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

FIRST SUMMARY REPORT

July 1, 1966 – December 31, 1966

AMERICAN SOCIETY OF MECHANICAL ENGINEERS

Research Committee On Corrosion And
Deposits From Combustion Gases

Prepared by
BATTELLE MEMORIAL INSTITUTE
Columbus Laboratories

FOREWORD

This Summary, like those preceding it that reported on thermochemical reactions, is divided into two parts. The first part, the GENERAL REVIEW section, describes only the essential results of this six months of work. It is not burdened with the many considerations and arguments concerned with carrying on the experimental work. Rather, it highlights the most important findings of the research and is intended for those who need only a broad picture of what has been done. The second part, the TECHNICAL DETAILS section, describes the experimental work in detail. It is provided for those seeking specific information on experimental methods, analytical procedures, test data, calculations, assumptions, and the like. Although the entire picture can be seen only by reading both parts, the first section can be considered to contain the main substance of this report.

FIRST SUMMARY REPORT

on

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

to the

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

July 1, 1966 – December 31, 1966

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

ASME Research Committee on Corrosion and Deposits From Combustion Gases

Enclosed is a copy of the First 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 from July 1, 1966 to December 31, 1966. It is sent to you in recognition of your support of the Committee's work.

It is believed that progress has been made in this study. Sulfates have been successfully formed in the laboratory under flue gas conditions, and it has been demonstrated that SO_3 concentrations much higher than measured in the bulk gas stream exist adjacent to surfaces such as are found in gas passages.

The work planned for the next six months is outlined in the report, and another report will be sent to you in July, 1967.

Please do not hesitate to contact me if you have any questions or suggestions concerning the report.

Very truly yours,

George C. Wiedersum
Chairman

Encl.

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First Summary Report

on

FORMATION OF ALKALI IRON SULFATES

AND OTHER COMPOUNDS CAUSING CORROSION

IN BOILERS AND GAS TURBINES

Sulfates, formed by the interaction of SO_3, SO_2, and O_2 in flue gas with alkalies from the fuel and iron oxides are invariably found in corrosion areas. Alkali sulfates, such as Na_2SO_4, are formed rapidly. Iron sulfates, both $FeSO_4$ and $Fe_2(SO_4)_3$, can also occur, although the thermodynamics are unfavorable in a low-SO_3 atmosphere. Alkali sulfates and iron sulfates can react to form alkali iron trisulfates, for example $Na_3Fe(SO_4)_3$. These are highly corrosive but their formation also requires more SO_3 than is found in bulk flue gas. Recent work has shown that the high SO_3 level needed to produce these complex sulfates can be provided by catalysis at surfaces, even though the SO_3 is too low in the bulk gas stream. Studies reported here show quantitatively that the SO_2 concentration immediately next to an Fe_2O_3 surface can be many times higher than in the bulk stream of gas, and can be ample to provide the SO_3 necessary to form the trisulfates.

GENERAL REVIEW

by

William T. Reid

Although it has been known for nearly 25 years that the alkali iron trisulfates are involved in the corrosion of heat-receiving surfaces in boiler furnaces, the exact mechanism by which these objectionable compounds are formed or what their exact role in corrosion may be has never been adequately explained. What has been learned essentially over those years is that sodium and potassium, separately or in combination, react with iron oxides and sulfur oxides to produce

compounds of the type $Na_3Fe(SO_4)_3$. The iron oxides can be supplied at the expense of the parent metal, or they may come from the iron oxides present in coal ash.

It has also been known for many years that this reaction occurs only beneath layers of ash or slag. Exposed surfaces, such as bare superheater elements, are not subject to severe wastage, whereas metal loss beneath ash deposits can be so severe in the worst cases as to cause outages within a few months. It has been evident further that the overlying layer of ash or slag does not contribute directly to metal loss. At the temperatures involved, usually about 1100 F, coal ash is chemically inert, as is oil ash except for the special case of liquid fuels high in vanadium. The lowest-melting constituent provided by fuel ash, excepting vanadium compounds, is Na_2SO_4 with a melting point of 1630 F. A solid solution of $3Na_2SO_4 \cdot K_2SO_4$ melts at 1530 F, but even this is about 400 F higher than the maximum metal temperature of superheater elements that have experienced corrosion. Because reactions between solids are almost invariably extremely slow, there is no indication that solid Na_2SO_4 leads directly to metal wastage. The trisulfates, however, are molten at temperatures over 1160 F depending on the SO_3 available to keep these compounds stabilized. It is evident, then, that the trisulfates can produce the environment leading to rapid loss of metal.

Even though these points have been made many times by numerous investigators, the exact procedure by which the trisulfates are produced has not been demonstrated. Many workers have speculated on the reaction sequence, but as yet no one has demonstrated conclusively exactly what occurs on the superheater elements of a boiler furnace that leads to the trisulfates and thereby to metal wastage. Providing that knowledge will show precisely what steps can be reasonably taken to break the reaction sequence. Lacking that knowledge will lead only to continued speculation and costly cut-and-try experimentation in operating boiler furnaces.

The first four years of research at Battelle for the ASME Committee on Corrosion and Deposits from Combustion Gases investigated intensively the thermochemical reactions leading to SO_3 in furnace gases, on the basis that sulfates were inextricably tied up with most corrosion processes, and that the trisulfates require a level of SO_3 in the order of 250 ppm for their existence at 1100 F. At the end of that research, the next logical step was to investigate reactions involving surfaces. The new program along those lines was begun in July, 1966, with the objective of investigating "---the interactions between such solids as Fe, (FeO) Fe_3O_4, and Fe_2O_3 and such gases as O_2, SO_2, and SO_3 in the presence of alkalies and other ash constituents". A further objective was to investigate physical factors occurring within deposits that lead to the formation of trisulfates.

This is the first report on that new program, covering the first six months of work. It is an interim report because the questions raised here can be answered only after a great deal of intensive research. However, an important finding during this period has shown quantitatively the large difference in SO_3 concentration near a surface compared with the SO_3 found in the bulk stream of gas passing over that surface. These data constitute an important step in providing quantitative measurements to explain how corrosion takes place.

As with earlier reports, this one is organized by sections covering specific parts of the overall study - surface investigations, fuel-burning furnace studies, and the mechanism of corrosion. The common objective of all three sections is the same - only the means of achieving those objectives experimentally and analytically is different.

RESEARCH ACCOMPLISHMENTS
OVER THE PAST SIX MONTHS

The present laboratory investigation has proceeded much along the same general lines as the earlier work, except that emphasis has been shifted from gas-phase reactions to reactions in which solids are involved - specifically surfaces representing idealized parts of a corrosion system. New experimental techniques have been developed in some cases, and others are being devised.

Surface Investigations

When the trisulfates were first identified as a major factor in metal wastage, it was found also that these compounds would not form unless at least 250 ppm SO_3 was present at metal temperatures of 1100 F or higher. However, because normal flue gas contains only about a tenth this much SO_3, the difference has been attributed to catalysis. Gross effects of catalysis have been demonstrated frequently, but what has been lacking is an exact understanding of the conditions affecting these surface reactions - the broad objectives of the present Battelle work.

Quantitative measurements have now been made of some of the factors leading to high SO_3 levels at surfaces. The data demonstrate, for the low gas velocity of just under one inch per second used in these experiments, that the SO_3 in the boundary layer can be as much as 30 times greater than in the main body of gas flowing over the surface. This SO_3 concentration can be high enough that the trisulfates will be stable.

Some of the test data reported in the Technical Details section show that no such increase in SO_3 occurs when NaOH is added to an otherwise catalytic surface of Fe_2O_3. Two premises are possible: (1) that the alkali destroys the catalytic capabilities of Fe_2O_3, or (2) that the alkali is capturing SO_3 as rapidly as the SO_3 is formed. When Na_2SO_4 rather than NaOH is added to Fe_2O_3, an increase occurs in SO_3 next to the surface, suggesting that the second premise is correct.

Other tests have demonstrated the difference in catalytic ability of Fe_3O_4 compared with Fe_2O_3, where Fe_3O_4 is again shown to be relatively noncatalytic. Essentially no gain in SO_3 occurred near the boundary layer when the surface consisted of Fe_3O_4.

With FeSO₄ applied initially to the surface, over 2000 ppm SO_3 was found later immediately next to the surface. A complicated situation exists here that will be investigated in more detail later.

The catalytic activity of vanadium as V_2O_5 or as crushed commercial catalyst containing 11 percent V_2O_5 was shown to be appreciably less than Fe_2O_3.

Other surface studies are being carried out with radioactive S^{35}. Their objective is to isolate the effects of SO_2 from SO_3, so that the relative importance of these two forms of sulfur can be assessed as far as corrosion is concerned. The first work in this field was done in England in 1954. Since then, no one seems to have used S^{36} in this way, although it has obvious advantages for following sulfur reactions. An AEC-approved test set-up has been assembled and preliminary tests have been made. Some trouble has been experienced in getting the proper $S^{36}O_2$ supply from commercial sources, but a new shipment is on order.

A quantity of relatively pure $Na_3Fe(SO_4)_3$ was made at Battelle to permit measurement of optical properties, X-ray diffraction pattern, and chemical characteristics. These properties will be helpful as a standard for later phases of the project where extremely small quantities of the trisulfate must be identified in test samples.

Fuel-Burning Furnace Studies

This phase has continued as an intermediate step between the chemical laboratory and a full-scale boiler furnace. Over the past six months, the fuel-burning furnace has been used mainly to evaluate conditions in an actual flue-gas atmosphere leading to the formation of sulfates and trisulfates.

For reasons of economy, tests in the fuel-burning furnace generally have been limited to a single shift, giving test periods at operating conditions of somewhat more than five hours. Equilibrium thermal conditions are established rapidly in the furnace, and surfaces usually come to a stable condition, as noted by changes in the SO_3 in the flue gas, within two to three hours. Nevertheless, in such a short test period, only extremely small quantities of solid products may be formed on the specimens. Usually these are too little to be checked by X-ray diffraction with its limit of 5 percent trisulfate in the sample for positive identification. Hence the tests that have been made to check conditions leading to the trisulfates have not been conclusive. When many such specimens had been accumulated, attempts were made to refine the detection method, leading to the use of pH-indicating paper to produce a "pH print" of the specimen.

In this procedure, a strip of pH-indicating paper with a range of pH 1.0 to pH 2.5 is wrapped tightly around a specimen tube and fastened at the ends with masking tape. The specimen is then placed in a high-humidity environment so that the pH paper becomes slightly damp. Under these conditions, such substances as $FeSO_4$, $Fe_2(SO_4)_3$, and $Na_3Fe(SO_4)_3$ and $K_3Fe(SO_4)_3$ hydrolyze to release H_2SO_4 which then changes the color of the paper. By using just the right

amount of dampness, a sharply defined spot of color is obtained precisely over the specimen where the hydrolyzable sulfate had been. Distinct color patterns have been obtained in this way for quantities of iron sulfates or trisulfates f:r tco small to be detected by X-ray diffraction.

Although the pH paper cannot distinguish between iron sulfates and trisulfates, it shows the presence of substances that may be closely related to corrosion, and it provides a means of evaluating specimens after quite short test periods. Two series of tests where specimens were coated with different mixtures showed in every case a pH of 1.5 or less when alkali sulfates were added initially, and only 3.5 when they were absent. Pure $FeSO_4$, $Fe_2(SO_4)_3$, and $Na_3Fe(SO_4)_3$ all give a pH of 1.0 under similar print-out conditions, pointing strongly to these compounds as the source of color in the pH print. And, since alkali sulfates were not present in the one series of tests where the pH was 3.5, it can be inferred that the trisulfate could have been formed in the other series where alkali sulfate was available because the pH then was 1.5 or less.

The form in which the alkalies is present must be important, for, in another test series with synthetic fly ash containing alkalies added as Na_2CO_3, no such low pH was observed.

Using the pH print scheme to check the surface of superheater elements during outages may be helpful in locating areas where corrosion may be occurring. It would only be necessary to chip off adhering ash deposits, hold the properly dampened pH paper tightly against the tube for a minute or two, and read the color change directly.

Another detection method has been tried whereby the formation of a liquid melt around the ends of two dissimilar metals separated a short distance produces a "battery" which provides easily measurable voltage. Two preliminary models tried have been too crude to decide whether the system has merit, but both showed an abrupt rise in voltage at 1000 F to 1050 F when the cell was heated gradually with SO_3 present and a mixture of Na_2SO_4, K_2SO_4, and Fe_2O_3 surrounding the separated junction of the two metals. This suggests strongly that a liquid phase was formed to act as a molten-salt electrolyte. In addition, a pH print showed a pH of 1.0 for this material. It is likely that this salt was $Na_3Fe(SO_4)_3$.

The Technical Details section recounts many tests which at first appeared to be of doubtful value in assessing conditions to form the trisulfates, but which were shown later by pH prints to be more meaningful. Limitations of these two detection methods are not yet well defined, but both the pH paper and the electrochemical cell show promise in evaluating later tests.

Other tests made during this period measured the catalytic characteristics of various fly ashes. Such data are needed to answer questions related to the formation of sulfates and trisulfates beneath layers of ash. It was found that no simple relation existed between the catalytic behavior of fly ash and its iron content expressed as Fe_2O_3 or the amount of alkalies it contained. Rather, it was concluded that surface conditions, particle size, distribution of ash constituents, and particularly the manner in which iron oxides had been complexed by heating with other ash minerals all would affect fly-ash catalysis.

Mechanism of Corrosion

Corrosion as a result of electrochemical reactions involving a molten electrolyte and a cathode and an anode within a tube surface has been reviewed critically during recent months. Considerable work has been done in other fields where melts are highly ionized that explain corrosion reactions adequately. Although the situation in boiler furnaces is more complex because conditions cannot be well defined, the concept of electrochemical attack is worth more attention.

Along these lines, a probe for detecting corrosion conditions using a different principle from the one now being tried at Battelle has been constructed and tested in Germany.

THE NEXT STEPS

Based on the results summarized here, work for the next six months will be directed toward:

1. **Positive identification of sulfur compounds.** Optical methods, pH printing, X-ray diffraction, and IR absorption will be used to differentiate as accurately as possible among $FeSO_4$, $Fe_2(SO_4)_3$, and $Na_3Fe(SO_4)_3$ as formed in deposits. Teamed with conventional chemical analyses for sulfate ion, it is expected that procedures can be developed to show the occurrence of these three compounds. High detection sensitivity will be sought, that the test duration can be as short as possible.

2. **Effect of flow conditions on formation of SO_3.** Geometry of the catalytic surface, its arrangement with respect to the gas flow pattern, the effect of laminar and turbulent flow, and the influence of temperature need to be evaluated in measuring the SO_3 profile over catalytic surfaces. Data are needed covering a wide range of Reynolds numbers.

3. **Relative importance of SO_2 and SO_3 in corrosion mechanism.** Tests with $S^{35}O_2$ will be made to learn whether SO_3 must be available to form iron sulfates and the trisulfates, or whether SO_2 is capable of forming intermediate compounds which are then oxidizable to the corrosive form.

4. **Formation of trisulfates associated with deposits.** Additional effort needs to be spent establishing a test procedure whereby trisulfates associated with ash deposits can be formed reliably. Thin slabs of coal ash will be prepared to cover the surface of a simulated superheater surface. By controlling diffusion through such a slab, or by fixed dimensions of voids or cracks, enough flue gas may enter the space between metal

and ash to lead to formation of the trisulfate. The sensitive detectors of reaction products expected to be available make such tests appear feasible. Duration of the test required to give measurable results will not be known until preliminary tests are completed.

5. Corrosion detector. As time is available, the electrochemical corrosion indicator will be tested further to learn its limitations. Possibly a "one-shot" device, it will be interesting to learn if the cell shows initial voltage output when a liquid phase is first produced between the electrodes, and if prolonged exposure under noncorrosive conditions at the same temperature reduces the output voltage to zero.

6. Profilometer measurements. Extremely small changes in surface roughness can be detected with a profilometer. To determine if this instrument can detect metal loss caused by corrosion in a surface originally electropolished, a few tests are planned with parts of metal specimens heated in contact with various substances, for example alkali iron trisulfate and mixtures of Na_2SO_4 and Fe_2O_3 in a flue-gas atmosphere containing SO_3. If the results are promising, the profilometer might be useful for measuring metal loss quantitatively over periods of only a few hours.

7. Mechanism of corrosion. Current literature on corrosion and deposits will continue to be reviewed critically in the search for new concepts.

SURFACE INVESTIGATIONS

by

A. Levy and H. H. Krause

Earlier studies on this program showed consistently that from 1 to 2 percent of the sulfur in fuel will be converted to SO_3 during combustion, the rest going only to SO_2. This finding in itself might be considered somewhat trivial except that it points up many important, unanswered questions on the formation of deposits on boiler tubes. Under usual coal- and oil-burning conditions, the SO_2 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. It is equally recognized, however, that SO_3 can be produced catalytically when SO_2 and O_2 are in contact with ferric oxide. The dilemma then is, if all the SO_3 found in flue gases is produced in the combustion zone, what occurs between the furnace and the stack when the combustion gases are in contact with the surfaces of the superheater elements, economizer tubes, and the air heaters?

The surface investigations being made here are aimed at determining the answer to this question. More specifically, the surface investigations hope to explain what reactions occur between SO_2, SO_3, O_2, and iron surfaces - the types of reactions, the order of the reactions, and the mechanisms leading to the formation of the simple alkali and iron sulfates and the complex alkali iron trisulfates. Recognizing that these simple and complex sulfates hold the answer to the corrosion and deposit problem, special attention to them is warranted.

Earlier work at Battelle defined the conditions under which SO_3 is formed in the bulk gas phase. With that background information, the investigation can now proceed to the special case of reactions occurring on surfaces.

INSTABILITY OF THE IRON SULFATES AND THE TRISULFATES

One of the knottiest problems being faced in the study of surfaces is connected with the instability of iron sulfates and the trisulfates in boiler-furnace atmospheres. This instability is important because it determines the likelihood of the compound being formed, and, once formed, of remaining active. A typical reaction,

$$Fe_2O_3 + 3SO_3 \rightleftharpoons Fe_2(SO_4)_3 ,$$
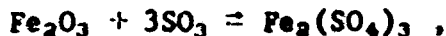
will proceed in one direction or the other depending upon the amount of SO_3 available and the temperature. Almost no data are available in the literature showing how the amount of SO_3 in equilibrium with these compounds changes with change in temperature. Indeed, there are only limited data showing the amount of SO_3 required in the surrounding atmosphere to allow these compounds to form, or conversely, to prevent them dissociating once they are formed.

Thermodynamic calculations have been made recently at Battelle[*] of the thermal decomposition of $FeSO_4$ and $Fe_2(SO_4)_3$ to form SO_3, neglecting the formation of SO_2 and O_2. Table 1 summarizes these calculations for the SO_3 partial pressure above $FeSO_4$ and $Fe_2(SO_4)_3$ at different temperatures.

TABLE 1. CALCULATED PARTIAL PRESSURE OF
SO_3 OVER IRON SULFATES[a]

Temperature, F	SO_3, ppm	
	$FeSO_4$	$Fe_2(SO_4)_3$
800	-	60
900	-	700
1000	<10	5,000
1100	15	35,000
1200	90	>10%
1300	700	-
1400	3800	-

(a) Neglecting the reaction $SO_3 \rightleftharpoons SO_2 + \frac{1}{2}O_2$

It is evident, at least theoretically, that ample SO_3 is available in the bulk flue gas stream to form $FeSO_4$ at temperatures between 1100 F and 1200 F. Contrariwise, 5000 ppm SO_3 is necessary if $Fe_2(SO_4)_3$ is to form even at temperatures as low as 1000 F; the concentrations of SO_3 needed at higher temperatures are even greater.

An "apparent partial pressure" of 23,000 ppm SO_3 over $Fe_2(SO_4)_3$ at 1161 F can be calculated based on Anderson's[1] studies, while a dissociation pressure of 35,000 ppm at this same temperature can be calculated from Warner and Ingraham's[2] work. Recognizing that SO_3 dissociation is not taken into account, it is still apparent that large quantities of SO_3 are necessary to stabilize $Fe_2(SO_4)_3$ at temperatures over 1000 F. Corey and his coworkers[3] showed that 10,000 ppm SO_3 was necessary at 1000 F to form $Fe_2(SO_4)_3$, somewhat more than the calculated value, but still in the same general range. The only published data on dissociation of the trisulfate are those reported by Corey, showing that 250 ppm SO_3 is necessary at 1100 F to form either sodium or potassium iron trisulfate.

Based only on thermodynamic principles, it is expected, then, that $FeSO_4$ is most likely to form under furnace conditions, that the trisulfates can be produced if the SO_3 is moderately high, and that there is little likelihood for $Fe_2(SO_4)_3$ to exist except under the most unusual conditions.

It must be emphasized that these conclusions are based on a maximum of suppositions and a minimum of facts. The experimental program now under way at Battelle is intended to put this on firmer ground, on the basis that to control corrosion will require a complete understanding of how such compounds are formed.

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[*] Dr. J. J. Ward, Materials Thermodynamics Division

SO_3 CONCENTRATION GRADIENTS

The study of surface reactions is considered important to this program because the concentration of SO_3 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 presently on superheaters, or many years ago, on wall tubes. As has been pointed out in earlier basic studies, both iron sulfates are unstable at 1200 F. Based on available thermodynamic data, $FeSO_4$ is more stable than $Fe_2(SO_4)_3$, but even it requires theoretically that 90 ppm SO_3 be present in the surrounding atmosphere at 1200 F. With $Fe_2(SO_4)_3$ at this temperature, the calculated equilibrium SO_3 level is 20 percent. Experimental measurements made by Corey[3] and his coworkers show that $Na_3Fe(SO_4)_3$ requires 250 ppm SO_3 at 1100 F. Under some conditions, then, $FeSO_4$ 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 sulfate products, it is necessary to explain why these "unstable" sulfates are found in corrosion areas.

It is generally recognized that thermodynamic requirements and kinetic requirements do not necessarily go hand in hand. Thus, it is quite conceivable that metastable sulfates can exist under certain boiler conditions, especially if some of the sulfate-deposit products can be built up from beneath an oxide coating. It is also recognized that SO_2 and SO_3 are strongly adsorbed gases, and as has been shown over the last few months in laboratory experiments, SO_3 concentrations immediately next to the surface can be much higher than those in the bulk gas stream. Experiments have been set up to measure this SO_3 concentration above various surfaces, as an indication of the conditions that can exist leading to the formation of relatively unstable sulfates.

Apparatus

The experimental apparatus used in this study is a microprobe arranged for sampling the gas mixture at a carefully measured level above the surface to be investigated. The equipment is shown in Figure 1. The coating material to be studied is placed on a small Vycor plate 0.6 inch x 1 inch and equilibrated with the gas stream by passing the desired gas mixture over it for an hour at 1100 F. The flow rate used in these runs is 40 cc/sec, providing a linear velocity of 0.79 inch per second. Hence the residence time is 1.3 seconds. The gas stream consists of nitrogen, oxygen, and SO_2, humidified by bubbling through water. Distance of the probe from the surface is measured by a cathetometer, with the probe kept in a fixed position and the furnace adjusted upward or downward as required by a micrometer screw arrangement. During sampling through the microprobe, SO_3 is trapped at 0 C as H_2SO_4 and SO_2 is trapped at -196 C. The remaining nitrogen and oxygen expand into a measured volume, where the pressure is observed on a McLeod gauge. Analysis of the SO_3 in the gas sample is determined by the barium chloranilate method.
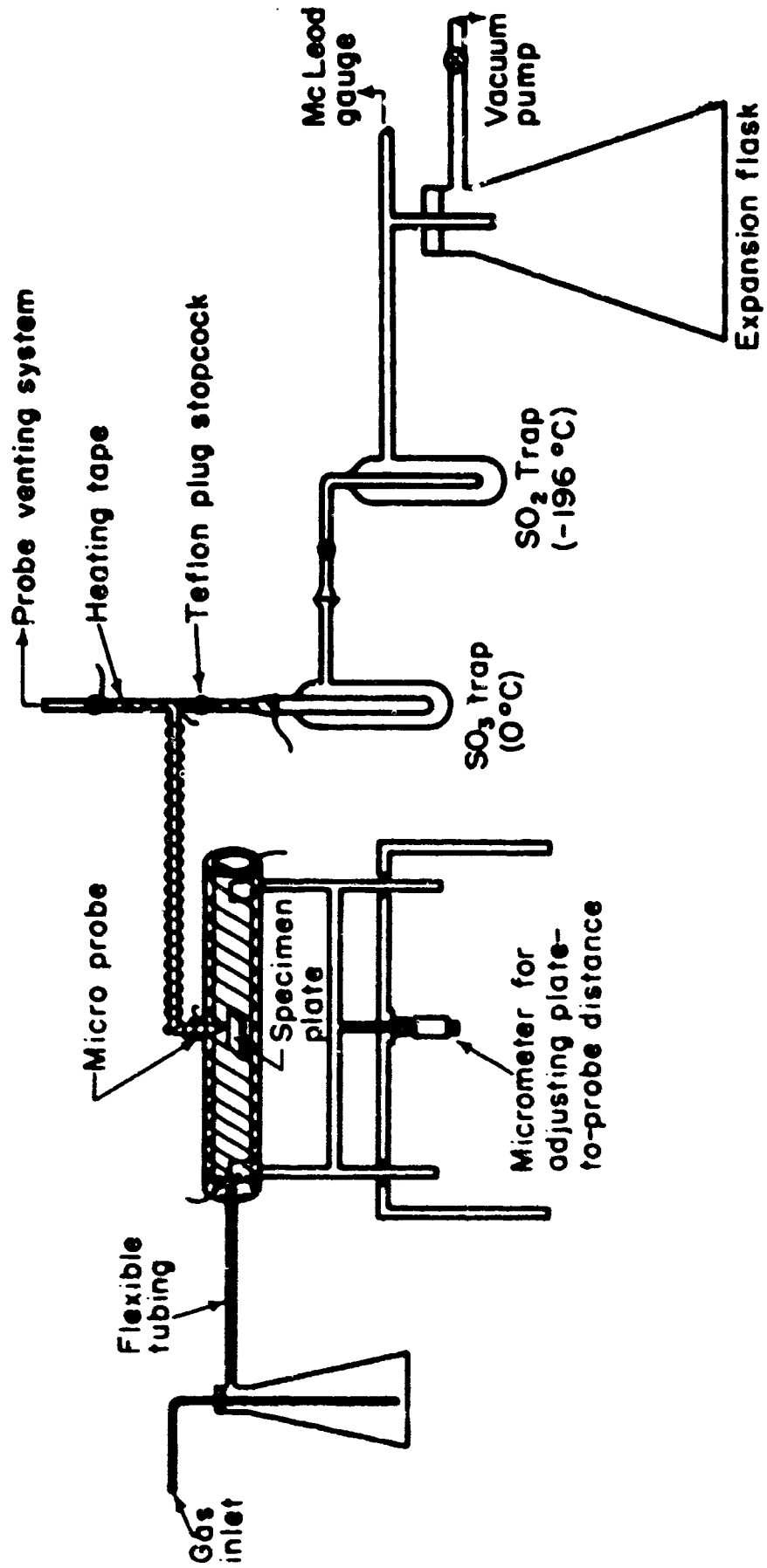
FIGURE 1. APPARATUS FOR MEASURING SO₃ PROFILES

SO₃ Profiles Above Fe₂O₃ Surfaces

Figure 2 shows the SO_3 concentration above an Fe_2O_3 surface with different amounts of SO_2 in the gas stream. High levels of SO_2 were used in these tests to demonstrate the basic relationships; the same general factors would apply with the lower concentrations of SO_2 found in flue gas. The two curves with 6 percent SO_2 are representative of the reproducibility of the microprobing technique, differing by only 5 to 10 percent at distances from the surface less than 2.5 mm. At the point of closest approach to the surface, the SO_3 values for the three levels of SO_2 are almost proportional to the square of the SO_2 concentration, but the value found for 3 percent SO_2 is too high to fit this relation. At any rate, these results indicate that near a catalytically active surface the SO_3 concentration can increase at a significantly greater rate than the SO_2 concentration in the bulk of the gas stream. As the distance from the surface increases, the SO_3 concentrations converge, and they become approximately equal at 5 mm or 0.2 inch from the surface.
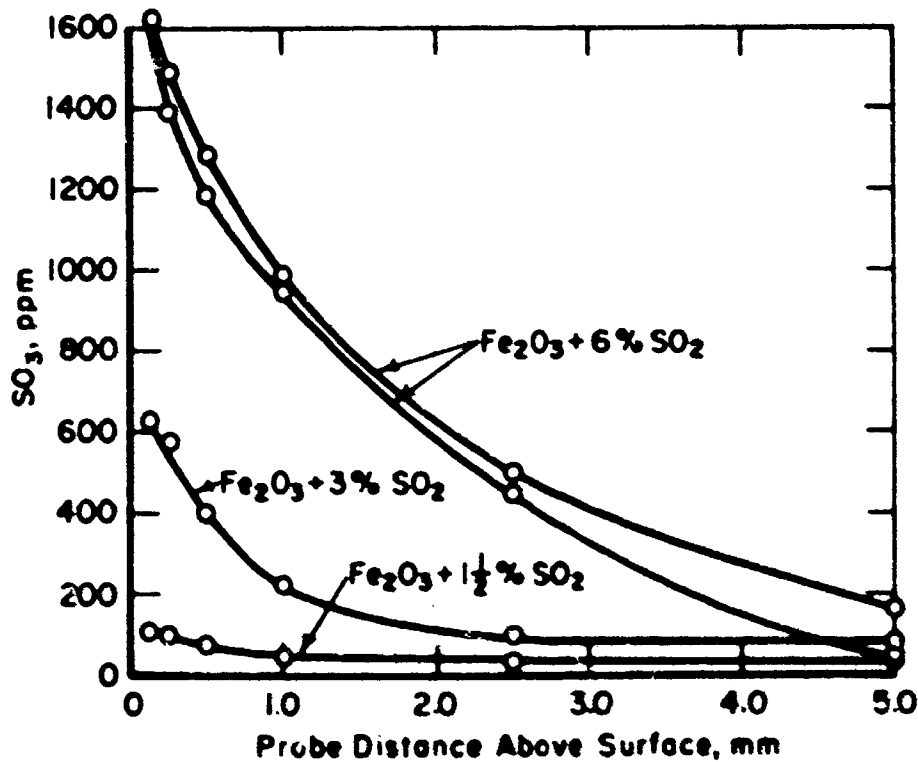
FIGURE 2. EFFECT OF SO_2 LEVELS ON THE SO_3 CONCENTRATION ABOVE Fe_2O_3 SURFACES AT 1100 F

SO$_3$ Profiles Above Mixtures Containing Fe$_2$O$_3$

Figure 3 shows several profiles over mixtures containing Fe$_2$O$_3$. The SO$_3$ profile above the mixture of Fe$_2$O$_3$ and Fe$_3$O$_4$ is similar to that above the oxidized iron surface, suggesting that the oxidized iron surface also consisted of Fe$_2$O$_3$ and Fe$_3$O$_4$, as would be expected. Indeed, the reduced catalytic effect in the profile for oxidized iron as compared with pure Fe$_2$O$_3$ indicates that there was Fe$_3$O$_4$ in the surface. For probe distances near the surface, 0.5 mm and less, the SO$_3$ concentrations with the 50 percent Fe$_2$O$_3$-Fe$_3$O$_4$ mixture were almost exactly half that found for the Fe$_2$O$_3$ alone. Such a result is in line with the negligible catalytic activity observed earlier with Fe$_3$O$_4$. At the 1-mm probe distance, the 2-to-1 relation almost holds, and from there out to 5 mm the SO$_3$ values converge. An SO$_3$ value of 50 to 60 ppm has been found frequently at the 5-mm level under the current experimental conditions. At the center of the tube above the specimen, SO$_3$ levels normally are 10 to 20 ppm.

Except for some slightly erratic values at 2.5 and 1 mm, the SO$_3$ levels observed above the Fe$_2$O$_3$-NaOH mixture in the proportion to form the trisulfate were almost constant at 60 ppm. The lack of a y substantial quantity of SO$_3$ in the gas above the surface suggests that if SO$_3$ were formed catalytically on the surface, it never left the surface, and must have reacted immediately with the NaOH to form Na$_2$SO$_4$.
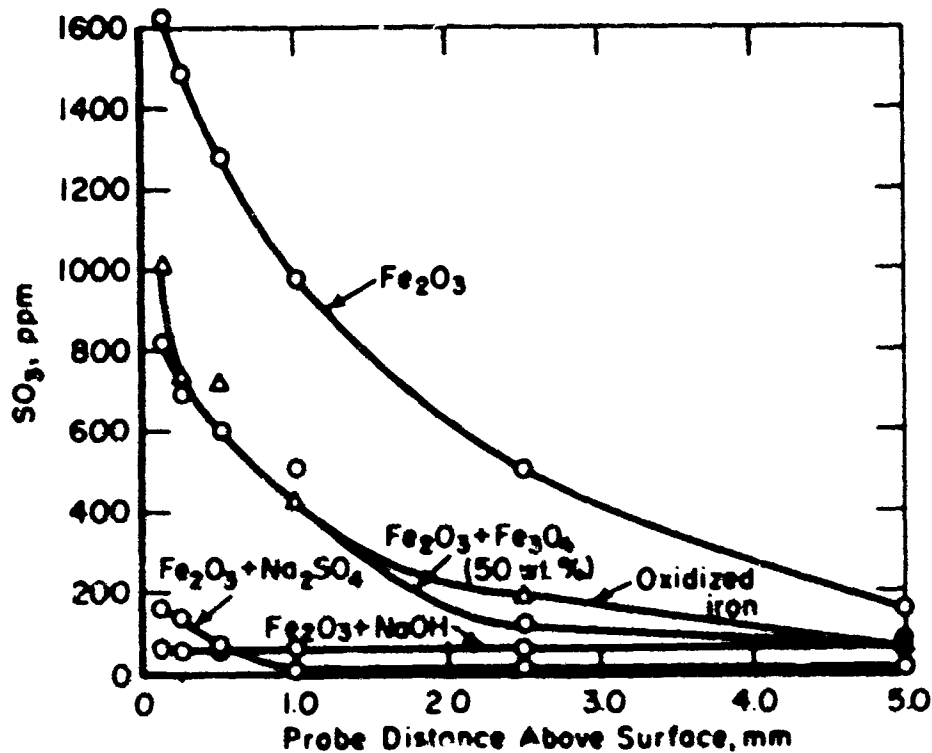
FIGURE 3. SO$_3$ PROFILES ABOVE MIXTURES CONTAINING Fe$_2$O$_3$ AT 1100 F IN 6 PERCENT SO$_2$

Addition of Na_2SO_4 to the Fe_2O_3 reduced the SO_3 concentration near the surface to a tenth of the value for Fe_2O_3 alone, although there was approximately half as much Fe_2O_3 present. These results can mean either that the Na_2SO_4 has a "poisoning" effect on the catalytic ability of Fe_2O_3, or that the SO_3 is being consumed as by forming the trisulfate. Analyses of these surfaces have not shown significant gains in the quantities of sulfate. However more extensive examination and longer runs will be required before a positive conclusion can be reached.

SO_3 Profiles Above Fe_3O_4 and $FeSO_4$ Surfaces

Figure 4 shows the SO_3 concentration gradients above Fe_3O_4 and $FeSO_4$. The relatively low catalytic activity of Fe_3O_4 is well demonstrated by these data. The SO_3 observed may be the result of slight oxidation of the Fe_3O_4 to Fe_2O_3 in the presence of an appreciable excess of oxygen.

With $FeSO_4$, the SO_3 concentration is the highest observed for the materials studied to date. Even though the temperature here was 1100 F, where $FeSO_4$ is thermodynamically stable in only 15 ppm SO_3, some decomposition may have occurred to furnish SO_3, and in the presence of oxygen the FeO could have oxidized to Fe_2O_3. Hence the SO_3 concentration observed can be the cumulative result of that formed by $FeSO_4$ decomposition and by Fe_2O_3 catalysis.
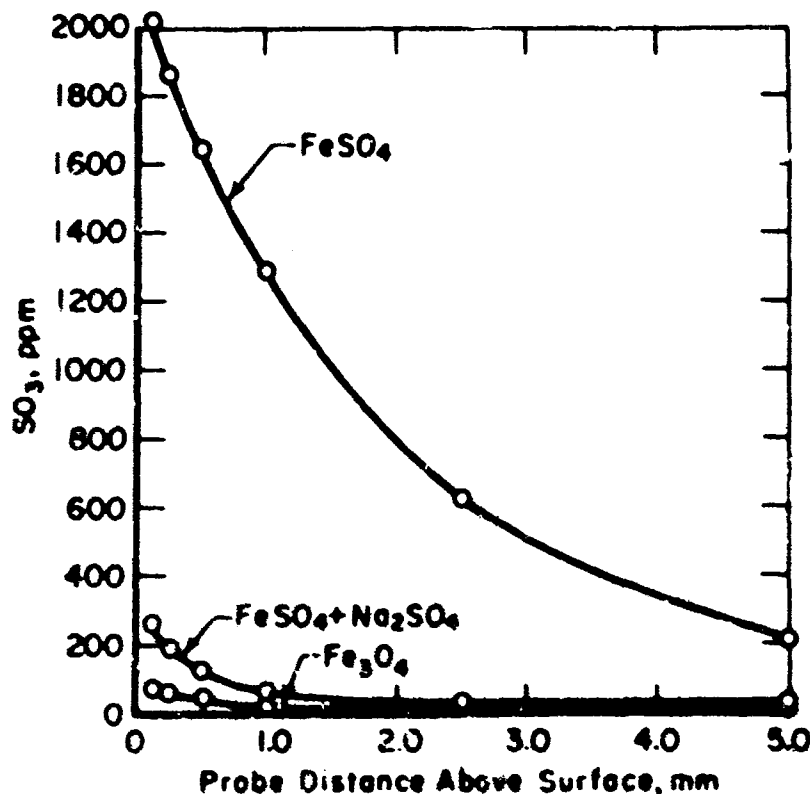
FIGURE 4. SO_3 PROFILES ABOVE SELECTED OXIDE AND SULFATE SURFACES AT 1100 F IN 6 PERCENT SO_2

Addition of Na_2SO_4 to $FeSO_4$ resulted in a drastic lowering of the SO_3 concentration above the surface. The amount of $FeSO_4$ in the mixture was approximately half that when the $FeSO_4$ was run alone, but the SO_3 was reduced to one-eighth the amount for $FeSO_4$ at the 0.125 mm position. Concentrations dropped off even more at greater distances from the surface. This must be the result either of "poisoning" the otherwise catalytic surface by the Na_2SO_4, or the reaction of any SO_3 so formed to produce a complex sulfate. Analysis of the samples will be made later to show which of the two cases predominates.

SO_3 Profiles Above V_2O_5 Surfaces

Figure 5 shows the results obtained with two surfaces containing V_2O_5. One of these materials, cp-grade V_2O_5, proved to be a poorer catalyst for SO_3 formation than was Fe_2O_3. This result does not agree with data by Wickert[4], who found V_2O_5 to be slightly more catalytic than Fe_2O_3 at 1100 F. Because of this discrepancy, another experiment was run with a crushed commercial catalyst containing 11 percent V_2O_5 on a support of Al_2O_3.* A 50 percent increase in SO_3 concentration near the surface was observed under these test conditions, but this confirms only that there can be significant differences between V_2O_5 catalyst surfaces.
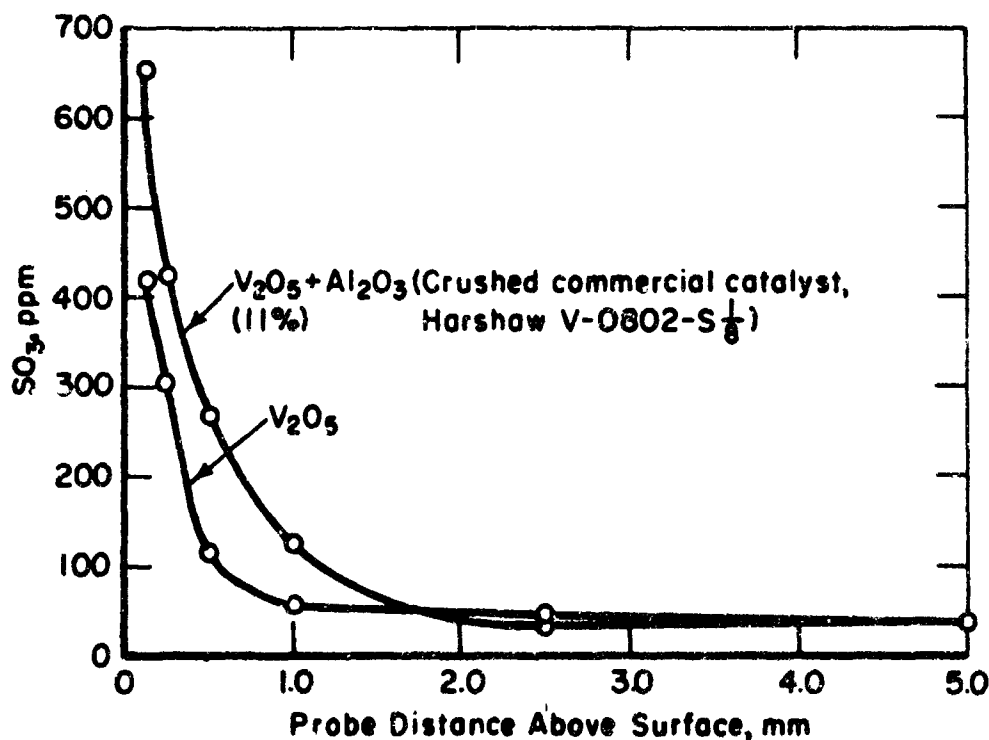
FIGURE 5. SO_3 PROFILES ABOVE SURFACES CONTAINING V_2O_5 AT 1100 F IN 6 PERCENT SO_2

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* Harshaw V-0802-S-1/8.

Fe^{2+} and Fe^{3+} Ions in Iron Oxide Coatings

Five iron oxide coatings previously exposed to sulfur oxide gases were analyzed for soluble ferric and ferrous ions in the coatings. The results are given in Table 2.

TABLE 2. Fe^{2+} AND Fe^{3+} IONS IN IRON OXIDE COATINGS AFTER EXPOSURE TO SULFUR-BEARING GASES AT 1110 F

			Mgs Water-Soluble Ions	
No.	Sample	Gas Mixture	Fe^{2+}	Fe^{3+}
1	Fe_3O_4 on Vycor, 1% NaOH	N_2-O_2-SO_3	0.7	0.7
2	Fe_3O_4 on Vycor, 1% NaOH	N_2-O_2-H_2O-SO_2	0.9	0.4
3	Fe_3O_4 on Vycor, 1% NaOH	N_2-SO_3	0.7	0.2
4	Fe_3O_4 on Vycor, 8.5% NaOH	H_2S-O_2-N_2 flame	1.4	1.6
5	Fe_2O_3 on Fe, 0% NaOH	H_2S-O_2-N_2 flame	1.5	0.2

It appears from these data that the water-soluble Fe^{2+} state of iron is present in equal or larger amounts than water-soluble Fe^{3+} in the samples. This would seem to indicate that more ferrous sulfate may be found in the samples than ferric sulfate, in agreement with the relative stability of ferrous and ferric sulfate at 1110 F. Increasing the NaOH content appears to have resulted in a considerable increase in the amount of Fe^{3+} found in solution (Sample No. 4); this in turn might have resulted from the formation of an alkali iron sulfate such as $Na_3Fe(SO_4)_3$, but this compound has not been identified in this sample.

Future Work

Additional effort will be spent learning more about the physical factors influencing SO_3 profiles, such as gas velocity and temperature. More work also will be done on the reactions involving Fe_2O_3 and sulfates, in an effort to determine how the trisulfates form. Some experiments also will be made on the V_2O_5-sulfate systems to shed light on formation of corrosive alkali vanadyl sulfates.

One way of detecting the influence of various factors on the formation of corrosive deposits would be to use specimens of superheater alloys in the form of polished flat plates. Electropolishing or simple mechanical polishing could produce surfaces with a roughness of, say, 10 microinches rms as measured with a profilometer. Such specimens, made perhaps an inch square, could then be exposed to furnace conditions after a small speck of supposedly corrosive material had been placed on its surface. After the test, another profilometer run would show

whether the surface had changed where the speck had been placed. The specimen probably would have to be cleaned in an inhibited acid solution to remove physical traces of the added material and to remove ordinary scale. Nevertheless, the profilometer measurement, because it can show quite small differences in height, should be able to demonstrate quantitatively how various materials behave under different conditions.

A typical use of such a procedure would be to investigate the effect of changes in gas velocity over a surface. It has already been shown at Battelle that a steep concentration gradient occurs in the SO_3 over a catalytic surface when SO_2 and O_2 flow over that surface. The SO_3 so produced is ample to form ferrous sulfates or alkali iron trisulfate at the expense of the iron oxide on the metal surface. A question yet unanswered is what influence does velocity have on this reaction? Since diffusion through the boundary layer and the thickness of the boundary layer itself are involved as well as the chemical kinetics, the problem becomes difficult to solve analytically. It would be relatively simple, however, to pass mixtures of gases simulating flue gas over polished surfaces at different velocities and temperatures. If the profilometer could indeed measure the amount of metal lost by comparing the exposed surface with a protected part of the original surface, a powerful tool would be available for determining quantitatively exactly what was occurring.

For example, the loss of 0.1 inch of metal per year by corrosion in an operating furnace is equivalent to about 11 microinches per hour. Hence, a 5-hour test at this rate would show a metal loss of 55 microinches, ample to be detected at the edge of the corroded area by a profilometer. A series of tests investigating a great many variables could be made in a relatively short period. With the background now accumulated at Battelle on the basic factors leading to corrosion, this would seem to be a logical extension for demonstrating under measurable conditions exactly which factors are important in corrosion and which can be ignored in practice. This same scheme should be useful in operating boilers, where a partially protected polished specimen could be attached to a controlled-temperature probe and inserted in suspected areas of a superheater circuit. Exposure of only a day or two might give meaningful and useful results.

RADIOACTIVE TRACER STUDIES

Radioactive sulfur (S^{35}) is being used in a series of tests to shed further light on the mechanism by which the alkali iron trisulfates and other corrosive materials are formed in an environment normally rich in SO_2 but deficient in SO_3.

The only previous study in which radio tracers were applied to the problems of boiler furnaces was that of Fletcher and Gibson,[5] published in 1954. In their work with S^{35}, combustion products from the burning of water gas were mixed with SO_2 and $S^{35}O_3$. This gas mixture was passed over sodium chloride at temperatures from 572 F (300 C) to 1382 F (750 C). The sodium chloride was converted to sodium sulfate, and because one of the sulfur oxides was radioactive, it was possible to distinguish their relative participation in the reaction.

Figure 6 summarizes the results of their research. Between 572 F (300 C) and 1112 F (600 C) the bulk of the sodium sulfate was formed from sulfur trioxide, but above 1112 F (600 C), the rate of sulfate formation from sulfur dioxide increased rapidly with temperature, while that from sulfur trioxide remained almost constant. In experiments in which 2 percent Fe_2O_3 was added to the sodium chloride, the rate of sulfate formation from sulfur trioxide was unaffected by the presence of the catalyst, while that from sulfur dioxide was greatly increased.

The Battelle program proposes to go much beyond the Fletcher and Gibson study. First of all, Fletcher and Gibson investigated only the formation of Na_2SO_4 with NaCl an important part of their system. Alkali sulfate formation, as shown by earlier work in this Battelle study, is fairly rapid and direct. Of primary interest in furnace corrosion is the formation of iron sulfates and ultimately the alkali iron trisulfates. It is the goal of the current program to identify these factors, including differentiating between SO_2 and SO_3 as they enter into the reaction mechanism.

If the premise can be accepted that alkali sulfates are produced rapidly in a combustion system, then a mechanism must be proposed whereby the simple iron sulfates are produced prior to the formation of the complex alkali iron sulfates. Although iron sulfates have been bypassed in some mechanisms proposed by others, the presence of iron sulfate and sodium sulfate together with ample SO_3 can lead directly to alkali iron trisulfate.

FIGURE 6. FORMATION OF SODIUM SULFATE AS OBSERVED BY FLETCHER AND GIBSON[5]

Three general steps may be surmised for the formation of iron sulfates;

1. The sulfidation of iron

$$3Fe + SO_2 \rightleftharpoons FeS + 2FeO$$

$$4Fe + SO_3 \rightleftharpoons FeS + 3FeO$$
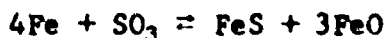
2. The oxidation of iron

$$Fe + O_2 \rightarrow FeO, Fe_3O_4, Fe_2O_3$$
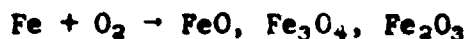
3. The sulfation reactions

$$FeO, \ Fe_3O_4, \ Fe_2O_3 \ \xrightarrow[SO_3]{SO_2} \ FeSO_4, \ Fe_2(SO_4)_3$$

$$SO_2 + \tfrac{1}{2}O_2 \rightarrow SO_3$$
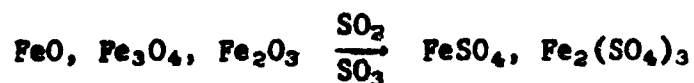
It is apparent that by labeling the SO_2 or the SO_3 with S^{35}, either the SO_2 or the SO_3 leading to sulfation could be identified, and ultimately it should be possible to determine the specific steps by which the alkali iron sulfates are formed.

The low-energy beta radiation (0.167 mev) of S^{35} is particularly suit-able 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 statisti-cally significant radioactive count over reasonable time 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-tagged sul-fur makes detection at these levels feasible.

Apparatus and Procedure

Figure 7 shows the apparatus for the S^{35} tracer studies. Desired mix-tures of nitrogen, oxygen, SO_2 carrier gas, and radioactive $S^{35}O_2$ are provided from gas cylinders with SO_3 generated by thermal decomposition of sulfuric acid. This gas mixture is passed over the surfaces to be studied, maintained at 1100 F. The initial S^{35} concentration in the gas cylinder is 1 microcurie per liter, thus providing 2.2×10^6 counts/min for each liter of the gas introduced into the re-action chamber. The presence of very small amounts of S^{35} in the reacted surface should be detectable, because the scintillation counter techniques are capable of detecting 5-10 counts per minute above the natural background of 25-30 counts per minute.

The SO_3 which remains in the gas stream is trapped out as sulfuric acid at 32 F (0 C) and the amount of SO_3 is determined by the barium chloranilate method. The SO_2 is absorbed by reaction with H_2O_2 solution in several bubblers, to prevent escape of any unreacted S^{35} from the system.

Experimental Results

Experimental work had barely gotten under way during this report period. For the initial experiment, conditions used were similar to those employed in the SO_3 profile studies and some of the earlier flame work to compare data. The gas mixture contained 74.8 percent N_2, 19.4 percent O_2, and 5.8 percent SO_2 at a flow rate of 40 cc/sec. Iron oxide deposited on a Vycor plate (1" x 4") was used as the catalytic surface, at a temperature of 1100 F. However, no radioactivity was
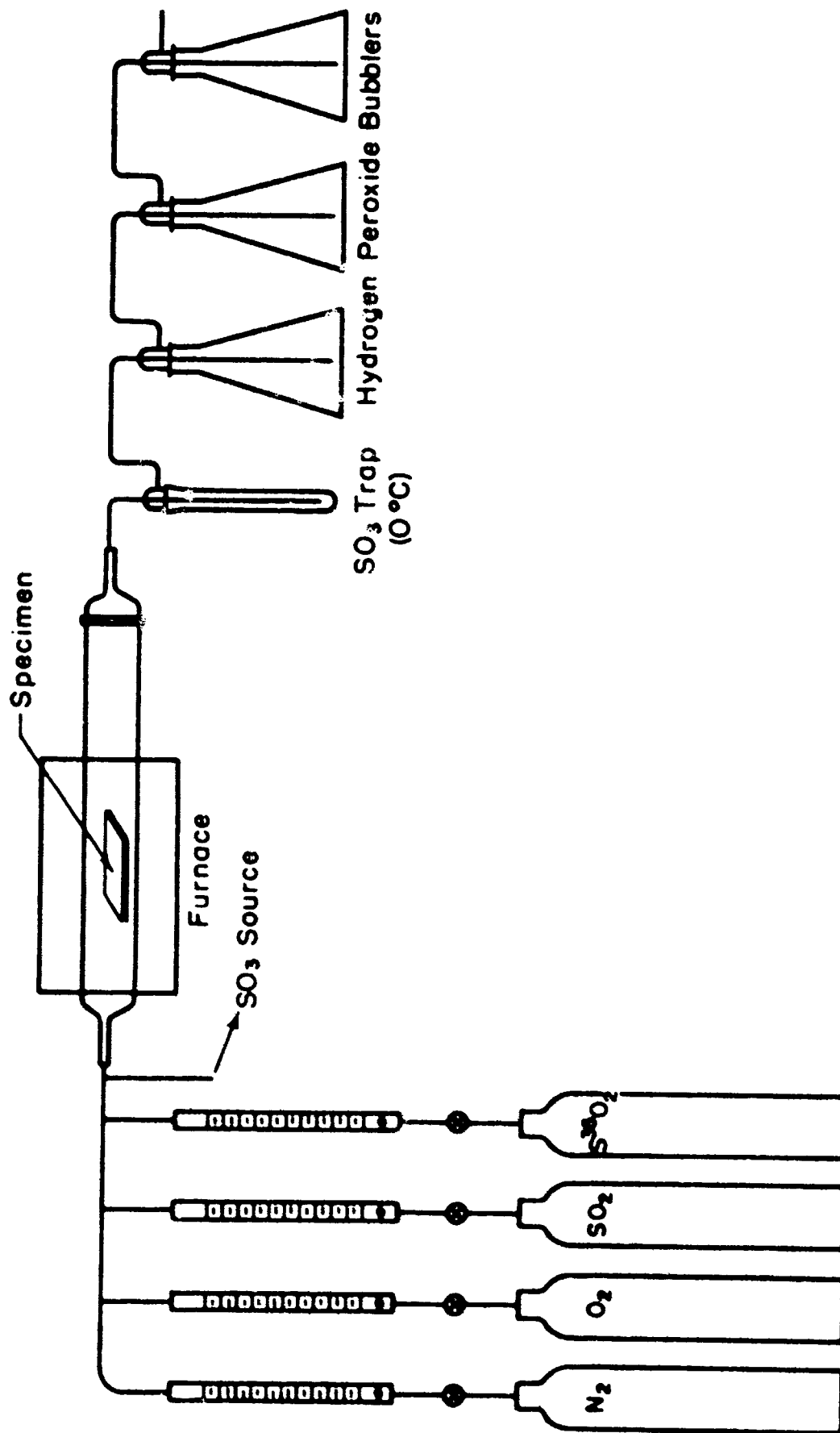
FIGURE 7. S³⁵ REACTION SYSTEM.

found in the catalytic surface, in the SO_3 trapped out as H_2SO_4, or in the unreacted SO_2 absorbed in the H_2O_2 solution. In addition, a filter on the effluent gas stream showed that no radioactivity was leaving the system. As a consequence of these negative results, the cylinder of gas which supposedly contained $S^{35}O_2$ in nitrogen was checked directly and no radioactivity could be detected in the gas mixture. The supplier was unable to give any good reason for the lack of activity and is making a new shipment. There is a possibility that the $S^{35}O_2$ could have been adsorbed on the container walls; to minimize this possibility, the new shipment has been requested in a smaller cylinder with only SO_2 as the diluent.

Future Work

The S^{35} tracer work will be resumed as soon as the new supply of $S^{35}O_2$ is received. The test procedure then will be that planned earlier, to follow the course of sulfur in forming the trisulfates and to distinguish the reactions of SO_2 from those of SO_3 in the system.

PREPARATION OF PURE ALKALI IRON TRISULFATES

Although the alkali iron sulfates have been known for many years, they are not chemical reagents that can be bought from usual laboratory supply houses. Trisulfates have been made by others in the temperature range of 1000 F to 1100 F. The same general procedures also have been used at Battelle to obtain samples for comparison with deposits formed on test specimens. Because there has been some question about the time required for the reactions to take place, in one case trisulfates were produced by placing a quantity of an Fe_2O_3-Na_2SO_4-K_2SO_4 mixture in a porcelain boat in an electric muffle furnace at 1100 F to 1150 F. A mixture of oxygen and SO_2 was bled into the muffle and over the boat; the resulting SO_3 concentration was not measured, but white fumes could be seen. The mixture melted within 2 hours, with an x-ray diffraction analysis showing what appeared to be small quantities of alkali iron trisulfates. The fact that some trisulfate was formed over this short period demonstrates that there is no "induction period" in forming these compounds. The quantity of trisulfate formed will increase with longer tests, suggesting that more sensitive means than X-ray diffraction for identifying trisulfates would make short-duration tests as meaningful as long ones.

To obtain a sample of relatively pure alkali iron trisulfate for use as a standard, a small amount was prepared at Battelle. A mixture of Na_2SO_4 (2.13 g), K_2SO_4 (2.61 g), and Fe_2O_3 (1.60 g) was placed in a boat and maintained at 1100 F in an atmosphere of SO_3, SO_2, and O_2 for 122 hours. This mixture provided the stoichiometric mol ration of 1.5:1.5:1.0 required for the pure compound. After being subjected to these conditions for 5 days, the upper half of the mixture, which was in contact with the gas stream, had been converted to a white crystalline mass. The lower half of the mixture was brick-red and had a sintered appearance.

The white crystalline product when examined by X-ray diffraction was found to be $Na_3Fe(SO_4)_3$ of rather good purity. Agreement with the standard pattern for the trisulfate was good. All of the lines in the X-ray pattern of the product appear in the standard, although the standard lists some additional lines. The X-ray diffraction data for the standard and the sample are shown in Table 3.

TABLE 3. X-RAY DIFFRACTION DATA
FOR $Na_3Fe(SO_4)_3$

d,Å	Relative Intensity	Lines Found In Reaction Product
6.80	75	X
4.27	2	X
3.93	40	
3.60	20	X
3.18	100	X
3.04	75	X
2.94	4	X
2.76	15	X
2.64	20	
2.56	15	
2.39	20	X
2.31	3	
2.25	15	X
2.14	3	X
2.03	20	X
1.98	10	X
1.94	8	X
1.86	30	X
1.80	15	
1.76	4	
1.73	10	X
1.68	8	X
1.63	10	X
1.58	20	X
1.54	20	X
1.47	15	

Values of the index of refraction of the $Na_3Fe(SO_4)_3$ product were checked by optical microscopy and found to be close to that recorded in the literature for $Na_3Fe(SO_4)_3 \cdot 3H_2O$, the mineral "ferrinatrite". Approximate values of 1.55 and 1.61 were found for the indices of the two axes. These are sufficiently different from those of other components likely to be present that the occurrence of small amounts of trisulfate might be detected by microscopic examination.

Figure 8 compares the infrared spectrum of the $Na_3Fe(SO_4)_3$ prepared here with that of other sulfates. If the trisulfate is present in quantities greater than 5 percent, it should be possible to get a clue to its presence from the absorption band at 7.9 microns, which would not be masked by the other sulfates.

Tests of this pure trisulfate with pH paper, using the technique being tried on specimens, showed a pH of 1 to 1.5. However it was not possible to distinguish the trisulfate from ferric sulfate on the basis of these pH values alone.

The red material from the bottom half of the boat obviously had not undergone complete reaction. However, the infrared spectrum of this material showed that a substantial portion had been converted to the trisulfate. Further analytical examination will be carried out on this product to try to distinguish the trisulfate from other components of the partially reacted mixture.
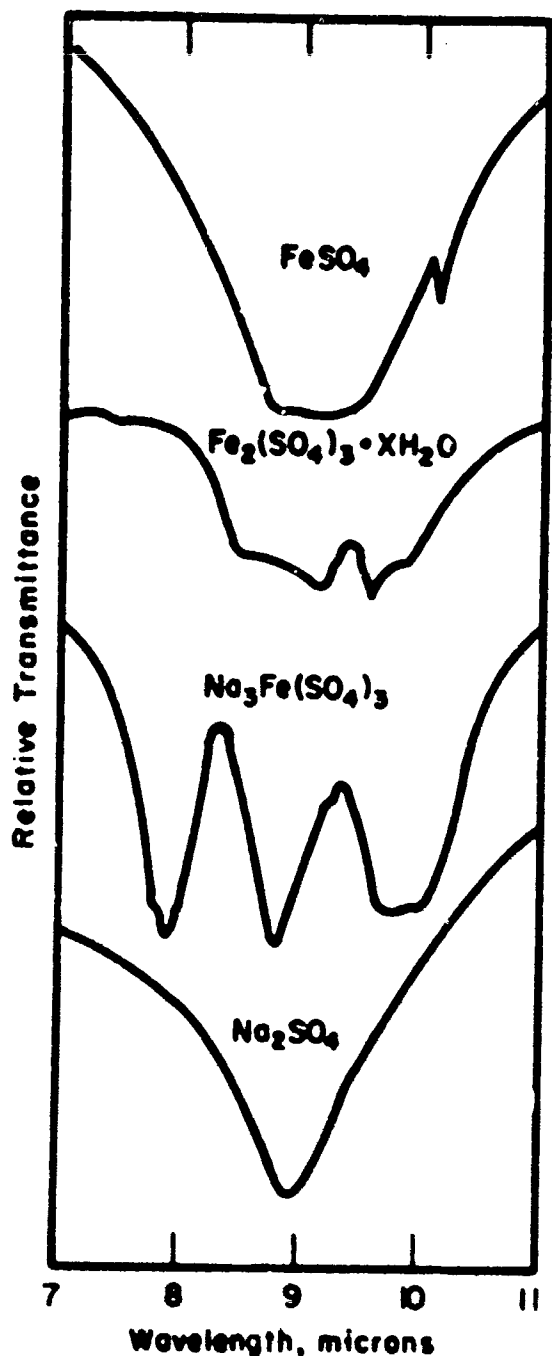
FIGURE 8. INFRARED SPECTRA OF VARIOUS SULFATES

FUEL-BURNING FURNACE STUDIES

by

R. E. Barrett

These fuel-burning furnace studies are intended to bridge the gap between the fundamental studies of reactions occurring at surfaces, and the application of such data to systems more nearly simulating large boilers and gas turbines. Recent work in the fuel-burning furnace has stressed investigation of the conditions leading to formation of alkali iron trisulfates. It is generally accepted that alkali iron trisulfates at superheater temperatures can form only when the SO_3 concentration is many times that available in the bulk flue-gas stream of a boiler furnace. Catalytic formation of high concentrations of SO_3 in localized areas around superheater tubes could explain this discrepancy, and indeed this has been the explanation suggested by many researchers. What has been lacking in that earlier work is quantitative data showing specifically what the SO_3 concentration can be immediately next to a catalytically active surface. The Battelle work on surface studies has now provided that information. This section of the report describes further work on catalysis and the effect of SO_3 produced catalytically on a surface in forming iron sulfates and alkali iron trisulfates even when the SO_3 in the bulk gas stream is relatively low.

EQUIPMENT AND TECHNIQUES

The fuel-burning furnace used for the furnace studies has been described in detail.[6,7] In general, it consists of a stainless steel combustion chamber with its walls at 500 F to prevent unwanted formation of SO_3 by catalysis, which otherwise would occur on hotter walls. The specimens are closed-end 3/16-inch-diameter mild steel tubes supported in a framework so that the combustion gases pass over the specimens in a controlled manner. Temperature of the specimens is determined by their location in the furnace. All tests reported here were made when burning No. 2 fuel oil containing sufficient carbon disulfide to give a 5¼ percent sulfur content.

Figure 9 shows the catalyst arrangement constructed to increase the SO_3 concentration of the combustion gas flowing over the test specimens from its nominal value of 30 to 40 ppm to about 200 ppm. It consists of a stainless steel holder which supports two rows of oxidized mild steel tubes, so arranged that all gas passing over the specimens must first pass over these tubes. Catalytic activity of the tubes is provided by oxidizing the tubes in flue gas at moderate temperatures, so that the tubes are covered with Fe_2O_3. A V_2O_5 coating could be used, but oxidation produces a uniform surface well adapted to forming SO_3 by catalysis.

One problem causing continued concern involves the positive identification of alkali iron trisulfates on specimen surfaces. Observations such as melting point, evolution of SO_3 on heating, and the pH of an aqueous solution are not
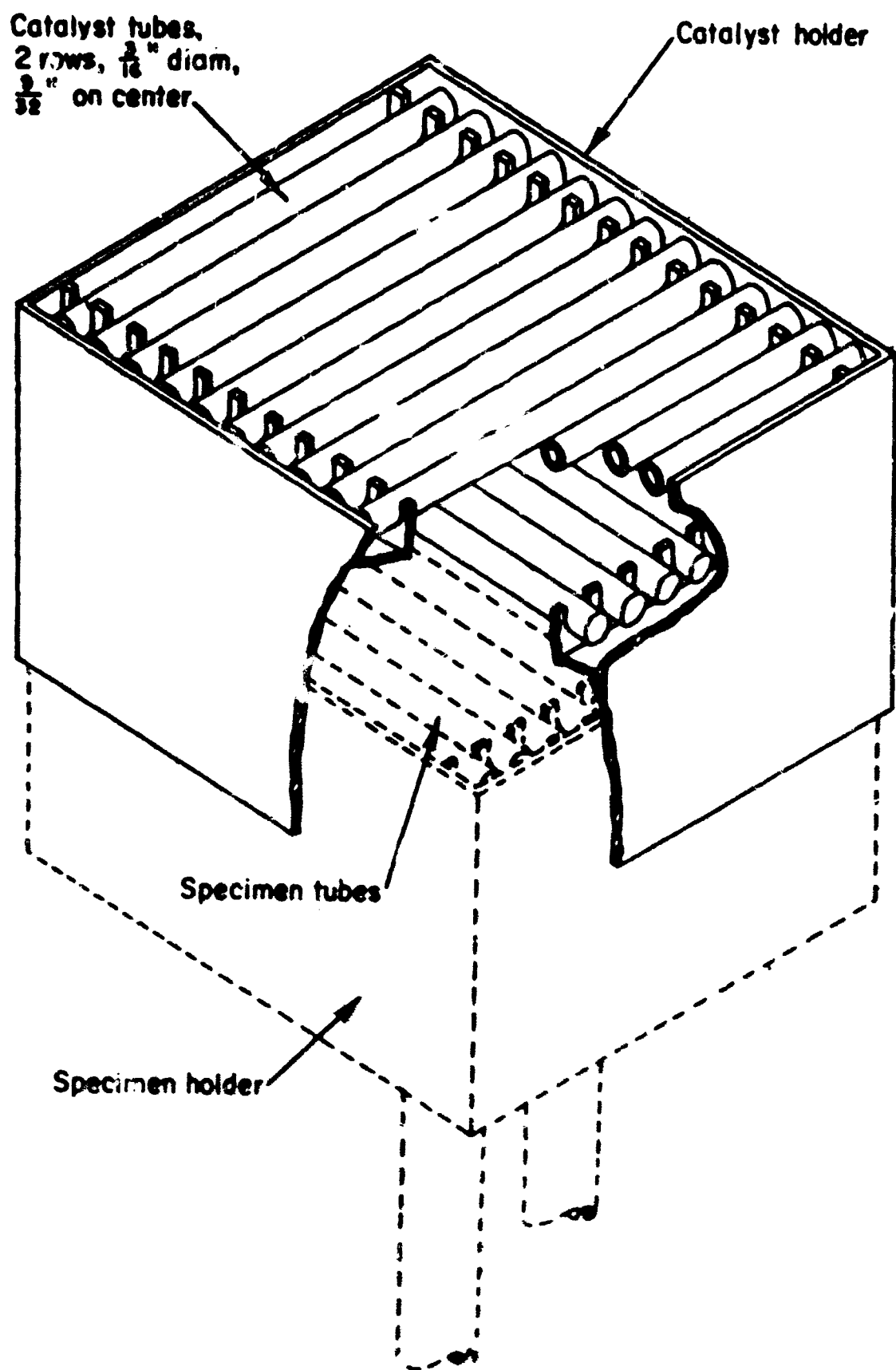
FIGURE 9. CATALYST HOLDER WITH TUBES

completely reliable because other compounds interfere, such as ferric sulfate and ferrous sulfate. Sophisticated detection techniques including X-ray diffraction are expensive for use on a daily basis, so that some compromise has to be made. Also, X-ray. diffraction requires at least 5 percent trisulfate in the sample to enable a positive identification.

Consideration was given to indirect qualitative schemes for detecting the alkali iron trisulfates. Two schemes investigated are pH "prints" and the use of an electrochemical cell.

pH Prints

Using pH-indicating paper* to show the presence of extremely small spots of iron sulfates or alkali iron trisulfate is based on hydrolysis of even the most minute particles of these sulfates to produce an acid reaction. To make such a test, a piece of dry pH paper of the range of 1.0 to 2.5 pH is wrapped firmly around a specimen tube and held in position by masking tape at the ends. The tube is then placed in a high-humidity environment so that the pH paper barely becomes damp. This provides enough moisture that any iron sulfates or trisulfates hydrolyze, and hence change the color of the paper locally. Too much water will show a pH of 7 and will mask the effect of small amounts of sulfates; it will also allow diffusion to occur so that the tiny spots of color representing the presence of sulfates are lost by being spread out over too large an area.

Spots only a few thousandth of an inch in diameter apparently can be made visible in this way, and since the paper is not completely wet, diffusion is not a problem and a fairly sharp outline is obtained. Although as yet the pH paper cannot distinguish between iron sulfates and alkali iron trisulfates, it does an excellent job of showing radical differences in the surface layer on specimen tubes after various test conditions. For example, pH values as low as 1.0 have been found in this way in localized areas on a number of specimen tubes.

Electrochemical Cell

As a method of detecting the presence of trisulfates while r test is in progress, a device was conceived that acts as a battery to produce a low voltage when a molten electrolyte is present between two electrodes. It consists of a simple electrochemical cell where two dissimilar metals are separated by a slight gap, with the metals connected to a potentiometer by wires of the same materials. When a molten electrolyte bridges the gap, a voltage is produced showing that corrosion is occurring. At temperatures in the range of 1000 F to 1200 F, the most likely molten salt will be the alkali iron trisulfate. Hence the appearance of a voltage indicating that a molten salt is bridging the gap between anode and cathode also can be taken as a fair indication that the trisulfate has been formed. A first trial made in the laboratory with such a device used mild steel and

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* pHydrion paper with ranges of 1.0 to 2.5 and 3.0 to 5.5 from Micro Essential Laboratory, Inc., Brookly, New York.

stainless steel tubing surrounding a porcelain rod, with the gap between the two metals about 1/32 inch. A better system would use an oxidized nickel tube and an alloy similar to those in superheaters.

The first trial of this system was made by inserting the two metals in a boat containing Na_2SO_4, K_2SO_4, and Fe_2O_3 in the stoichiometric proportions to form the trisulfate. When the temperature of this system was raised gradually in an atmosphere containing SO_3, no voltage was produced until the temperature reached 1020 F. Here there was an abrupt rise in voltage, almost exactly where a liquid phase should have formed.

Another test was made in the fuel-burning furnace by placing the combination of an oxidized nickel tube and a steel tube in one of the positions of the regular specimen holder, again with the two metallic elements separated slightly and maintained in position by a porcelain rod. This "cell" was coated with the usual mixture of Na_2SO_4, K_2SO_4, and Fe_2O_3. The furnace was then heated gradually, with the SO_3 concentration about 30 ppm in the bulk gas stream. Voltage output of the cell was essentially zero until the temperature reached about 1000 F, when the voltage rose abruptly to 0.5 volt, measured with a 20,000-ohm-per volt meter. When the specimen was removed from the furnace, the coating was found to have melted. A check with pH paper showed spots with a pH of 1.0.

Further work under better contolled conditions is warranted to evaluate the electrochemical cell more exactly.

FORMATION OF TRISULFATES ON FURNACE SPECIMENS

Three paths were followed in seeking to form significant quantities of alkali iron trisulfates under controlled conditions in the fuel-burning furnace.

Table 4 shows the results in tests G 08 through G 19 of initial attempts to form trisulfates. In the first tests, G 08 to G 10, the tubular specimens were coated with a mixture of sodium sulfate, potassium sulfate, and ferric oxide, and exposed in the furnace for five hours at 1100 F. The furnace atmosphere contained roughly 60 to 90 ppm SO_3 in the bulk gas stream. At the temperature of these experiments, about 70 F above the reported melting point for alkali iron trisulfate with a 1:1 mol ratio of sodium and potassium, there was some evidence of melting on the surface of the specimens, but only in extremely small spots. A 1 percent solution of the deposit in distilled water had a pH of 3.6 This pH value indicates a more acidic deposit than any reported in the Seventh Summary Report.

A pH print of Specimen G 10 showed a pH of 1.0 to 1.5 in spots, confirming that either iron sulfate or alkali iron trisulfate had formed during the test. It was likely, however, that less than 5 percent sulfate was present so that it would not have been detected by X-ray diffraction.

Test Series G 15 through G 19 was run to determine the influence of temperature on the formation of alkali iron sulfates. As before, a mixture of Na_2SO_4, K_2SO_4, and Fe_2O_3 in the mol ratio of 1.5:1.5:1.0 was coated on clean unoxidized tubular metal specimens. The amount of mixture applied varied between

TABLE 4. SUMMARY OF TESTS PRODUCING SULFATE SURFACES

Test	Specimen Coating	Average Specimen Temperature, F	Average Bulk SO_3 Concentration, ppm		Average Specimen Weight Loss, mg	pH By Damp Hydrion Paper
			Upstream	Downstream		
G 08	Alkali Mixture (a)	-	60	64	-	-
G 09	"	1115	61	66	-	-
G 10	"	1075	88	87	127	1.0-1.5(b)
G 15	Alkali Mixture (a)	1200	174	124	345	-
G 16	"	1160	198	148	274	-
G 17	"	1110	180	122	194	-
G 18	"	1030	124	85	160	1.0-1.5
G 19	"	1060	76	92	-	1.0-3.0
G 32	Alkali Mixture (a)(c)	1125	37	51	154	1.5
G 33	"	1030	29	33	72	1.5
G 34	Alkali Mixture (a)(d)	1065	33	37	94	1.5
G 35	"	1055	113	113	103	1.5

(a) Alkali Mixture = 1.5:1.5:1.0 mol ratio of Na_2SO_4, K_2SO_4, Fe_2O_3.
(b) pH of 3.6-3.75 measured for 1 percent of deposit in water.
(c) With kaolin covering alkali mixture.
(d) With kaolin + Na_2SO_4 covering alkali mixture.

0.05 and 0.13 gram per square inch, enough to provide a coherent layer over the entire surface of the specimens. To increase the SO_3 level in the bulk gas stream, two rows of catalytically active tubes were placed above these specimens in the arrangement shown in Figure 9. With these tubes, the SO_3 level in the bulk gas stream approaching the specimen tubes varies between 75 and 200 ppm, rather than the 30 to 40 ppm normally present in the gas from flame reactions.

Specimen temperatures in these tests were established between 1060 F and 1200 F. In tests at 1060 F and 1075 F, the alkali sulfate-Fe_2O_3 mixture melted in small areas to produce reddish nodules and partially fused surface layers. There was no evidence of such melting in tests made at 1105 F, 1165 F, and 1200 F, suggesting that the SO_3 concentration was not high enough to produce the trisulfate at these temperatures. The bulk SO_3 level in the gas stream below the catalyst tubes was 75 ppm for the test at 1060 F, 145 ppm at 1075 F, and ranged between 175 and 200 ppm for the tests between 1105 F and 1200 F. Such variations are expected because of the influence of temperature on the catalytic formation of SO_3.

Analysis by X-ray diffraction of a melted nodule from the lower temperature test showed no positive indication of $Na_3Fe(SO_4)_3$ or $K_3Fe(SO_4)_3$. The analysis was not entirely satisfactory because relatively large amounts of a substance were present that could not be identified positively. It is fairly certain, however, that if trisulfates were present, they must have been in concentrations of less than 5 percent. Paper pH prints of specimens G 18 and G 19 showed a pH as low as 1.0 in some spots, confirming that iron sulfate or the trisulfate had been formed.

These tests confirmed earlier expectations that the trisulfates did not form at moderate bulk SO_3 concentrations when the temperature exceeded 1100 F. They do not indicate how much SO_3 must be present under furnace conditions except that it must be greater than 200 ppm at 1100 F to 1200 F. Because trisulfates are known to form on superheaters when the bulk SO_3 concentration is as low as 35 ppm, these data support the distinction between SO_3 levels in the bulk of the flue-gas stream and those occurring on the surface of corroding metals covered with layers of ash or slag.

In the second attempt to form trisulfate, Tests G 32 through G 35, clean steel specimen tubes were coated with the usual mixture of Na_2SO_4, K_2SO_4, and Fe_2O_3 in the mol ratio 1.5:1.5:1.0. A second layer consisting of kaolin or a mixture of 95 percent kaolin and 5 percent Na_2SO_4 by weight was applied on top of the first layer. Table 5 lists the details of the four tests made in this series. In the first two tests, the coating mixtures were not ball milled. In the last two, both the Fe_2O_3-sulfate mixture and the kaolin-sodium sulfate mixture were ball milled for 2 hours before the tests. Metal specimen tube temperatures ranged between 1030 F and 1150 F. For Test G 35, two rows of Fe_2O_3-covered catalyst tubes were placed above the specimen tubes, increasing the SO_3 concentration to 70 to 115 ppm in the flue gas approaching the specimens. For the other tests, the SO_3 level was about 30 to 40 ppm.

In none of these tests was there any visual evidence of melting of the Fe_2O_3-sulfate mixture. It was concluded that not enough alkali iron trisulfate was formed under these conditions to be identified positively. Nevertheless,

TABLE 5. TEST CONDITIONS FOR ATTEMPTS TO FORM
ALKALI IRON TRISULFATES BENEATH EXTERIOR COATING

Test	First Coating	Second Coating	Coating Materials Ball Milled	Temperature, F	Uostream SO_3 Concentration, ppm
G 32	Sulfate Mixture	Kaolin	No	1105-1150	37
G 33	"	"	"	1030	29
G 34	"	95 Kaolin + 5 Na_2SO_4	Yes	1050-1075	32
G 35	"	"	"	1045-1090	7C-115

pH prints showed spots with a pH of 1.5 on each of these specimens. Providing a
surface coating of kaolin over the sulfate mixture, to simulate an ash covering
on a superheater element, apparently had no radical action here whether or not
the kaolin coating contained Na_2SO_4 which might have migrated through the deposit.

Another attempt during this period to produce identifiable trisulfates
in the fuel-burning furnace was made with an open-top stainless steel box con-
structed with a porous stainless steel sheet one-half inch below the top edge of
the box. The gas-analysis probe and suction lines were connected to holes in the
bottom of the box so that combustion gas could be drawn through the porous plate.
This porous plate was covered first with a 3/16-inch layer of the Fe_2O_3-sulfate
mixture, then a 1/16-inch-thick layer of Fe_2O_3, and finally, a 1/4-inch-thick
layer of a 95 percent kaolin-5 percent Na_2SO_4 mixture. A continuous stream of
combustion gas was drawn slowly through the three layers while they were main-
tained at about 1050 F in the furnace. Although no molten zones were found in
these layers at the end of the test, the Fe_2O_3-sulfate mixture was sintered
strongly enough to suggest that small quantities of a liquid phase might have
been present. This material had a pH of about 3.C when checked with damp pH paper.

CATALYTIC ACTIVITY OF FLY ASH

Questions have been raised with regard to earlier work in this study
which showed a typical fly ash to be relatively noncatalytic in oxidizing SO_2 to
SO_3. Hence several tests were conducted to investigate the catalytic ability of
fly ashes in more detail. Table 6 shows the source and the composition of the
three fly ashes tested. Ferric oxide varied from 16.0 to 30.4 percent. Table 7
summarizes these tests as well as others involving catalysis on surfaces.

Figure 10 shows the SO_3 concentration in the bulk gas measured down-
stream of specimen tubes coated with Fe_2O_3 and with each of these fly ashes.
None of the fly ashes is nearly as catalytic as Fe_2O_3 at the test temperature of
1200 F. Indeed, the Joppa fly ash with 30.0 percent Fe_2O_3 had almost no effect
on SO_3 except for the usual brief dip when the specimens were first placed in the

TABLE 6. COMPOSITION OF FLY ASHES TESTED FOR
CATALYTIC ACTIVITY, WEIGHT PERCENT*

Component	Astoria, Consolidated Edison	Port Jefferson, Long Island Lighting	Joppa, Electric Energy, Inc.
SiO_2	47.7	48.6	38.0
Al_2O_3	29.2	28.8	17.4
Fe_2O_3	16.0	17.0	30.4
CaO	2.3	1.9	6.5
MgO	1.2	0.7	3.6
Na_2O	0.7	0.4	0.6
K_2O	2.0	2.5	1.8
SO_3	0.1	0.1	1.6
P_2O_5	-	-	0.1
	100.0	100.0	100.0

* Adjusted to 100.0 percent.
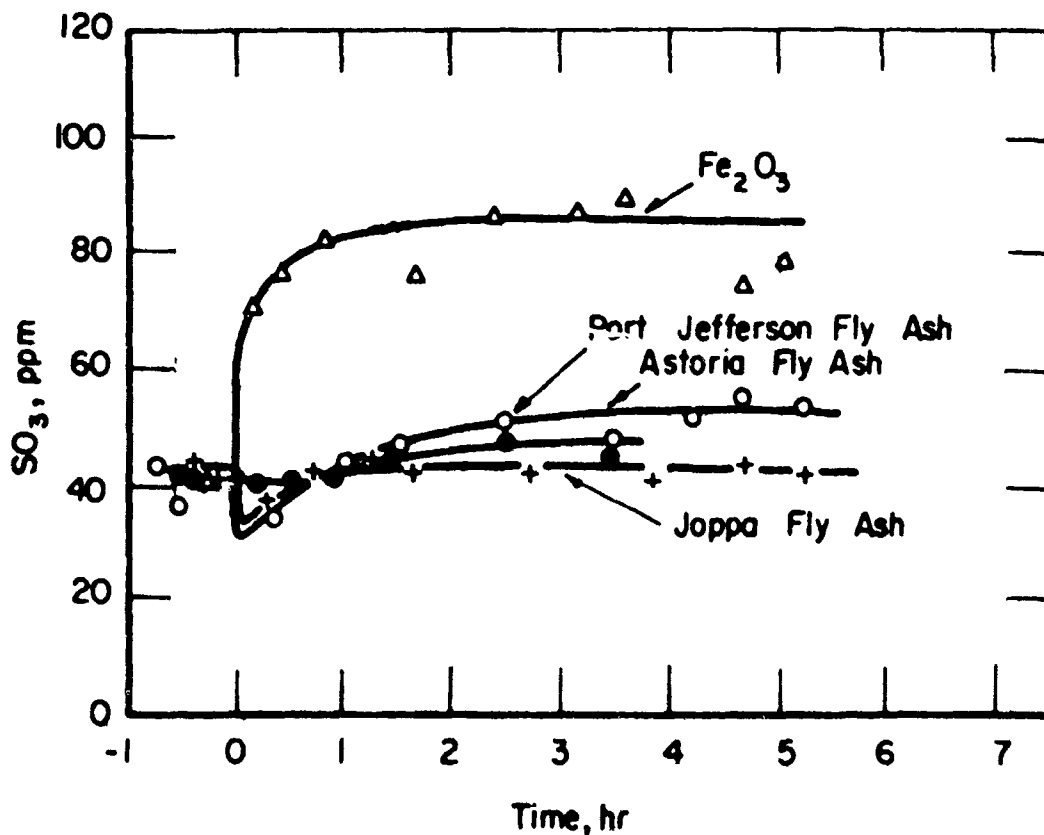
FIGURE 10. SO_3 CONCENTRATION DOWNSTREAM OF MILD STEEL SPECIMENS
AT 1200 F COATED WITH FLY ASH AND WITH Fe_2O_3

TABLE 7. SUMMARY OF TESTS ON CATALYTIC NATURE OF SURFACES

Test	Specimen Coating	Average Specimen Temperature, F	Average Bulk SO_3 Concentration, ppm		Average Specimen Weight Loss, mg	pH By Damp pHydrion Paper
			Upstream	Downstream		
G 24	None	1170	5C	93	-	3.5-4.5
G 29	Fe_2O_3	1220	37	82	-	3.0-3.5
G 26	1:2 Fe_2O_3:kaolin	1200	51	77	-	3.5
G 27	2:1 Fe_2O_3:kaolin	1180	46	36	-	3.5
G 30	1:2 Fe_2O_3:kaolin (a)	1185	31	35	-	3.5
G 31	2:1 Fe_2O_3:kaolin (a)	1180	33	42	-	3.5
G 21	Port Jefferson Fly Ash	1190	41	51	-	4.5
G 22	Astoria Fly Ash	1195	41	45	-	4.0-4.5
G 28	Joppa Fly Ash	1230	41	42	-	3.0
G 36	Syn. Fly Ash 0% Na (a)(b)	1175	47	43	58	4.5
G 37	" 3% Na (a)(b)	1170	47	46	60	3.5-4.5
G 33	" 10% Na (a)(b)	1180	39	44	76	3.5-4.5

(a) Heated for 16 hours at 2000 F prior to test.
(b) Sodium added as carbonate.

furnace, On the other hand, Port Jefferson fly ash with only 17.0 percent Fe_2O_3 increased the SO_3 level from 40 ppm with no specimens present, to 53 ppm after 5 hours exposure, or about a third as much as Fe_2O_3 alone. Astoria fly ash was less effective as a catalyst, increasing the SO_3 concentration by 7 ppm, or about one-seventh as much as Fe_2O_3.

It is interesting to compare these results with data reported by Nelson and Lisle.[6] In their tests, a measure of catalysis can be taken as the percentage conversion of SO_2 to SO_3 under their specialized laboratory test conditions. Table 8 compares the Nelson and Lisle data with these recent results from Battelle. On this basis, although the Battelle curves seem to indicate little catalytic activity for fly ash, the increase in SO_3 level with some fly ashes is comparable to or even greater than that reported by Nelson and Lisle. These data also show, of course, the wide difference in behavior of fly ashes, a not unexpected conclusion.

TABLE 8. CATALYTIC ACTIVITY OF FLY ASH

Nelson and Lisle[8]:	Observed Percentage Conversion of SO_2 to SO_3, 1100 F	Percentage of Conversion With Fe_2O_3
Fe_2O_3	38.0	100
Fly Ash "B"	7.03	18
Kaolin	0	0

Battelle:	Increase in SO_3 at 1200 F, ppm	Percentage of Level With Fe_2O_3
Fe_2O_3	45	100
Port Jefferson Fly Ash	13	29
Astoria Fly Ash	8	18
Joppa Fly Ash	2	4

Figure 11 shows the results of tests to compare the catalytic behavior of mixtures of Fe_2O_3 and kaolin in the Battelle fuel-burning furnace. The decrease in SO_3 with the mixtures after 3 to 4 hours exposure can be attributed partially to an unexplained decrease in temperature of the test specimens. Within the variations expected for such tests, the two mixtures were equally as catalytic as Fe_2O_3 alone. Hence it appears that mixing Fe_2O_3 with the principal ash constituent, kaolin, does not decrease the effectiveness of Fe_2O_3 as a catalyst in this type of test.

It was concluded, therefore, that the catalytic nature of fly ash depends on other factors than its Fe_2O_3 content, and that the presence of moderately large amounts of Fe_2O_3, as shown by chemical analysis, does not necessarily result in high catalytic effectiveness. The way in which Fe_2O_3 occurs in fly ash, as a constituent of melted particles for example, must be more important. Surface
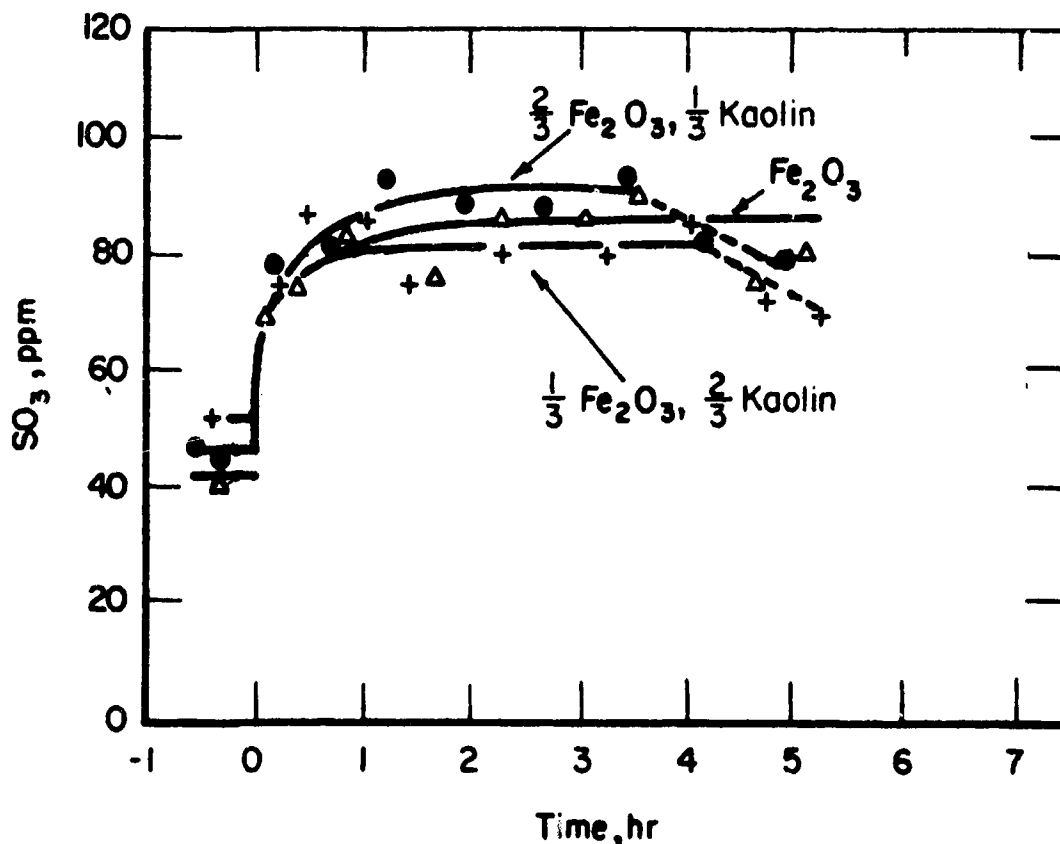
FIGURE 11. SO₃ CONCENTRATION DOWNSTREAM OF MILD STEEL
SPECIMENS AT 1200 F COATED WITH Fe_2O_3 AND
WITH Fe_2O_3-KAOLIN MIXTURES

conditions, particle size, and distribution of ash constituents in different
parts of the heterogeneous mixture called "fly ash" all must play a part in
affecting its catalytic ability.

To examine the effect of prolonged heating on the catalytic activity
of fly ash, two samples of (a) 1/3 Fe_2O_3 and 2/3 kaolin, and (b) 2/3 Fe_2O_3 and
1/3 kaolin were ball milled and then heated for 16 hours at 2000 F. The resul-
tant product was ground and applied to clean specimen tubes. Tests of these
tubes showed essentially no catalytic activity compared with specimens coated
with unheated mixtures of the same materials.

Figure 12 shows the SO₃ concentration down stream of the tubes coated
both with the unheated and with the heated mixtures. The unheated coatings in-
creased the SO₃ level by 32 to 44 ppm; the heated coatings resulted in an SO₃
increase of only 5 to 12 ppm. Apparently, Fe_2O_3 can be readily complexed by
silicates to the point where it loses most of its catalytic properties. The re-
sults of these additional tests suggest that the drop in catalytic activity ob-
served in the final hours of the earlier tests could have been due partly to a
change in the nature of the coating when heated. Likely it is this action that
explains the variation in catalytic activity of fly ash, and that makes it im-
possible to correlate the chemical composition of fly ash with its observed
catalytic activity.
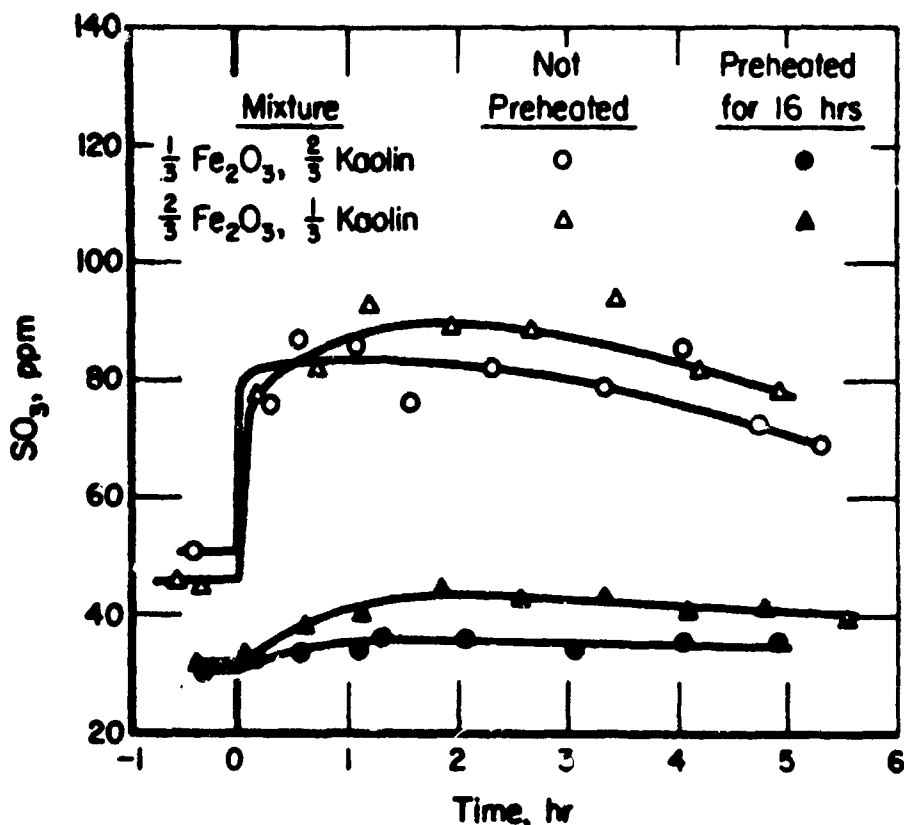
FIGURE 12. SO₃ CONCENTRATION DOWNSTREAM OF MILD-STEEL SPECIMENS
AT 1200 F COATED WITH Fe₂O₃-KAOLIN MIXTURES

In other tests, three synthetic fly ashes with differing sodium contents
were made by ball milling and then heating the mixtures shown in Table 9 at 2000 F
for 16 hours. The resultant synthetic fly ashes were ground and applied to clean
specimen tubes. Figure 13 shows the results of tests with these tubes in the
fuel-burning furnace. None of the three synthetic fly ashes were significantly
catalytic and no pattern of catalytic activity could be determined as a function
of the composition of the mixture, showing that the alkali level apparently does
not influence catalytic activity.

TABLE 9. COMPOSITIONS OF SYNTHETIC FLY ASHES WITH
VARYING SODIUM CONTENT, WEIGHT.PERCENT

Ash Component	Composition A	Composition B	Composition C
SiO₂	31.5	30.5	28.4
Al₂O₃	26.8	26.0	24.1
Fe₂O₃	36.6	35.5	32.9
CaO	5.1	5.0	4.6
Na₂O	0.0	3.0	10.0
	100.0	100.0	100.0
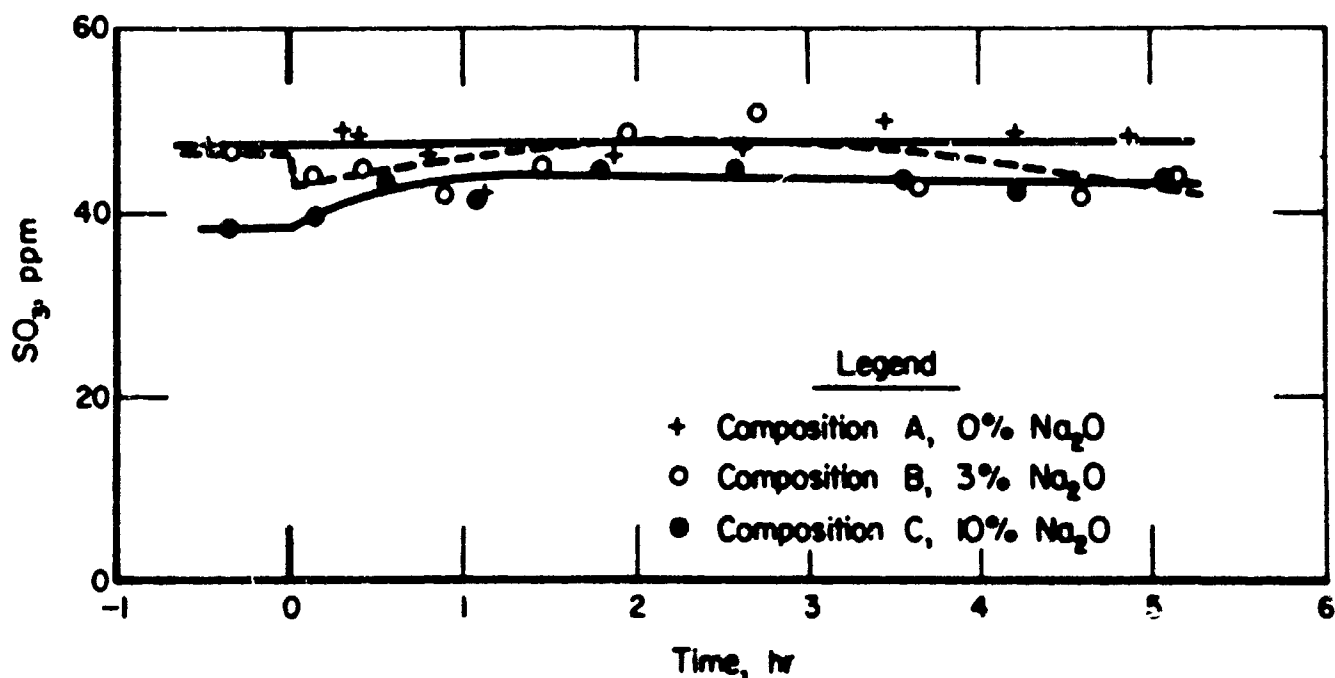
FIGURE 13. SO₃ CONCENTRATION DOWNSTREAM OF MILD-STEEL SPECIMENS AT 1200 F
COATED WITH SYNTHETIC FLY ASH CONTAINING VARYING AMOUNTS OF SODIUM

FUTURE WORK

No further tests of specimens to measure catalytic activity are planned at present. The test program has defined the conditions where catalysis occurs well enough to guide later experiments where catalytically formed SO₃ on surfaces can be expected to lead to the trisulfates.

Other factors related to the formation of alkali iron trisulfates under furnace conditions will need to be investigated. Further development appears to be worthwhile of the electrochemical cell technique of determining the presence of trisulfates. The pH print method also is worth further study, even though at present it cannot distinguish between iron sulfates and the trisulfates. If warranted, a 100-hour test may have to be made on the basis that longer periods may be needed to allow reactions to go more nearly to completion and for larger quantities of trisulfates to form. Probably most important in the near future, in addition to better pre . . . . in determining the presence of trisulfates during a test and in the final products, is to learn exactly why corrosion is found only in practice beneath ash deposits. This is thought at present to be dependent on poor diffusion of flue gases into and away from the surface of a superheater element with a moderately well attached layer of ash. Experiments to support this hypothesis would seem to be justifiable.

MECHANISM OF CORROSION

by

P. D. Miller

THE ELECTROCHEMISTRY OF HIGH-TEMPERATURE DEPOSITS

An interesting area, which has been explored to some extent by several investigators during the past few years, is concerned with high-temperature electrochemistry of deposits in boilers. The subject is of particular importance to power-station corrosion technology because all examples of severe high-temperature corrosion, i.e., alkali trisulfates, pyrosulfates, and vanadium salts, are associated with a molten phase. Thus, any research which contributes to a better understanding of reactions at high temperature in molten salts is significant. 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 example) is oxidized, i.e., loses electrons by the reaction:

$$Fe^o - 3e \rightarrow Fe^{+++} . \tag{1}$$

Several reactions are possible at the cathode as illustrated by:

$$SO_4^{=} + 8e \rightarrow S^{=} + 4O^{=} , \tag{2}$$

$$O_2 + 4e \rightarrow 2O^{=} . \tag{3}$$

A broad review of the subject was presented by Reddy.[9] Several recently reported experimental studies relate to this subject.

Corrosion Mechanism

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.

Real progress is being made in the field of molten salt corrosion by research such as that recently reported by Burrows and Hills[10] along with Inman and Wrench[11]. 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 flcw 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:

$$E_{Fe} = E_{Fe}^{O} + \frac{RT}{3F} \ln a_{Fe^{+++}} \quad , \tag{4}$$

where

E_M = measured potential

E_M^O = 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^{+++} .

A later section in this report summarizes such measurements in systems related to those in boiler furnaces.

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

$$\begin{array}{ccc} \text{base} & \text{acid} & \text{base} \\ SO_4^= \rightleftarrows SO_3 & + & O^= \end{array} \quad . \tag{5}$$

Concentratio- of the SO_3 determines the acidity of the melt and the extent of the corrosion ol e metals in contact with the melt. Disassociation of the sulfate ions as noted above will be determined by the value of the disassociation constant, K, as in:

$$K = \frac{a_{SO_3} \cdot a_O^=}{a_{SO_4}^=} \tag{6}$$

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 by means of a platinum electrode in an atmosphere of oxygen and carbon dioxide, according to Flood.[12,13] 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 as:

$$E_R = E_{O^=}^O + \frac{RT}{2F} \ln \frac{a_{O_2}^{\frac{1}{2}}}{a_O^=} \tag{7}$$

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 (5) will tend to move to the right if SO_3 or $O^=$ are removed. It is suggested that SO_3 can be reduced at the cathode by reactions such as:
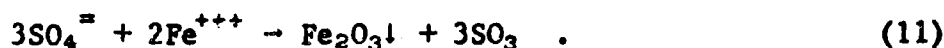
$$SO_3 + 2e \rightarrow SO_3^= \tag{8}$$

or

$$SO_3 + 2e \rightarrow SO_2 + O^= \quad . \tag{9}$$

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

$$O^= - 2e \rightarrow \tfrac{1}{2}O_2 \quad . \tag{10}$$

Oxide ions will not build up in the melt and Equation (5) will not reach equilibrium if the oxide is precipitated according to equation:

$$3SO_4^= + 2Fe^{+++} \rightarrow Fe_2O_3\downarrow + 3SO_3 \quad . \tag{11}$$

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.

Standard Electrode Potentials

As mentioned previously, the tendency of a metal to become oxidized (give up electrons) and go into solution is indicated by measurement of its potential with reference to some standard electrode. Unfortunately such measurements have not yet been made in iron-trisulfate systems. Table 10 lists such potentials for various metals in the molten Li_2SO_4-K_2SO_4 system at 1155 F as given by Burrows and Hills[10].

TABLE 10. STANDARD POTENTIALS IN MOLTEN Li_2SO_4-K_2SO_4 AT 1155 F WITH REFERENCE TO Ag-Ag$^+$ [10]

Electrode	Potential, volts
Au - Au$^+$	+0.837
Pd - Pd^{++}	+0.541
Cu$^+$ - Cu^{++}	+0.051
Ag - Ag$^+$	0.000
Cu - Cu$^+$	-0.202
Co - Co^{++}	-0.630
Fe - Fe^{++}	-0.930 (unstable)

It will be noted that metals more negative than cobalt do not establish stable reversible and reproducible potentials in the sulfate melt. Thus, it is predicted that iron, nickel, and chromium would be readily oxidized by this melt and would not be good construction materials.

Actually, metals are found to be oxidized at potentials more positive than those in Table 10. This fact is explained by the presence of SO_3 formed by the reaction:

$$SO_4^= \rightleftharpoons SO_3 + O^= \quad . \tag{5}$$

A curve is presented by Burrows which shows an increased current flow when SO_3 in the form of sodium pyrosulfate is added. It is concluded that oxidation of iron and steels will take place as long as traces of SO_3 are present.

Standard electrode potentials in molten Li_2SO_4-Na_2SO_4-K_2SO_4 with respect to Ag-Ag^+ were calculated by Johnson and Laitinen[14] as summarized in Table 11.
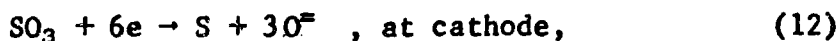
Possible important reactions are:

$$SO_4^= \rightleftharpoons SO_3 + O^= \quad , \tag{5}$$

$$SO_3 + 6e \rightarrow S + 3O^= \quad , \text{ at cathode,} \tag{12}$$

$$O^= - 2e \rightarrow \tfrac{1}{2}O_2 \quad , \text{ at anode.} \tag{13}$$

TABLE 11. STANDARD REDUCTION POTENTIALS ON THE Ag^0/Ag^+ SCALE IN Li_2SO_4-Na_2SO_4-K_2SO_4 MELTS[14]

Electrode	Temperature, F	Potential, volts
Pd - Pd^{++}	1075	+0.441
Rh - Rh^{+++}	1065	+0.267
Ag - Ag^+	1000-1075	0.000
Cu^+ - Cu^{++}	1065	-0.099
Cu - Cu^+	1075	-0.220
Co - Co^{++}	1020	-0.764

Liu[15] has found that sulfate is oxidized at the anode in Li_2SO_4-K_2SO_4 melts at 1150 F according to the reaction:

$$SO_4^= \rightarrow \tfrac{1}{2}O_2 + SO_3 + 2e \quad . \tag{14}$$

The cathodic processes are thought to be:

$$SO_4^= + 2e \rightarrow SO_3^= + O^= \quad , \tag{15}$$

$$SO_4^= + 6e \rightarrow S + 4O^= \quad , \tag{16}$$

$$SO_4^= + 8e \rightarrow S^= + 4O^= \quad . \tag{17}$$

Potential Measurements

A significant experiment was described by Hart[16] in which potentials at inert platinum electrodes in a molten mixture of sulfates at 1110 F were found to be a function of the SO_3 present in equilibrium with SO_2 and O_2 in the cover gas. It was concluded that the SO_3 concentration on boiler tubes coated with sulfate deposits should be the equilibrium concentration rather than the nominal values usually found in flue gas. Thus, it would appear that sufficient SO_3 would be present to allow for alkali trisulfate formation.

Electrochemical concepts have been put to a very practical use by Littlewood[17] and others who have developed an oxygen meter based on potential measurements. The instrument can be used for measuring the oxygen content of hot gases over an extremely wide range, i.e., from 100 percent oxygen down to an oxygen partial pressure of only 10^{-20} atmosphere. The probe as illustrated in Figure 14 consists simply of a closed end zirconia tube with platinum electrodes inside and outside. The zirconia becomes conductive at about 900 F. The oxygen partial pressure within the tube is held constant (P_{const}) by maintaining a flow of oxygen or air. The outside of the tube is placed in the furnace atmosphere.
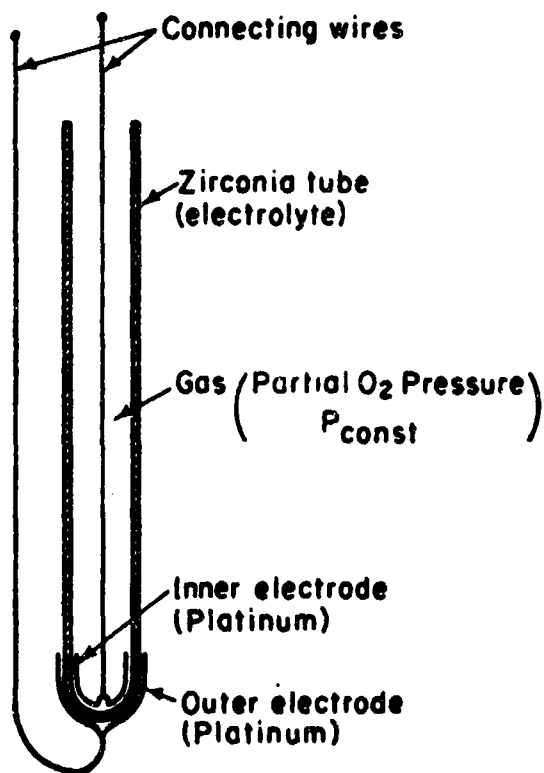
The resulting cell potential gives a direct measure of the partial pressure of the oxygen in the flue gas (P_1) by the equation:

$$E = \frac{2.303RT}{4F} \log \frac{P_1}{P_{const}} \qquad (18)$$

It has not been reported that the probe has been used in power stations, but it should prove to be of value if it can be shielded from fly ash deposits.

A further development of considerable practical value, which has been used successfully in several operating power stations in Europe, is described by Pfeiffer[18,19]. He has constructed a probe which indicates the corrosive tendency of flue gas at high operating temperatures. Electrochemical corrosion reactions are used to activate the probe and furnish voltage readings which can be interpreted for combustion control to minimize corrosion. More involved than the electrochemical cell now being tried by Battelle, Pfeiffer's probe is intended to perform the same general function.

FIGURE 14. LITTLEWOOD'S[17] PROBE FOR MEASURING PARTIAL PRESSURE OF OXYGEN

The metallic electrodes in his probe are 3 mm diameter and are constructed from the same material used for boiler tubes. The wires are encased in

a semisolid electrolyte retained in a smooth pyrometer tube 24 mm in diameter. One wire is completely enclosed by the semisolid electrolyte, the other wire protrudes from the end which is placed in contact with the flue gas. External ends of the two wires are connected to leads going to a potentiometer.

Figure 15 shows the construction of this high-temperature corrosion probe. The reactions which are believed to occur at the wire-ash layer, when the probe is used under oxidizing conditions, are indicated. Those which occur under reducing conditions are shown in Figure 16. It should be pointed out that sulfide also can occur under reducing conditions.
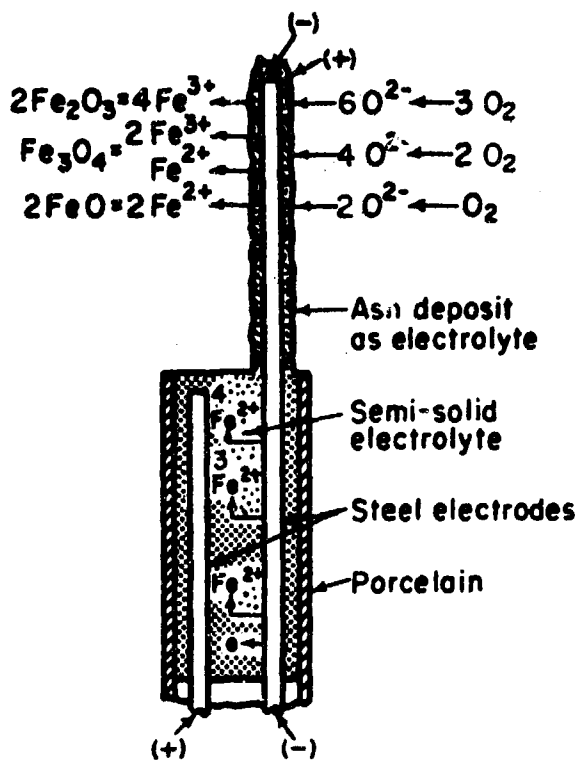

FIGURE 15. ACTION OF HIGH TEMPERATURE
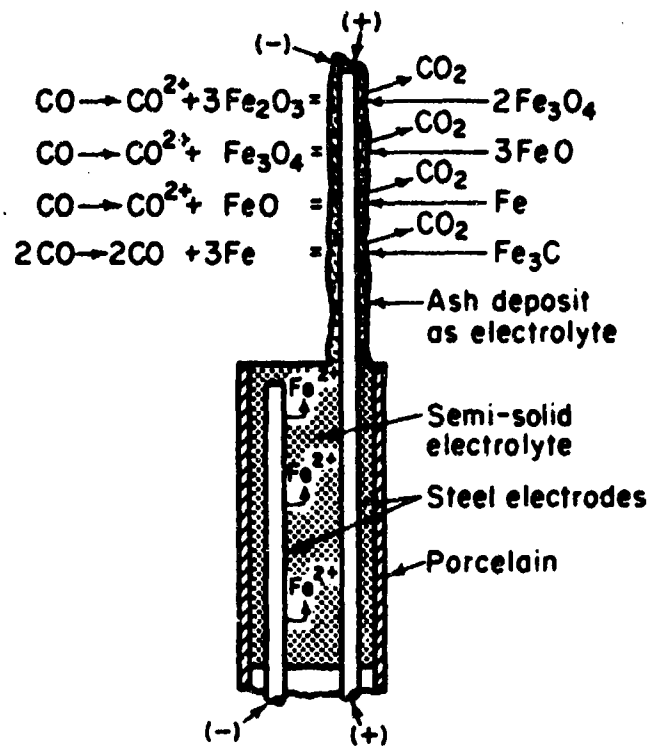   PROBE IN OXIDIZING FLUE
            GAS ATMOSPHERES[18,19]

FIGURE 16. ACTION OF HIGH TEMPERATURE
            PROBE IN REDUCING FLUE GAS
            ATMOSPHERES[18,19]

Practically, it has been found that corrosion can be avoided if the combustion controls are adjusted so that the probe readings are within the range ±50 mv at operating tempei_tures. The probe gives fairly rapid response to changes in combustion conditions so any departure from the low-potential range indicates that dangerous conditions have been produced.

Successful operation of boilers for up to 16,000 hours by means of this probe are reported. The probe can be used for coal as well as oil and is being studied for application to gas tuxbines. Several detailed descriptions both for oil and coal firing illustrate the practical value of the probe to station operators since they could correct for conditions not apparent by any other measuring devices they were using.

Conclusions

Recent research on the electrochemistry of fused salts has been of value in two areas of interest in high-temperature power station corrosion. First, useful probes have been developed which indicate those conditions of combustion furnace operation which prevent corrosion and deposits. Second, a better understanding is being obtained of the reactions which take place while molten salts are corroding metal surfaces. Electrochemical measurements offer a new approach as a control system for observing corrosion while it is occurring in boiler furnaces.

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