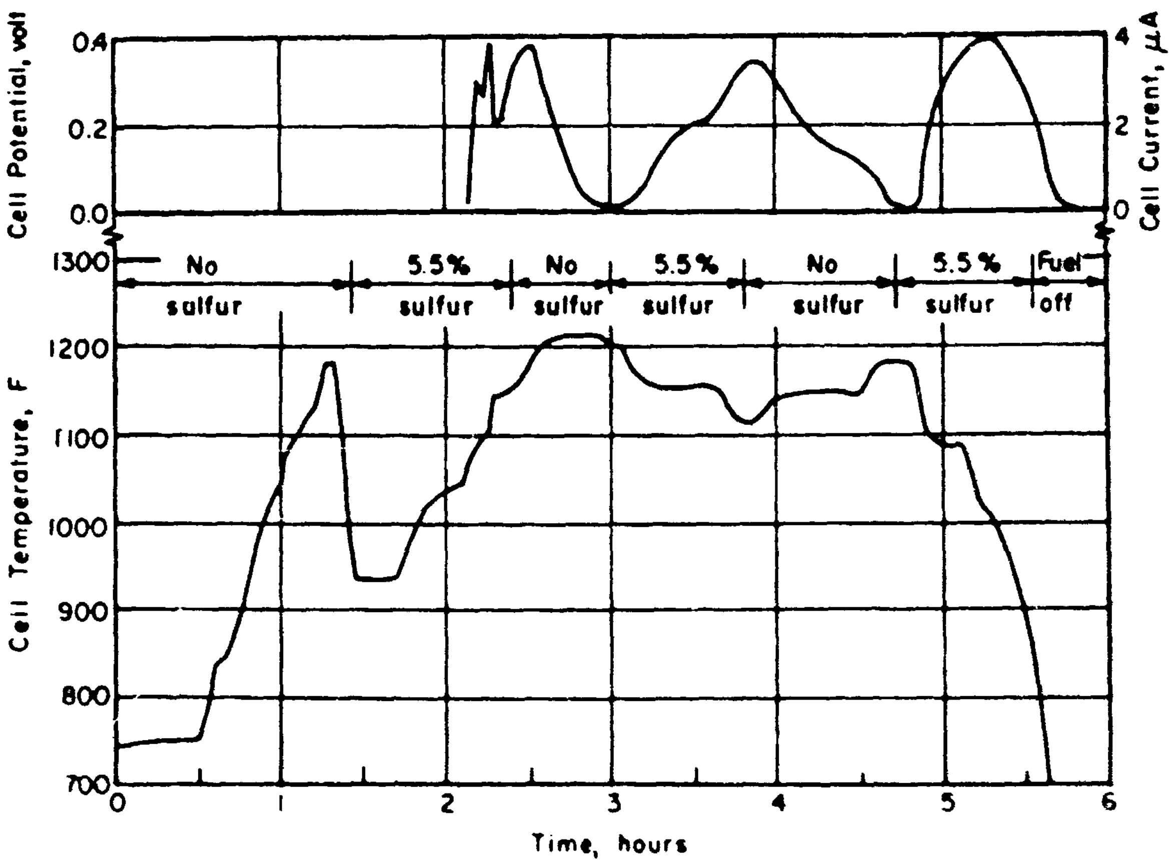


FIGURE 8. TEST OF IRON:NICKEL OXIDE ELECTROCHEMICAL CELL

Figure 8 shows the voltage developed by this electrochemical cell at various temperatures when the electrodes were covered with a thin layer of alkali sulfate-ferric oxide mixture capable of forming the trisulfate. During the initial heating period, no voltage was produced in the absence of sulfur oxides in the flue gas even though the temperature was raised to 1182 F, showing that no molten phase was being produced when no SO_2 or SO_3 was present. The temperature was then decreased to 947 F and the sulfur-containing fuel was fired. As the temperature increased, no voltage was observed until the cell reached 1070 F when the voltage suddenly increased to 0.3 volt, showing that corrosion was then occurring with about 3200 ppm SO_2 and 40 ppm SO_3 in the bulk flue gas. Shortly after changing back to sulfur-free fuel, the voltage dropped to zero. Obviously, the coating was no longer corrosive, confirming that the trisulfate must have been converted back into alkali sulfate and ferric oxide at 1200 F when no sulfur oxides were present in the flue gas. When sulfur-bearing fuel was burned again, 3 hours after the test had started, the voltage once more increased to over 0.3 volt. The voltage dropped to zero again when the furnace was switched to sulfur-free fuel. In all, three such cycles were demonstrated during this test.

These data showed convincingly that an electrochemical system could indicate variations in apparent corrosion rate depending on the presence of sulfur oxides, and that corrosion may be occurring long before any metal loss or other changes can be detected by conventional means. Later problems with reversed polarity led to discarding this cell in favor of the iron:platinum cell.

Iron:Platinum Cell

Table 1 tabulates all tests conducted with iron:platinum electrochemical cells. The conditions that have been varied in these tests are:

1. Sulfur content of fuel: 0.25 or 5.5 percent.
2. Initial condition of iron: clean or oxidized.
3. Corrodent mixture: various alkali, Fe_2O_3, and fly ash combinations.
4. Cell temperature: 745 F to 1200 F.
5. Duration of test: 1.3 to 4.7 hours.

Most tests were conducted at temperatures of 890 F to 1200 F while burning fuel containing 5.5 percent sulfur, using initially clean iron specimens coated with alkali sulfates as the corrodent in the boat. In all cases, Fe_2O_3 was present either in the corrodent mixture or on the iron surface, as even the initially clean iron specimens oxidized rapidly in the flue-gas environment.

Figures 9 through 21 show the cell potential and current and the specimen temperatures for Table 1. Tests are shown in the same order as listed in Table 1.

SiO_2

Figure 9 shows the result of a test with the electrochemical cell containing SiO_2 to bridge the gap between the iron boat and the platinum electrode. Its purpose was to establish the voltage produced by gas-phase oxidation of the iron with no alkali present. The absence of any voltage undoubtedly shows that SiO_2 was too good an electrical insulator to provide any current flow even through a 100,000-ohm circuit.

TABLE 1. SUMMARY OF TESTS WITH IRON:PLATINUM ELECTROCHEMICAL CELL

						Cell Potential			Analysis of Specimen After Test	
Figure	Sulfur in Fuel, percent	Initial State of Iron	Corrodent Mixture	Average Iron Temp., F	Length of Test, hrs	Peak, volts	1 hr After Peak, volts	Rate of Change in 1 hr, volts/hr	pH	Sulfides
5	5.5	Clean	SiO_2	1100	3.5	0.0	- (a)	-	5.0	None
6	"	"	Na_2SO_4, K_2SO_4	890	2.4	0.61	0.43	-0.18	5.0	Much
7	"	"	"	975	3.0	0.80	0.43	-0.37	3.5	Much(c)
8	"	"	"	1100	2.1	0.82	0.44	-0.38	3.5	Much
9	"	"	"	1120	2.6	0.73	0.47	-0.26	4.0	Slight
10	"	Oxidized	"	1075	2.1	0.77	0.41	-0.36	1.5	Some
11	"	"	"	1100	1.3	0.81	0.49(b)	-0.32	4.0	Much
12	0.25	Clean	"	1120	2.1	0.64	- (a)	-	5.5	Slight
13	5.5	"	"	745	3.8	0.26	- (a)	-	4.5	Much
				840		0.59	0.45(b)	-0.14		
				1000		0.68	0.41	-0.27		
				1200		0.70	0.05(b)	-0.65		
14	"	"	Na_2SO_4, K_2SO_4, Fe_2O_3	1175	4.7	0.36	- (a)	-	2.0	Some
15	5.5,0.25	Oxidized	"	1125	4.5	0.62	- (a)	-	-	-
16	5.5	Clean	Fly Ash 44-1, Na_2SO_4, K_2SO_4, Fe_2O_3	1130	2.7	0.09	- (a)	-	2.5	Some
17	"	"	Fly Ash 44-1	1120	2.6	0.0	- (a)	-	5.5	None

(a) No distinct peak.
(b) Extrapolated.
(c) Trisulfate crystals observed by optical microscopy.

Alkali Sulfates

Figures 10 through 15 show results of a series of tests with the electrochemical cell containing a 1:1 mol ratio of sodium sulfate and potassium sulfate at specimen temperatures of 890 F to 1120 F when burning a 5.5 percent sulfur fuel. Flue gas over the cell contained about 3200 ppm of SO_2 and 40 ppm of SO_3. Peak cell potentials ranged from 0.61 to 0.82 volt with the highest voltages occurring early in the tests followed by a gradual lowering to 0.4 volt after about two hours' exposure. Similar results were obtained whether the iron electrode in the cell was clean or oxidized at the beginning of the test. In each of these tests, significant corrosion was indicated at specimen temperatures considerably below the 1030 F(9) melting point reported for a mixture of sodium and potassium iron trisulfate. Others(8) have also observed this phenomenon.

Figure 16 is for a test with alkali sulfates in the cell and firing straight No. 2 fuel oil with no appreciable sulfur oxides present in the flue gas. Although a cell potential of over 0.6 volt was observed, the initial high peak voltage did not occur and there was no gradual voltage drop as when a sulfur-bearing fuel was burned. These data suggest that once alkali sulfates have formed on a tube, corrosion may occur even though the temperature is about 500 F below the melting point of the salt. No allowance is made here for the normal current flow in the electrochemical cell as iron oxides are being formed.

Figure 17 shows the results of a test in a cell containing alkali sulfates in which step changes of temperature were made during the test. Again, except at the lowest temperature of 750 F, each change in temperature was followed by a voltage peak and then a gradual drop in voltage. The magnitude of the peak voltage increased slightly as the temperature level was increased, and the rate of falloff in voltage also was greater as the temperature was increased.

Alkali Sulfate-Ferric Oxide Mixture

Figures 18 and 19 show the results obtained with a mixture of alkali sulfates and ferric oxide in the cell. The mol ratio of the mixture was 1.5:1.5:1.0 Na_2SO_4, K_2SO_4, and Fe_2O_3, respectively. Peak cell potentials were only about 0.4 and 0.6 volt. respectively, less than the potentials observed for the tests with only alkali sulfates present. A gradual drop in voltage was observed in the test shown in Figure 18, although the initial voltage drop was not as rapid as with the alkali sulfates alone. The temperature here averaged about 1175 F which should be sufficient for trisulfates to form. About half way through the test shown in Figure 19, the fuel was switched from doped 5.5-percent-sulfur fuel to regular No. 2 fuel oil. No large decrease in voltage was observed in two hours of firing with the sulfur-free fuel, indicating that any trisulfates that were present did not decompose rapidly when the SO_3 level was reduced. This may have been due to the thick layer (over 0.25 inch) of alkali sulfate-ferric oxide mixture placed on the specimen. Enough time probably was not available to dissociate this relatively large mass of material.

Fly-Ash Coatings

Figure 20 shows the cell potentials and currents observed in a test when the cell contained equal parts of fly ash and a mixture of alkali sulfate and ferric oxide, in the usual 1.5:1.5:1.0 mol ratio. A cell potential of only about

0.1 volt was observed. The fly ash used in this test, described in Table 2, contains 36.2 percent Fe_2O_3 and 1.8 percent CaO + MgO.

TABLE 2. COMPOSITION OF FLY ASH SAMPLE USED IN TESTS SHOWN IN FIGURES 20 AND 21.

Constituent	Weight Percent
SiO_2	38.0
Al_2O_3	14.6
Fe_2O_3	36.2
CaO	1.1
MgO	0.7
Na_2O	4.0
SO_3	0.1
C	2.1

Figure 21 shows the results of a similar test with the same fly ash but with no alkali sulfates or ferric oxide added; no voltage was observed during the entire test. This indicates either that corrosion was not occurring or that the fly ash was not sufficiently conductive electrically to permit electron flow.

Discussion of Results

The high initial peak voltages shown in Figures 10 through 15 and in Figure 17, which almost by definition mean a high corrosion rate, fall off with time at a constant temperature even when normal alkali sulfates alone are present. The rate of decrease in voltage apparently is greater as the temperature is higher, as is shown quite well in Figure 17. Figure 10 which shows a high rate of falloff in voltage at 890 F, and Figure 12 which shows a greater rate of falloff at 1125 F, seem to confirm this postulate when only normal alkali sulfates are in contact with the iron surface. The same rapid decrease in cell potential was not seen in Figure 16, when no sulfur oxides were present in the gas stream. Hence, in some as-yet-unexplained way, sulfur oxides contribute to the falloff in voltage during a test. When a mixture of the alkali sulfates and ferric oxide is present, as in Figure 18, no peak is observed, the total rate of corrosion of the iron electrode is low, and the rate decreases slowly with time, all suggesting that a reaction may be occurring in the mixture but that only a minor attack is occurring of the iron electrode. It may be that a peak voltage accompanied by a gradually decreasing cell voltage indicates corrosion, but that a constant voltage of about 0.4 volt may represent a contact potential or some other spurious effect.

Small samples from most of the tests reported above were examined for the presence of trisulfate by the index-of-refraction method. Trisulfate crystals were observed only in the sample from the test shown in Figure 11, but the spotty formation of trisulfates observed on specimens used in earlier tests suggests that the problem may be one mainly of sampling. Multiple samples will need to be

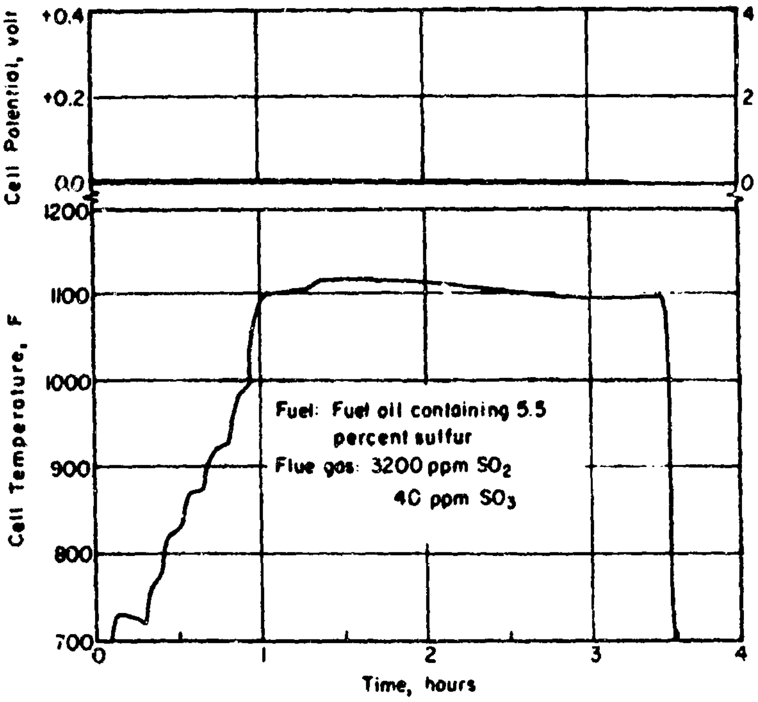


FIGURE 9. TEST OF IRON:PLATINUM CELL CONTAINING SiO_2

Note: All figures will include current on same plot with voltage.

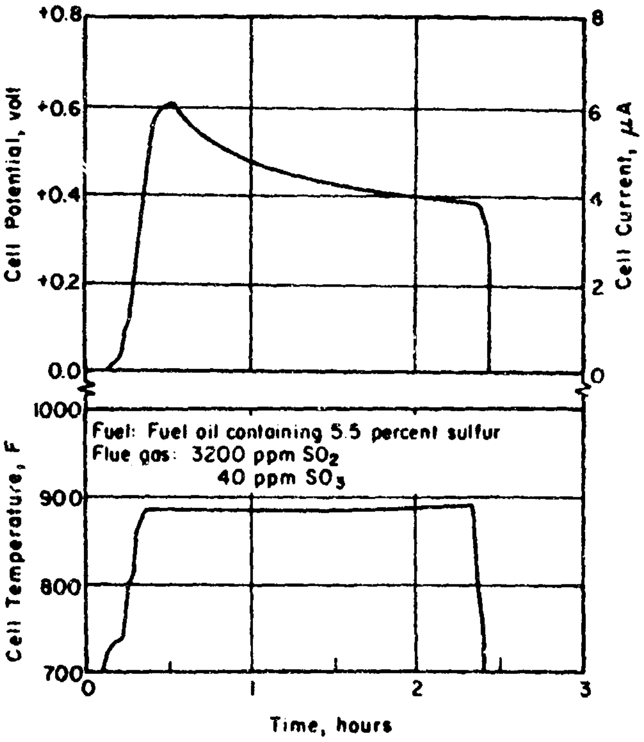


FIGURE 10. TEST AT 890 F OF IRON:PLATINUM CELL CONTAINING ALKALI SULFATES

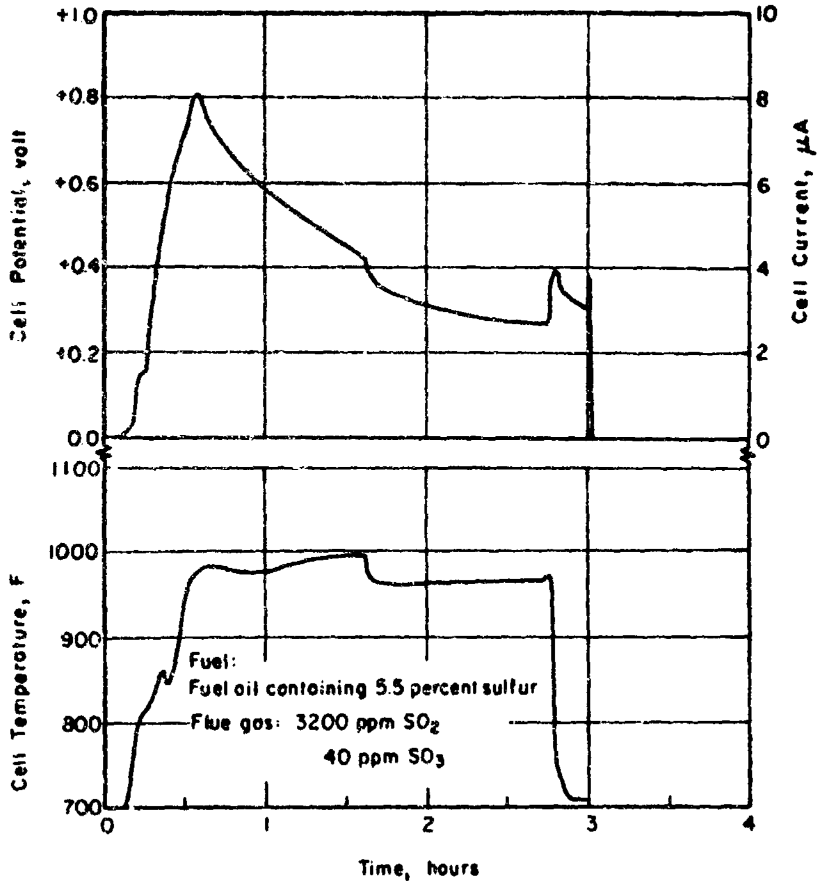


FIGURE 11. TEST AT 975 F OF IRON:PLATINUM CELL CONTAINING ALKALI SULFATES

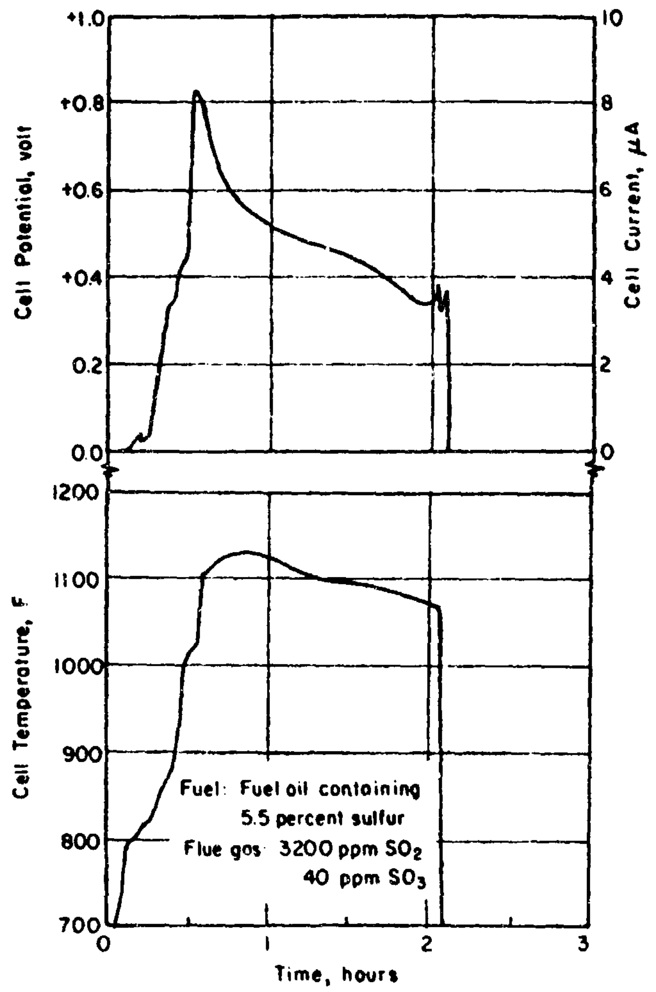


FIGURE 12. TEST AT 1100 F OF IRON:PLATINUM CELL CONTAINING ALKALI SULFATES

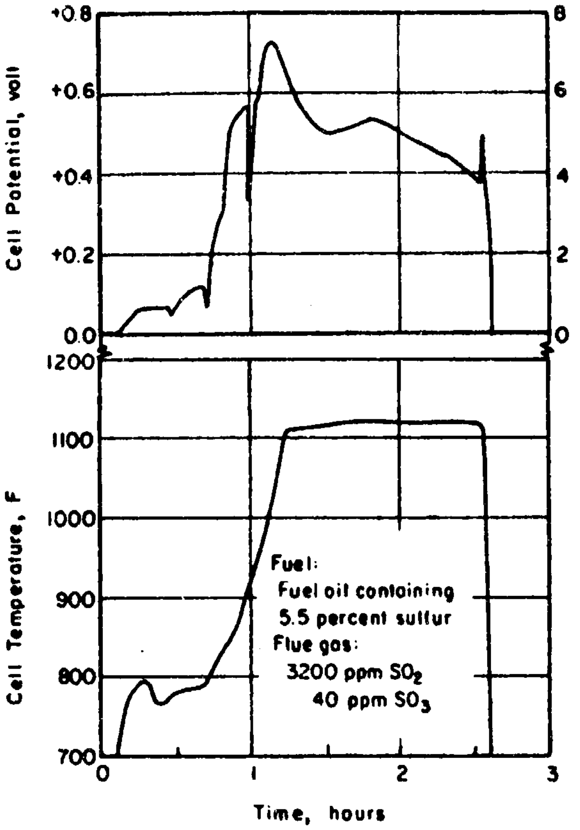


FIGURE 13. TEST AT 1120 F OF IRON:PLATINUM CELL CONTAINING ALKALI SULFATES

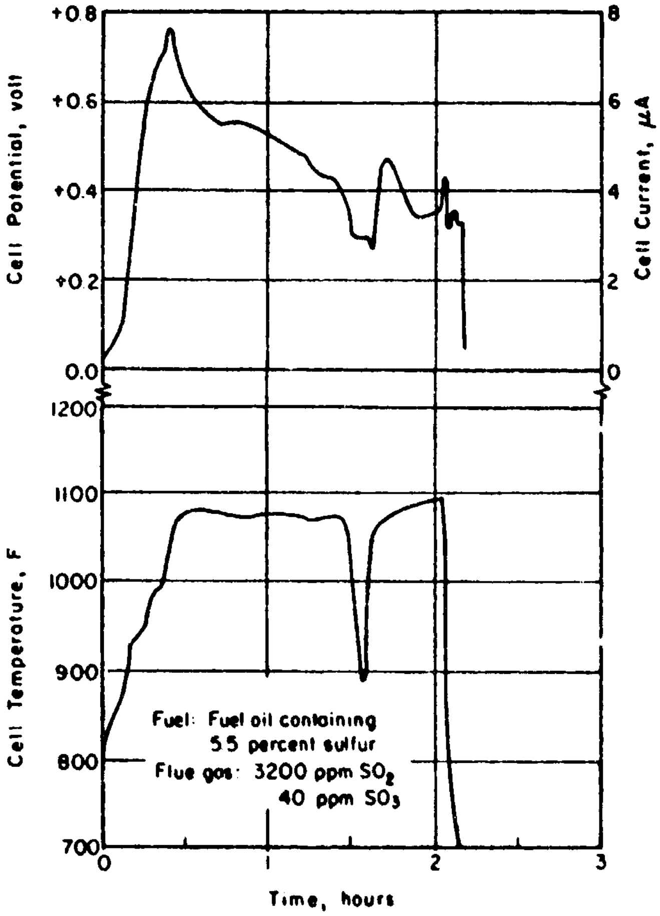


FIGURE 14. TEST AT 1075 F OF IRON:PLATINUM CELL CONTAINING ALKALI SULFATES WITH IRON INITIALLY OXIDIZED

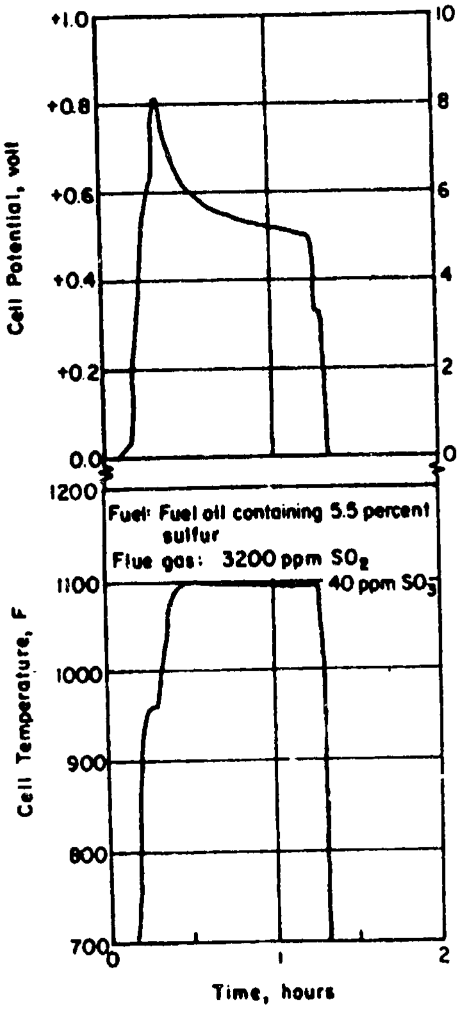


FIGURE 15. TEST AT 1100 F OF IRON: PLATINUM CELL CONTAINING ALKALI SULFATES WITH IRON INITIALLY OXIDIZED

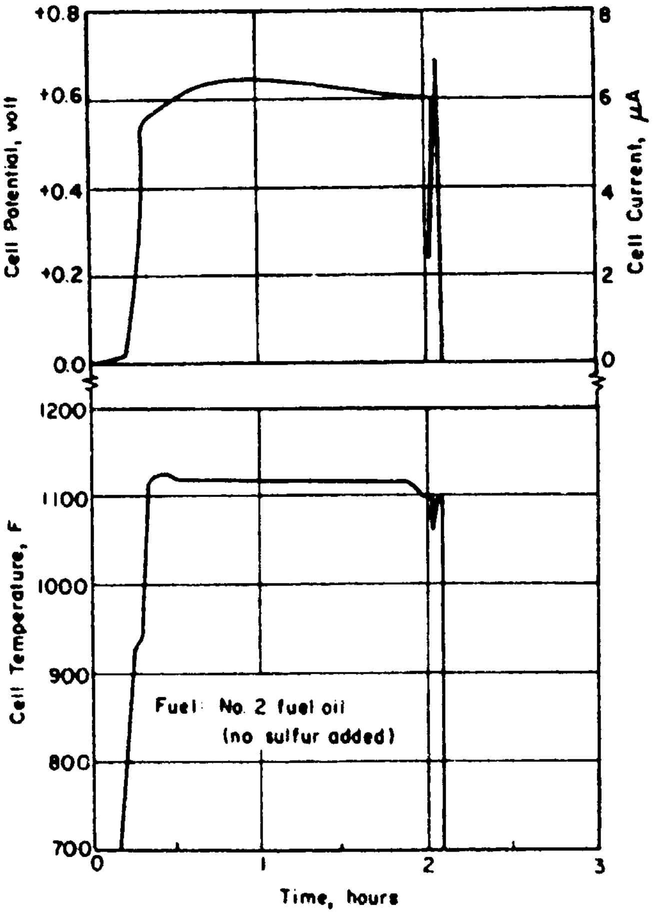


FIGURE 16. TEST OF IRON:PLATINUM CELL CONTAINING ALKALI SULFATES WHEN BURNING NO. 2 FUEL OIL WITHOUT ADDED SULFUR

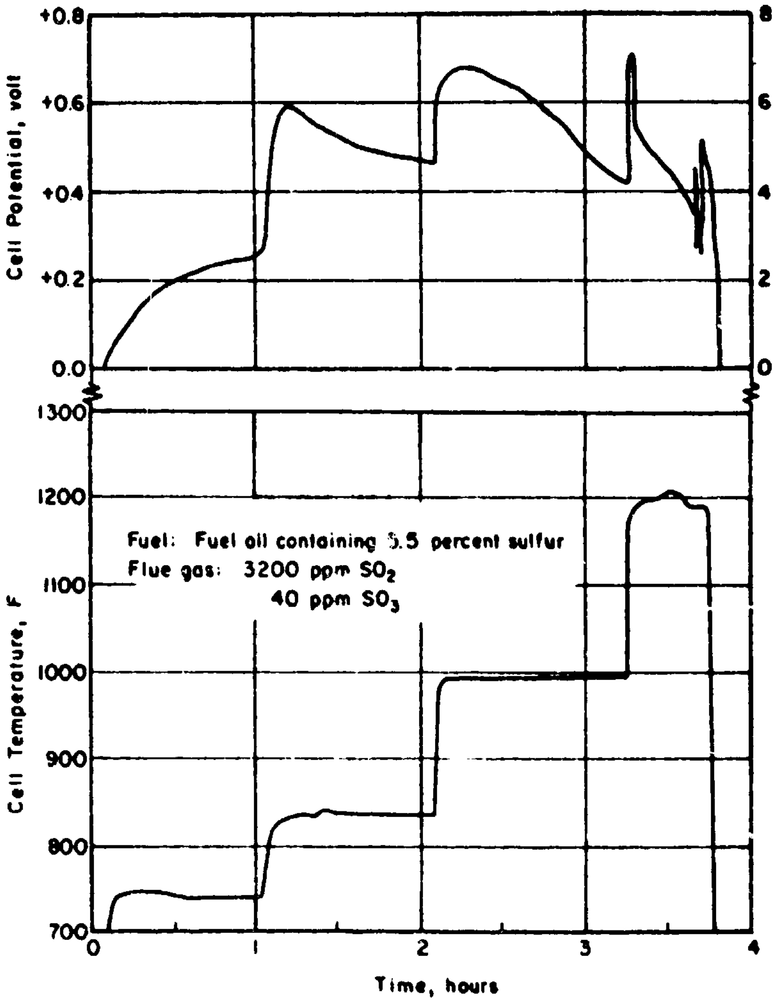


FIGURE 17. TEST OF IRON:PLATINUM CELL CONTAINING ALKALI SULFATES WITH SUDDEN TEMPERATURE INCREASES

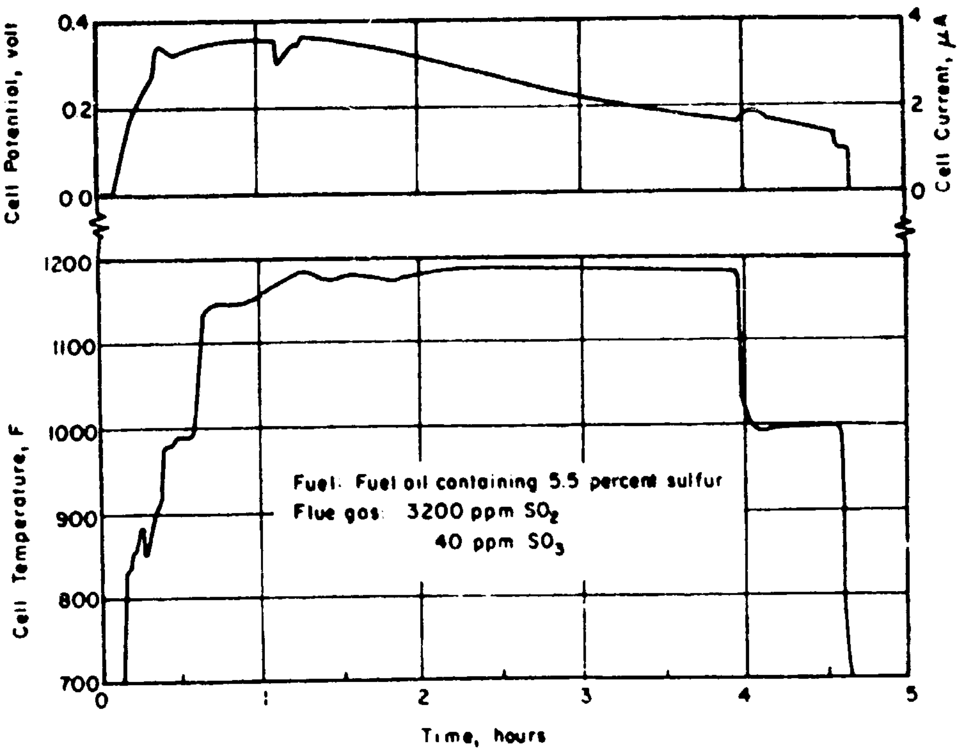


FIGURE 18. TEST AT 1175 F OF IRON:PLATINUM CELL CONTAINING AN ALKALI SULFATE-FERRIC OXIDE MIXTURE

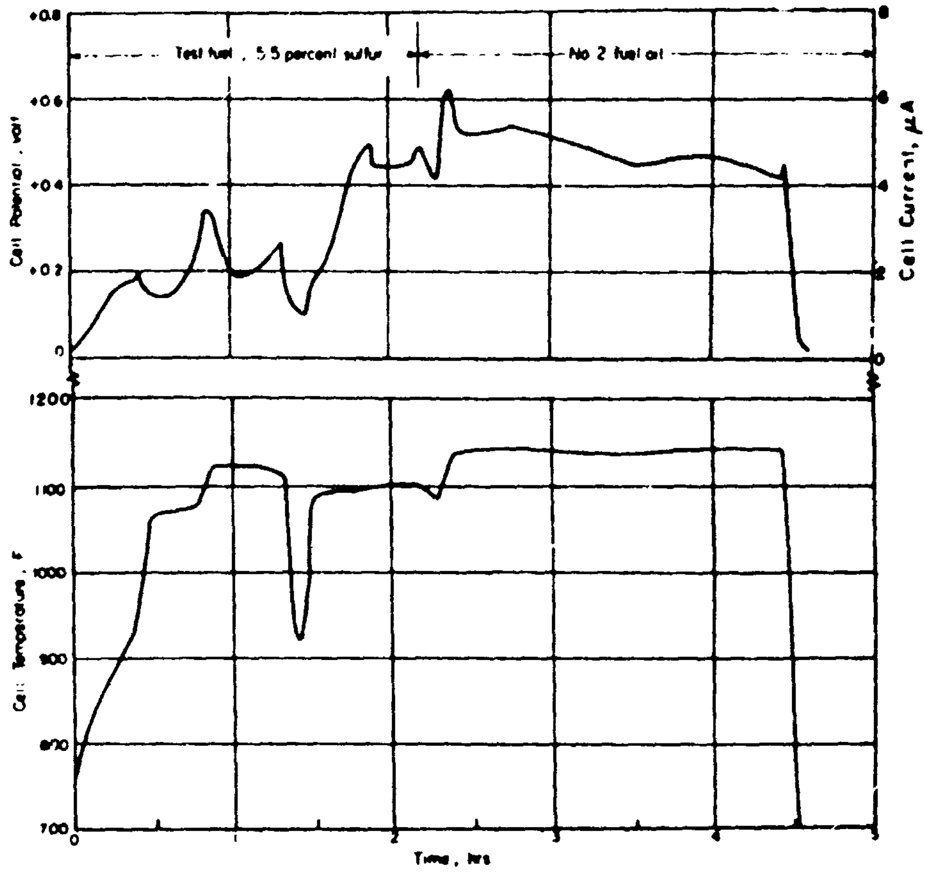


FIGURE 19. TEST AT 1125 F OF IRON:PLATINUM CELL CONTAINING AN ALKALI SULFATE-FERRIC OXIDE MIXTURE

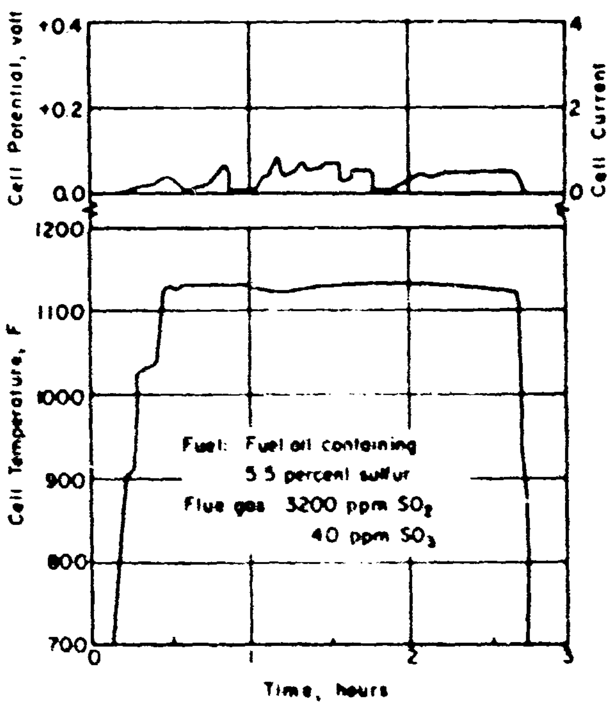


FIGURE 20. TEST AT 1125 F
IRON:PLATINUM
CONTAINING A F
ALKALI SULFATE
OXIDE MIXTURE

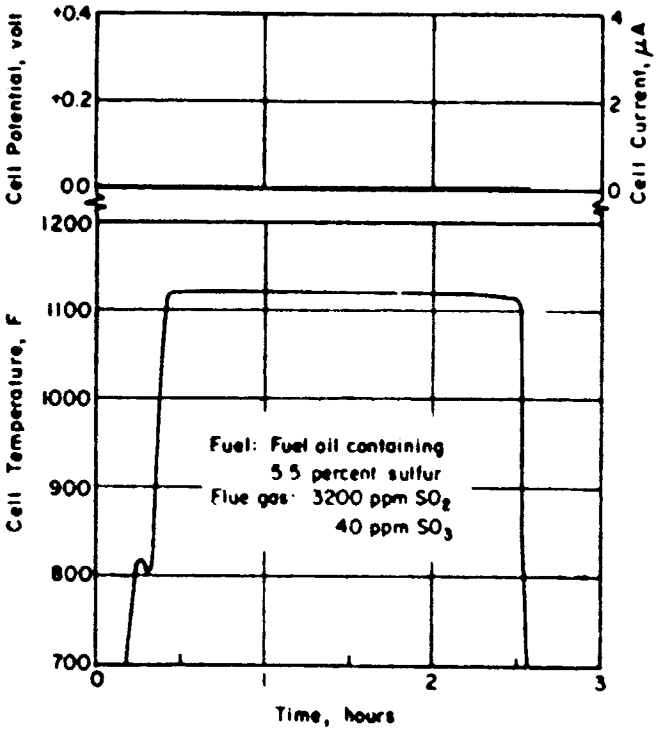


FIGURE 21. TEST AT 1120 F OF IRON:PLATINUM CELL CONTAINING FLY ASH

examined to increase the chances of observing the particular spots where initial trisulfate formation occurs. The ability of the electrochemical cell to indicate corrosion when only microscopic areas are involved may magnify this problem. The fact that trisulfate was definitely observed on one specimen indicates that the mechanism of corrosion may be similar to that occurring on superheater tubes.

FORMATION OF SULFIDES

An additional check on the presence of sulfides was made on several specimens from earlier tests. The specimens examined were from Tests G 18, G 19, G 24, and G 29, described in Table 4 and Table 7 of the First Summary Report. Deposits from Tests G 18 and G 19 had pH values as low as 1.0 and showed some visual evidence of melting, indicating that trisulfates were formed during the tests. Trisulfate crystals were observed in the scale from Test G 19 by the index-of-refraction technique. Tests G 24 and G 29 did not yield deposits with a low pH nor was there evidence of melting, indicating that trisulfates were not formed.

Using the sodium azide test described earlier, specimens from Tests G 18 and G 19, where the trisulfates were evidently present, gave strong indication that sulfides existed beneath the surface layer. Specimens from Tests G 24 and G 29 where trisulfates were not detected gave little or no indication of the presence of sulfides. The lack of sulfides from Tests G 24 and G 29 indicates that sulfides are not the result of reaction of the metal specimen with the sulfur oxides in the gas stream. Hence, these data support the conclusions of Nelson and Cain(8), that the corrosion reaction can be:

$$3Fe + SO_4^{=} \rightarrow Fe_3O_4 + S^{=} .$$

FUTURE WORK

No further development of the electrochemical cell appears necessary, and the present version will be used in studying factors affecting corrosion. It may be desirable to decrease the volume of corrodent, but the basic design appears satisfactory.

Two main fields need investigation during the coming year, the influence of alkalies deposited from the flame, and the effect of deposits on the formation of trisulfates. Based on probe studies in full-scale furnaces, it is generally agreed that alkalies condense readily on cool surfaces, but the same action has not been tried in this investigation. Hence, by adding alkalies to the flame, it may be possible to deposit a layer of Na_2SO_4 on a specimen to serve as the start of the corrosion process. This is expected to pose experimental problems because the alkalies will also deposit on the walls of the test furnace and on the specimen supports. Some ingenuity may be necessary to devise a practical technique.

One of the earliest objectives of this study was to investigate which constituents in fuel ash were involved in corrosion, and to evaluate the overall effects of deposits. It is now certain that the alkalies and sulfur in coal, together with vanadium in fuel oil, are the principal chemical contributors to corrosion. Much less is known about the physical effects of deposits. Hence, future experimental work in the fuel-burning furnace will be aimed principally at identifying exactly how deposits influence the formation of trisulfates specifically and corrosion generally. If the concept of a deposit acting by providing a relatively stagnant gas film to allow high concentrations of SO_3 is the correct one, it should be possible to demonstrate this by relatively short-duration tests. If migration of alkalies through deposits is the dominating factor, more troubles can be expected experimentally because this migration occurs slowly. In any event, the influence of deposits is worth detailed investigation and will be given major attention in the fuel-burning-furnace tests.

MECHANISM OF CORROSION

by

P. D. Miller

SULFIDATION CORROSION

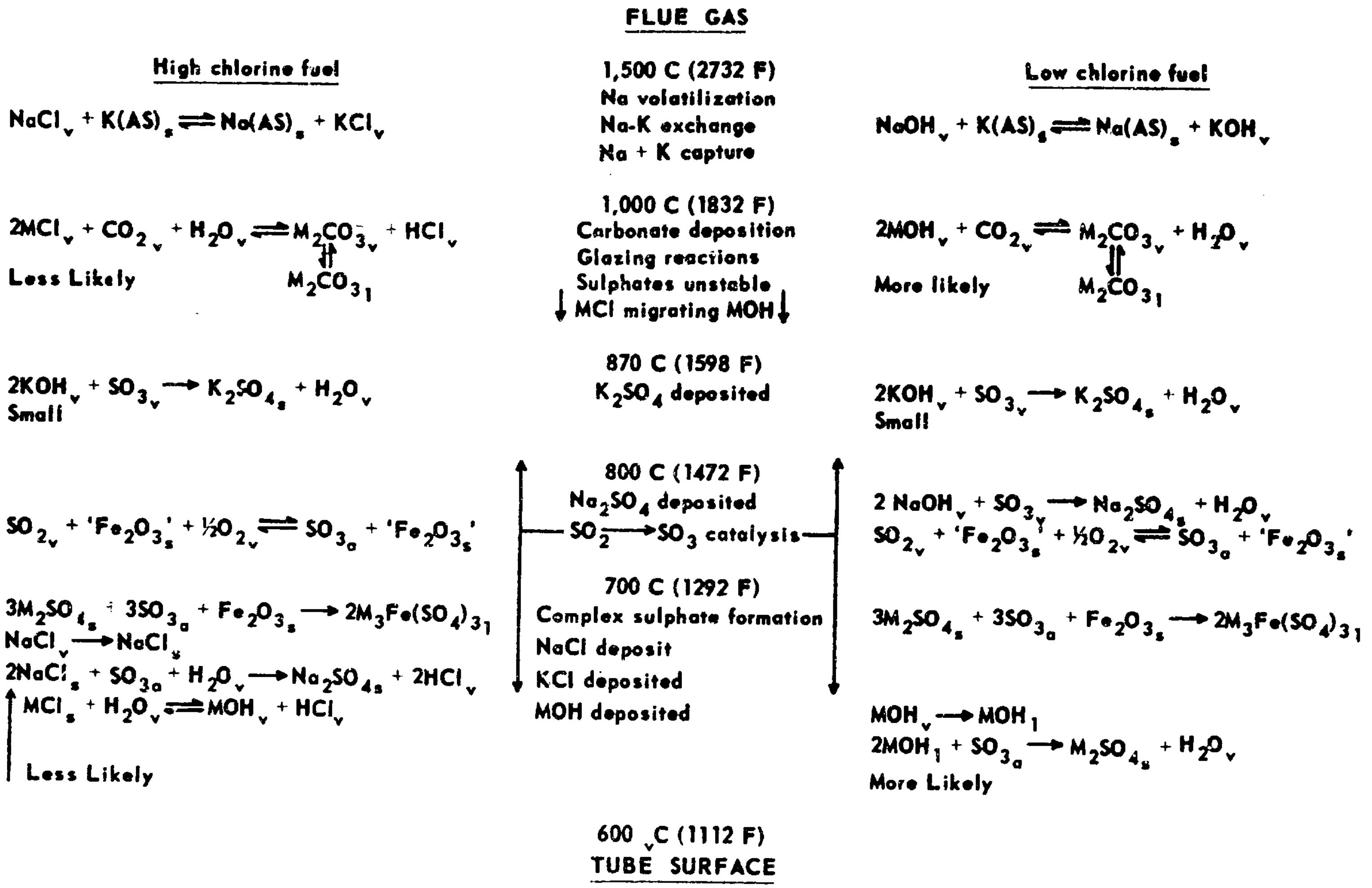
It has been shown by many investigators that the most severely corroded areas in operating boilers are those where molten deposits are formed. There has been considerable discussion of corrosion by sulfate-containing deposits that are molten at some period during the operating cycle. Such deposits with a sulfate base have been found to be extremely corrosive to superheaters of coal-fired central stations at temperatures of 1000 to 1300 F and in gas turbines at temperatures of 1400 to 1500 F. It is realized that the chemical composition of the deposits is not the same in the two instances, but the sulfate ion is common to each.

Another factor common to each is the presence of metal sulfides in the corroded areas. It is suggested that information as to how sulfidation takes place on a superheater will be of value in understanding a similar reaction on a turbine component. Recent studies reported in the literature concerning sulfidation reactions show the importance of this step in the overall wastage problem.

The Formation of Sulfate-Containing Deposits

Before discussing the properties and action of the sulfates, it is of interest to consider their mode of formation. It has been proposed by several investigators that the alkali-metal constituents in the fuel (considering coal first) are the primary starting materials. These constituents are volatilized as chlorides, oxides, or hydroxides because of the high temperature in the flame of at least 3000 F, and are then converted to the simple sulfate salts K_2SO_4 and Na_2SO_4, which enter into the reactions discussed later. Actually, many mechanisms for the formation of alkali salts have been proposed, and agreement has not been reached as to the most likely one. How and his associates in CEGB recently presented a brief summary of current theories explaining such salt formation.(10)

A fairly detailed treatment has been presented by Jackson.(11) He proposed an interesting and comprehensive hypothesis in which alkali-metal hydroxides or chlorides are the migrating species within porous deposits of fly ash. A possible sequence of reactions is shown in Figure 22. Reactions are separated according to whether the fuel is high or low in chlorine. Reactions at the top of the figure are those which are thought to occur at high flue-gas temperatures, while those at the bottom of the figure are those which occur in the deposits near the tube surface.



(AS) = aluminosilicate. Subscripts: a = adsorbed, 1 = liquid, s = solid, v = vapour.

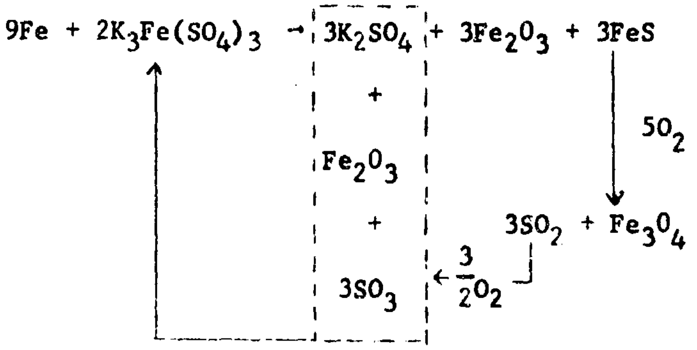
FIGURE 22. SEQUENCE OF REACTIONS WITH TEMPERATURE GRADIENT IN DEPOSIT. (11)

In the case of turbines, it has been proposed that the sulfate is in the form of sodium sulfate produced when salt is ingested with the incoming air. The reaction is

$$2NaCl + SO_2 + 1/2\ O_2 + H_2O \rightarrow Na_2SO_4 + 2HCl. \qquad (1)$$

It should be noted that somewhat different reactions are proposed for NaCl in Figure 22.

Most investigators now agree that corrosion in coal-fired boilers at temperatures of 1000 to 1300 F is caused by complex sulfates such as $Na_3Fe(SO_4)_3$ and $K_3Fe(SO_4)_3$, which are molten under these conditions. The Sixth Summary Report (October 31, 1965) on the earlier phase of the Battelle work discussed the alkali trisulfates in some detail and suggested the following cyclic corrosion mechanism patterned after the one proposed by Nelson and Cain (8,9):



(2)

It should be noted that FeS is a product of the above reaction, and that it is invariably found in corroded sections of boiler tubing.

An alternative and more recent suggestion of the steps that influence the formation and growth of deposits from combusion products of coal is given by Plumley and his associates.(12)

During combustion, the pyrites, FeS_2, and organic sulfur react with oxygen:

$$2FeS_2 + 5\text{-}1/2O_2 \rightarrow Fe_2O_3 + 4SO_2$$
$$RS\ (\text{organic sulfide}) + O_2 \rightarrow SO_2$$
$$SO_2 + 1/2O_2 \rightarrow SO_3\ . \qquad (3)$$

In the high flame temperature, the Na and K in the clays, shales, etc. react to form Na_2O and K_2O. (4)

The Na_2O and K_2O then react with SO_3 either in the gas stream or after deposition on the tube.

$$(Na_2\ \text{or}\ K_2)O + SO_3 \rightarrow (Na_2\ \text{or}\ K_2)SO_4\ . \qquad (5)$$

These alkali sulfates, iron oxide, and SO_3 then react to form the complex sulfate.

$$3(K_2 \text{ or } Na_2)SO_4 + Fe_2O_3 + 3SO_3 \rightarrow 2K_3Fe(SO_4)_3. \qquad (6)$$

The complex sulfate in the molten phase then reacts with the tube metal.

$$2K_3Fe(SO_4)_3 + 6Fe \rightarrow 3/2FeS + 3/2Fe_3O_4 + Fe_2O_3 + 3K_2SO_4 + 3/2\,SO_2. \qquad (7)$$

The First Summary Report in this series pointed out that most of the systems of interest in fuel-ash corrosion are composed of melts which are highly ionized and have high electrical conductivity. Thus, electrochemical reactions can occur freely. Reactions at boiler-tube surfaces are also quite rapid because of the high temperature. Furthermore, passive films are not as stable as in aqueous systems because of the good solvent properties of fused salts.

It is fairly well accepted that electrochemical reactions cause corrosion in such systems. Discrete areas on the surface are considered to act as anodes and cathodes. For example, at the anode, the metal (iron, for instance) is oxidized, i.e., loses electrons by the reaction

$$\overset{\circ}{Fe} - 3e \rightarrow Fe^{+++}. \qquad (8)$$

Several reactions are possible at the cathode as illustrated by

$$SO_4^{=} + 8e \rightarrow S^{=} + 4\,O^{=}\ , \qquad (9)$$

$$O_2 + 4e \rightarrow 2\,O^{=}\ . \qquad (10)$$

Real progress is being made in the field of molten-salt corrosion by research such as that recently reported by Burrows and Hills(13) along with Inman and Wrench(14). They explain corrosion in molten-salt systems on the basis of an oxidation-reduction equilibrium and of an acid-base equilibrium. The oxidation-reduction potential can be expressed electrochemically as the pressure buildup of electrons sufficient to cause flow from the metal (construction material) to the molten-salt system. This flow will continue until a common potential is reached. The metallic electrode potential for iron in sulfates can be expressed as

$$E_{Fe} = E^{\circ}_{Fe} + \frac{RT}{3F} \ln a_{Fe}{}^{+++}\ , \qquad (11)$$

where

E_M = measured potential
E°_M = standard state potential
R = gas constant (1.987 cal/deg mol)
T = absolute temperature
F = Faraday (23,000 cal/volt equivalents)
a = activity of the Fe^{+++} .

The acid-base equilibrium in a melt is expressed by the equilibrium

$$\overset{\text{base}}{SO_4^=} \rightleftarrows \overset{\text{acid}}{SO_3} + \overset{\text{base}}{O^=} \;.. \tag{12}$$

Concentration of the SO_3 determines the acidity of the melt and the extent of the corrosion of the metals in contact with the melt. Dissociation of the sulfate ions as noted above will be determined by the value of the dissociation constant, K, as in

$$K = \frac{a_{SO_3} \cdot a_{O^=}}{a_{SO_4^=}} \;. \tag{13}$$

Values for this constant have not been established for the sulfate systems. Research to determine them would be of value.

Oxygen-ion activities in fused salts, such as sodium sulfate-carbonate mixtures can be determined accurately with a platinum electrode in an atmosphere of oxygen and carbon dioxide, according to Flood(15,16). The method needs to be carried over to the sulfate-iron system.

Importance of the oxygen ion is further clarified by a consideration of the redox potential of a melt containing oxide ions and oxygen gas as given by

$$E_R = E^\circ_{O^=} + \frac{RT}{2F} \ln \frac{a_{O_2}{}^{1/2}}{a_{O^=}} \;. \tag{14}$$

It can be seen that the potential is a function of the ratio of the activities of the gaseous oxygen to the oxide ions. A metal placed in the melt will react with the melt if the potential of the metal is less than the redox potential of the melt. Reaction will continue until the two potentials reach the same value, i.e. $E_{Fe} = E_R$.

Reaction (12) will tend to move to the right if SO_3 or $O^=$ is removed. It is suggested that SO_3 can be reduced at the cathode by reactions such as

$$SO_3 + 2e \rightarrow SO_3^= \tag{15}$$

or

$$SO_3 + 2e \rightarrow SO_2 + O^= \;. \tag{16}$$

The oxide ion is correspondingly oxidized at the anode as shown by

$$O^{=} - 2e \rightarrow 1/2O_2 \ . \qquad (17)$$

Oxide ions will not build up in the melt and reaction (12) will not reach equilibrium if the oxide is precipitated according to

$$3SO_4^{=} + 2Fe^{+++} \rightarrow Fe_2O_3 \downarrow + 3SO_3. \qquad (18)$$

It can be seen that sulfur trioxide and oxygen are important constituents from the corrosion standpoint. Continuing research will be required to show the quantitative effect of each in the corrosion reactions.

Mechanism of Sulfidation

Many mechanisms have been proposed to explain sulfidation attack. It is generally agreed that the following conditions are present when the attack occurs in marine gas turbines:(17)

(1) A molten film primarily containing Na_2SO_4 is formed on the metal surface.

(2) Protective films, mainly oxide, on the metal surface are destroyed.

(3) Reaction occurs between the sulfur in the molten film and the metal surface, which stimulates subsequent rapid oxidation.

Several mechanisms have been proposed for the reaction of sodium sulfate with metals. Some of the earlier investigators were Simon and his associates.(18) They proposed that reducing agents trigger reactions that can become autocatalytic and destroy the alloy if sufficient sodium sulfate is present.

Recent research at the Westinghouse Electric Corporation(19) has combined knowledge from field results with that obtained in the laboratory. The primary concern again was with gas turbines. A high level of alkaline-metal sulfates is reported with melting points ranging from 1400 to 1550 F in normal deposits. In most cases, the alkaline metals seemed to come from the incoming air, whereas the sulfur was furnished by the fuel or by the air. These authors suggest, as do others, that alkaline-metal sulfates can react to break down the protective oxide surface films on the metals.

Interesting and significant results come from electron-beam analyses made on sulfided sections of alloys. These analyses show that sulfur reacts preferentially with chromium. There is also some reaction with other metals in the alloys, i.e., aluminum, molybdenum, titanium, and iron, to form complex chromium sulfides. As a result, the metal adjacent to the chromium sulfide complex becomes impoverished in chromium and aluminum and is more easily oxidized. Figure 23 taken from the Westinghouse report shows graphically an inner layer containing complex chromium sulfides located next to the base metal. The outer layer consists of oxides and porous corrosion products.

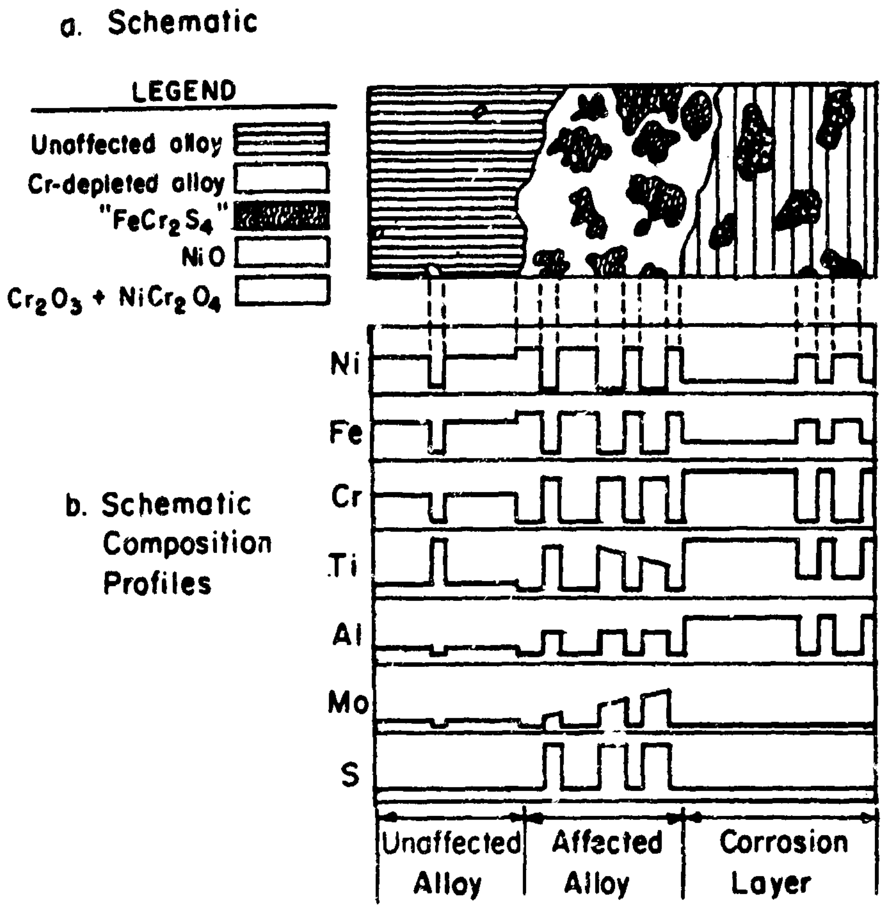


FIGURE 23. COMPOSITION PROFILE OF Ni + 13Cr + 6Al ALLOY--EXPOSED 90 HOURS AT 1450 F(19)

These studies with the electron-beam probe, coupled with more conventional metallographic studies, suggest that the attack proceeds by penetration at grain boundaries.

It is suggested that the corrosion proceeds by reactions in which free sulfur is formed as in

$$Na_2SO_4 + 3M \rightarrow Na_2O + 3MO + S \ , \qquad (19)$$

where M is a metal such as chromium, nickel, or iron or some other reducing agent, i.e., carbon. Then the sulfide is formed by

$$M + S \rightarrow MS. \qquad (20)$$

The electron-beam-probe examination of a nickel-base alloy showed that this sulfide phase could be a compound such as $FeCr_2S_4$ with a spinel-type structure.

It is postulated further that this sulfide phase reacts with oxygen by the following:

$$2MS + O_2 \rightarrow 2MO + 2S \tag{21}$$

$$MS + 3/2\,O_2 \rightarrow MO + SO_2 \tag{22}$$

$$2MS + SO_2 \rightarrow 2MO + 3S \tag{23}$$

In essence, it is proposed that a self-sustaining reaction is possible once the above cycles have been initiated and that a high level of sulfur in a gas stream is not required to maintain the reaction. The electron beam has identified the oxides NiO, Cr_2O_3, and $NiCr_2O_4$ in the corroded layer.

Other valuable, recent mechanisms have been tentatively formulated by Gambino and his coworkers.(20) In oxidation kinetic studies devoted to the system nickel and sodium sulfate, it was concluded that sodium sulfate reacts with nickel metal according to the reaction

$$Na_2SO_4 + 9/2Ni \rightarrow Na_2O + 3NiO + 1/2\ Ni_3S_2. \tag{24}$$

It was proposed that the main function of sodium sulfate is to provide a reservoir so that the Ni_3S_2 phase is continuously maintained at the metal surface by employing the following two reactions cyclically

$$Ni_3S + 9/2O_2 \rightarrow 3NiO + 2SO_3 \tag{25}$$

$$Na_2O + SO_3 \rightarrow Na_2SO_4\ . \tag{26}$$

Nickel is considered the reducing agent in Equation (24).

A nickel oxide film on nickel was penetrated by sodium sulfate at temperatures well below the melting point of sodium sulfate (880 C, 1616 F). Accelerated corrosion of the nickel was initiated as soon as sulfate reached the metal surface.

In a companion metallurgical-metallographic program, Seybolt(20) showed that nickel and nickel alloys can react directly with either solid or liquid Na_2SO_4 in the absence of another reducing agent.

It was proposed that unalloyed nickel is attacked readily because the eutectic Ni_3S_2-Ni is formed. This material is molten at a relatively low temperature (645 C, 1190 F) and can easily diffuse down grain boundaries. Thus, sulfur is readily transported into the base metal. It has been shown that nickel sulfide-rich areas oxidize more rapidly than the base metal which in turn helps to explain the catastrophic nature of the attack often encountered. The details of the oxidation reaction are not yet understood.

Seybolt carried the study to other possible constituents of high-temperature alloys.

He points out that the most stable sulfides will form at the expense of the less stable sulfides. Accordingly, in alloys containing chromium, it would be predicted that CrS would be formed preferentially. In such alloys, corrosion proceeds because the chromium sulfide is oxidized more readily than the base metal and also because in areas adjacent to the CrS, the chromium has been depleted and the base alloy is less oxidation resistant.

The importance of the formation of low-melting eutectic compounds appears to be greatest in the case of nickel since, as can be seen in Table 3, nickel sulfide melts at a temperature lower than other sulfides.

TABLE 3. MELTING POINTS OF EUTECTICS AND COMPOUNDS(20)

System	Eutectic	Compound	Melting Point	
			C	F
Ni-S	Ni_3S_2-Ni	-	645	1193
	-	Ni_3S_2	810	1490
Co-S	Co_4S_3-Co	-	877	1610
	-	Co_2S_3	930	1706
	-	CoS	1182	2160
Fe-S	FeS-Fe	-	988	1811
	-	FeS	1193	2180
	-	FeS_2	1171	2140
Cr-S	CrS-Cr	-	1350	2462
	-	CrS	1565	2849
Mn-S	MnS-Mn	-	1580	2876
		MnS	1610	2930

Additions of chromium to both nickel- and cobalt-base alloys improves corrosion resistance The function of the chromium was suggested to be that of aiding in the formation of a more corrosion-resistant surface layer, i.e., a chromium-rich surface oxide, as well as immobilizing the sulfur by forming a relatively stable and inert chromium sulfide.

Shirley(21), in essence, agrees with many of the observations and conclusions of the General Electric investigators. He points out that a study of many samples of high-nickel alloys revealed that sulfur penetration is followed by oxidation of the chromium-depleted layer. Oxidation of the chromium sulfide phase is not mentioned by Shirley.

It is pointed out that alkali-metal salts are more aggressive to high-nickel steels, and that calcium salts are more corrosive to carbon steels. Table 4 by Shirley is interesting in showing the importance of metal composition on the attack suffered from contact with various salt mixtures. Note in particular that mild steel is better than Inconel or Nimonic 80A in the Na_2SO_4-NaCl mixture.

TABLE 4. EFFECT OF METAL COMPOSITION ON ATTACK BY 9:1 SULPHATE:CHLORIDE MIXTURES AT 700 AND 750 C(22)

Exposure, 6 or 24 hours in air

			Loss in Weight, mg cm^{-2} (a)			
			9:1 Na_2SO_4-NaCl		9:1 $CaSO_4$-$CaCl_2$	
Type	Cr, percent	Ni, percent	700 C (24 hr)	750 C (6 hr)	700 C (24 hr)	750 C (6 hr)
FI 17 steel	17	-	14, 11	-	75, 85	-
FI 20 steel	20	-	-	9, 2	-	118, 152
Pyrista steel	28	2	9, 6	6, 6	4, 126	104, 129
FCB(T) steel	18	10	11, 9	5, 6	6, 74	47
FV 555 steel	16	10	7, 7	-	12, 183	-
Immaculate 5 steel	25	20	9, 5	3, 5	54, 31	95, 95
Experimental	-	25	-	85, 89	-	60, 64
steels	10	25	27	-	50	-
	20	35	16	-	49	-
Inconel	13	78	30, 14	184, 355	1, 2	2, 3
Nimonic 80A	20	74	-	294, 452	-	2, 3
Mild steel			-	143	-	112
Nickel			-	7, 6	-	10, 12
Chromium			-	1, 5	-	10, 12

(a) In the absence of sulphate:chloride mixtures weight losses of the following metals, in air at 750 C for 6 hr, were (in mg cm^{-2}):

Mild steel	49
25% Ni steel	11
Nickel	2
Others less than	1

An interesting study recently made at the Marine Engineering Laboratory(22) attempted to relate electrochemical measurements with sulfidation. Potentials were measured between a platinum electrode and an alloy sample immersed in Na_2SO_4 and in Na_2SO_4 plus NaCl at 1650 F. A sustained rise in potential was observed whenever sulfidation occurred. Oxide-film thickness had a definite effect on the elapsed time to the sustained rise in potential. The results with two nickel-base alloys were quite different.

The potential-measurement technique showed that one alloy was attacked in both Na_2SO_4 and Na_2SO_4/NaCl mixtures, while another suffered sulfidation in the Na_2SO_4/NaCl mixture only. It would appear that the procedure just described would be of value in screening experimental alloys for high-temperature service.

The role of NaCl in the corrosion process is not at all clear at this time since conflicting reports have been presented as to its action. It does appear, however, that it may be important in determining the melting characteristics of the mixture on the surfaces. Figure 24 shows a phase diagram by Danek(17) indicating that at about 35 percent NaCl the melting point of the Na_2SO_4/NaCl mixture can be as low as 1150 F.

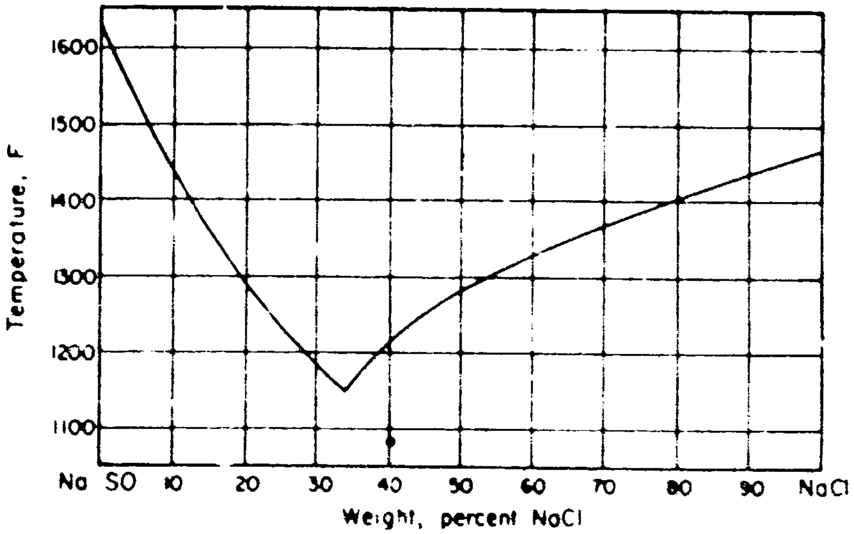


FIGURE 24. PHASE DIAGRAM, SODIUM SULFATE - SODIUM CHLORIDE(17)

A recent paper by Bergman(23) indicates that neither chloride salts nor externally introduced reducing conditions are needed for hot corrosion to occur. It was also significant that he found that a reduction of sulfur to 0.07 percent did not eliminate corrosion. However, chloride salts were present in these experiments.

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