EPA U.S. Environmental Protection Agency
Office of Research and Development

Industrial Environmental Research
Laboratory
Research Triangle Park, North Carolina 27711

EPA-600/7-77-041
April 1977

A SURVEY OF SULFATE, NITRATE, AND ACID AEROSOL EMISSIONS AND THEIR CONTROL

Interagency
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Contract No. 68-02-1323
Task No. 49
Program Element No. EHE624a

EPA Task Officer: W.S. Lanier

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Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
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ABSTRACT

The objective of this study was to evaluate the effects of fuel and combustion modifications on the formation of primary acid aerosols and their significance as combustion generated pollutants from large stationary sources. The term acid aerosol is used here in its broadest sense to include all sulfates, nitrates, chlorides, and fluorides in all their forms. Primary acid aerosols are those aerosols which are emitted directly from a source or formed, primarily by condensation reactants, in the immediate vicinity (0.5 mi); secondary aerosols, formed by reactions downstream in the plume, are not considered. Available field data, which were rather minimal, were collected and interpreted in view of current knowledge of mechanisms of formation of potential acid aerosols and their precursors. Although sulfates, nitrates, chlorides, and fluorides were considered, based on the available data, only sulfates appear to be significant as primary acid aerosols. All of the various combustion modifications for NO_x control are expected to have little effect on emissions of primary acid aerosols. The exception to this conclusion may be firing with low excess air which has the potential to abate both NO_x and acid aerosol emissions. Combustion modifications and fuel changes may lead to an increased formation of small particles which could increase the formation of acid aerosols through heterogeneous reactions. Most of the effects, however, are rather speculative due to the meager data available. Gaps in our information have been identified and directions for further research are indicated.

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A SURVEY OF SULFATE, NITRATE, AND ACID AEROSOL EMISSIONS AND THEIR CONTROL

SUMMARY AND CONCLUSIONS

The role of ambient acid aerosols, and in particular sulfates, as contrasted to SO_2, in health and environmental problems is of increasing concern. As a result of recent studies of the ambient atmosphere, particularly in northeastern United States, the contribution of primary acid aerosol or sulfates to the total ambient loading has been questioned. Historically, it has generally been stated that only about 1 to 3 percent of the sulfur in a fuel is emitted from the combustion system as SO_3 or acid. However, since such acid can lead to various sulfates which might be a part of the particulate emissions, it is important to consider these as well as SO_3 as part of the primary acid aerosol. Further, as various combustion modifications become more widely applied to control NO_x emissions one must be concerned that these previously-held postulations regarding SO_3 and sulfate emissions are valid. The purpose of this study has been to evaluate existing data to try to answer these questions.

It should be noted that throughout this study there was considerable uncertainty in correlating and interpreting such data as was available because of the difficulties in sampling and analyzing for acid aerosol components, especially as regards SO_2, SO_3, and sulfates. This has led to a great deal of uncertainty in much of the data and has made quantitative interpretation extremely difficult. A deep-rooted conclusion that underlies this entire study is that to objectively evaluate the sulfate issue additional work to enhance sampling and analysis capabilities is urgently needed.

The results of this study are best summarized by first addressing seven specific questions raised by the Environmental Protection Agency at the initiation of this program, then by assessing the specific effects of combustion modification procedures.

A. What are the primary acid aerosols being emitted?

The great majority of emissions which may lead to acid aerosols are sulfur compounds, sulfuric acid, SO_3, and sulfates although it is recognized that not all sulfates are acidic. Nitrates have not been observed nor are they expected in stack particles, but a small amount of nitrate may be formed in the near plume. The sparse information available on HCl or chlorides is in general agreement with basic thermodynamic considerations that the chlorine in fuel will be emitted primarily as gaseous HCl from the stack. Evidence indicates that total primary sulfates (i.e., those observed within the first half-mile) can be as high as 20 percent of total sulfur emissions or as low as 2 percent.

A significant fraction of the primary sulfates consist of H_2SO_4, based on field measurements. Equilibrium considerations for coal-firing indicate that the remaining sulfates are distributed among $CaSO_4$, $MgSO_4$, and $ZnSO_4$. Bisulfates are not formed. Specific sulfates are not identified but field data suggest Na_2SO_4, K_2SO_4 and $FeSO_4$ are also formed. For oil-firing, $NiSO_4$ and Na_2SO_4 are major components of the sulfated fly ash.

B. What is the effect of fuel composition?

A significant effect of fuel composition on sulfate emissions should be expected. Laboratory and field data indicate that as fuel sulfur level is decreased, the fractional conversion to H_2SO_4 is increased although total emission decreases. Moreover, based on fundamental data on catalytic activity of various metals, it is expected that the effect on total primary sulfate emissions of trace metal speciation in fuels will be large.

There are three effects related to trace metal composition; these are catalysis, sulfate capture, and size distribution. V, Mn, Fe, Ni, and other transition metals have been shown to catalyze the oxidation of SO_2 to SO_3, thus potentially increasing total sulfate emissions, The presence of other species, i.e., Na, Ca, Mg, etc., affects the distribution of sulfate in the fly ash.

In addition to affecting total $SO_4^=$ formation, fuel composition is expected to have a large effect on emitted particle size distribution. Volatile metals condense to form very small nuclei, giving a high surface to volume ratio and therefore accelerating catalysis. It should be noted

that volatile elements may not always form the most volatile combustion products. Furthermore, small particles may increase the $H_2SO_4/SO_4^{=}$ ratio, especially if large particles are removed.

Field data to support evidence for V, Ni, etc., catalysis of SO_2 oxidation in fly ash are lacking. There is a scarcity of field data on speciation of sulfate in fly ash, although a correlation exists between the Na, Ca, Fe, and Mg content of fly ash and sulfate content.

The effects of fuel composition and the use of additives is summarized in greater detail on page 7.

C. Are acid aerosols the result of combustion in general or are they the by-product of a limited class of equipment?

In general, the combustion of any sulfur-containing fuel will produce some primary acid aerosol but there doesn't appear to be, and one would not expect, a strong relationship between the type of equipment and acid aerosol formation. However, to the extent that the equipment influences the formation of fine particles (cyclone and pulverized firing of coal, for instance, emit finer particles than stoker firing) there may be an effect on acid aerosol formation resulting from catalytic reactions.

D. What are the mechanisms of acid aerosol formation and destruction?

Primary acid aerosols are formed by at least the following mechanisms:

(1) High temperature homogeneous SO_2 oxidation

(2) Dry gas-solid reactions converting SO_2 to $SO_4^{=}$.

There is no reason to expect solution chemistry kinetics to influence primary sulfate emissions.

In general, the acid species are not destroyed once formed. Some may be removed from the gas stream by adsorption on particles where they may be in part neutralized and some particles are removed by precipitators, for instance, but such processes are not completely effective.

E. Are sulfur compounds adsorbed by boiler deposits and subsequently released during soot blowing?

Yes, there is positive evidence for the adsorption of sulfur oxides, metal oxides, and chlorides by deposits and subsequent conversion of these compounds to sulfates. Soot blowing removes some such material and probably overloads the precipitator and results in emission of sulfates, vanadates,

and other species. Although field data are lacking in this regard, it is probable that such deposits catalyze SO_2 oxidation to some extent but carbon deposits probably do not contribute to the catalysis at deposit temperatures.

F. What percentage of the total acid aerosol is formed in the flame zone, in the convective passes, in the stack, in the plume, and in the atmosphere?

Available data does not allow one to quantify this. The investigators best estimate is:

Flame zone	10 percent of total S converted
Convective pass.	10 percent of total S converted
Stack.	0 percent of total S converted
Near plume	1 percent of total S converted
Atmosphere	80 percent of total S converted

These estimates of conversion refer to that part of the sulfur in the fuel contributing to aerosol emissions and do not include the sulfur retained in the ash, slag, etc. That is, it is estimated that of the sulfur in the stack effluent, up to 10 percent might be converted to acid aerosol constituents in the combustion zone. Similarly, another 10 percent may have been converted in the convective passes so that up to 20 percent of the sulfur in the effluent may contribute to primary acid aerosol. Probably 80 percent or more of the sulfur emitted in the stack gases will be SO_2, which will be further oxidized in the atmosphere at some later time.

G. What is the effect of CM on primary acid aerosol?

There is no evidence to indicate that CM (combustion modification) will, in general, be an effective procedure for acid aerosol abatement although low excess air firing, where practical, may be an exception. It might be expected, however, that standard CM techniques for NO_x abatement may adversely affect the quantity, speciation, and particle size of acid aerosol exhaust emissions through increases in the formation of fine particulates and carbonaceous materials. This is covered in more detail in the following section.

In brief, no definitive quantitative answers to the above questions exist at this time. There are some fundamental data and some field data that allow the conclusion to be drawn that acid aerosol emissions are a function of fuel composition and combustion conditions. However, quantitive interpretation is difficult because of three areas of uncertainty:

- lack of detailed fuel analyses
- undefined combusiton conditions
- uncertainty in particulate emission sampling and analysis.

SPECIFIC EFFECTS OF COMBUSTION MODIFICATION ON ACID AEROSOL

There are very little pilot or field test data which directly demonstrate that a particular combustion modification employed to reduce NO and NO_2 will have an effect, good or bad, on primary acid aerosol. The weight of the evidence is that anything which tends to reduce super-equilibrium oxygen atom concentration in the flame zone will tend to reduce SO_3. On the other hand if the production of particulate, especially very small particles, is increased then the production of acid and sulfate solids might be expected to increase through heterogeneous processes. In the temperature range of the convective zone SO_3 might be the result of heterogeneous oxidation of SO_2 on metallic or metal-containing particles and deposits, whereas at low temperatures in the stack and near plume it might occur predominantly on carbonaceous particles. At this time, conclusions regarding the effect of a particular combustion modification on specific equipment must be highly speculative.

The one case where the data clearly show that acid aerosol can be reduced is operation with low excess air. The reduction in NO and NO_2 is accompanied by reduced SO_3 formation in the flame and the reduced availability of oxygen pertains throughout the system. This implies extremely good combustion control and a level of excess air below that generally attainable in coal combustion at the present time. It must be kept in mind that in low excess air combustion there is the risk of increased particulate formation which might lead to an increase in catalytic oxidation of SO_2. However, from the standpoint of controlling both NO/NO_2 production and acid aerosol formation, this would appear to be the most fruitful approach at the present time.

In the case of staged combustion, there are essentially no data pertaining to total primary acid aerosol emissions for full-scale systems under staged conditions. During the first stage of combustion where conditions are fuel rich, SO_3 formation may be reduced essentially to zero. However

it has been demonstrated that it is possible to form more SO_3 when air is added to complete combustion than would have been formed by the same level of air in a single combustion step. It seems quite likely that metal speciation and size distribution in particulates and deposits will be different under staged conditions and vary from one type of staged combustion to another. Although changes in particulate and deposits are expected to have an effect, so little is known that it is difficult to even speculate what the effects might be except that in general an increase in particulates would be expected to lead to increased total sulfate at any given SO_2 level.

For flue gas recirculation there are essentially no data on sulfate emissions from practical systems. The effect of flue gas recirculation is to lower combustion temperature and one study reported a correlation between flame length and SO_3 production in the combustion zone. But the evidence on particulate formation was quite contradictory. Certainly the time-temperature history of material moving through the system will vary with flue gas recirculation and where and how, and to what extent, the recirculation is applied. Little is known about the effects of bringing previously formed SO_2 or particulates into the system early in the combustion process. One might speculate, also, that lowered temperatures will reduce metal volatilization with a subsequent reduction of very small, high metal content, catalytically active particles in the convection passes. This would be expected to reduce the oxidation of SO_2 to SO_3 in this regime. However, there is no data to substantiate such speculations.

Reburning, and particularly the use of ammonia, is another case where there is essentially no data pertinent to this study. Certainly any ammonium sulfate which might be formed will remain dissociated till low temperatures are reached. As will be discussed in the section on Early Plume Reactions, an increase in sulfate formation would be expected if there is a significant increase in pH.

EFFECT OF FUEL COMPOSITION

The nature of the fuel obviously will have an effect on acid aerosols and the increased propensity for sulfates with increasing fuel sulfur hardly needs to be stated. However, there are essentially no field data that indicates low concentration of trace species have a major effect on primary acid aerosols. Although there are apparent correlations between sulfates and certain metals in fly ash and deposits, it is difficult to state unequivocally that the sulfate resulted from the presence of the metals.

Based on fundamental data and experiments to show catalytic activity of fly ash constituents, it is to be expected that trace metals will have a large effect on sulfate emissions, but existing data from practical combustion systems do not allow trace metal effects to be quantified.

In the case of coal particulates, the major species are silicon and aluminum oxides which probably are inert. However, Fe, Na, K, and Ca oxides are also generally present in lesser quantities and these have been shown to have some catalytic activity for SO_2 oxidation under at least some conditions. Different metal distributions among coals in conjunction with different combustion modifications probably lead to variations in the distribution and speciation of these metals in the particulate, therefore variation in oxidation of SO_2 is to be expected.

In general, the sulfate in coal fly ash is less than 2 percent although occasional higher values are observed. It appears that the sulfur is largely on the surface and present as $SO_4^=$ rather than adsorbed SO_3. Studies of the particulate surfaces suggest the sulfate may be present largely as iron and/or calcium sulfates. Iron is a major constituent of fly ash along with sodium and lesser amounts of calcium. Furthermore, since studies of deposit chemistry have shown that ferric oxide can be an effective catalyst for SO_2 oxidation and sulfate formation, the fragmentary evidence available suggests iron and its eventual distribution and speciation may be an important factor in the effects of particulates on primary acid aerosol emissions.

Particulates from oil combustion, particularly high ash residuals, are in many respects similar to those from coal except that they are much more likely to be high in carbonaceous materials and the total amount of particulate will be smaller. The major difference is the presence of

vanadium and nickel oxides, which do not generally appear in coal particulates, and are known active catalytic materials for SO_2 oxidation. This occurence correlates with the generally higher sulfate levels found in particulate from oil combustion.

Fuel composition in conjunction with combustion conditions is expected to have a large effect on particle-size distribution. In general, the evidence suggests that the more volatile metals will be concentrated in the smaller particles and maximum flame temperature will effect the amount and species volatilized. These small particles with their relatively large surface area can be particularly effective catalysts for SO_2 oxidation and sulfate formation.

In addition to catalytic effects, differences in size distribution and speciation are also expected to effect the sorptive properties of fly ash and depostis for SO_2 and SO_3 which can effect the eventual formation of sulfates by noncatalytic mechanisms. However, at present it is virtually impossible to quantify these effects.

Another aspect of fuel composition is the use of additives, which in effect change the metal content of the fuel. Generally, materials are used containing either Mg or Zn, both of which readily form sulfates. The particles thus formed may be removed by precipitators thereby reducing the potential for acid aerosol emission. Various forms of the additive have been shown to be effective, i.e., metals, metal oxides, minerals, or organometallic compounds. The use of such materials does not reduce primary acid aerosol formed, as defined in this report, but does reduce the acid emission, that is SO_3/H_2SO_4, by forming $ZnSO_4$ or $MgSO_4$. If removing SO_3 from the flue gas is the goal, then inert materials such as SiO_2 have been shown to be effective. These probably act by forming high surface area particles, like cenospheres, which physically adsorb SO_3 and result in particles with sulfuric acid adsorbed on the surface. Overall this may not be as beneficial as forming magnesium or zinc sulfates.

RECOMMENDATIONS

Perhaps the most significant finding of this study is the recognition that clear, quantitative correlations between combustion modifications and the problem of acid aerosols do not exist. It is not even clear to what extent primary acid aerosols are a problem. Basic and field test data indicate the fraction of sulfur emitted as acid is generally small but the uncertainties are large. There is no evidence that nitrates or chlorides are major contributors to primary acid aerosols. Therefore, to the extent that there is a problem, it is a problem of formation of sulfuric acid and sulfates. In light of this general conclusion, the following recommendations are made. It is not our intent to define specific research tasks but rather to indicate directions for further research which should prove fruitful.

- Further research, at least in the form of field sampling/analysis of particulate emissions from CM-operated boiler facilities, is needed to define the severity of the acid aerosol problem.

- Sampling and analysis procedures need to be improved. Much of the uncertainty in this report results from the fact that such data as exists is ambiguous.

- In addition to sulfuric acid (SO_3) in the gas phase much more attention needs to be given to speciation in solids in order to determine how and to what extent solid sulfates contribute to the primary acid aerosol problem. Speciation as a function of particle size distribution is a particularly vexing problem but, from the standpoint of acid aerosol effects, it is an important problem area.

- The ratio of primary to secondary sulfate is not well established. The evidence points to a small value of this ratio but further work is needed to precisely establish its value and hence determine the extent to which primary acid aerosols are a problem.

- Overall, there is little data on the SO_3/SO_2 ratio with and without combustion modification for a given combustion system. In many situations the available data suggests that CM is not expected to have a major effect on primary acid aerosol but there is almost no documentation for practical systems. Such data is needed but it is recognized that the experiments will have to be very carefully defined in terms of choice of combustion systems, combustion modifications, fuels, etc., in order to provide useful data at reasonable cost.

- Laboratory studies on the formation and destruction of SO_3 and sulfates in combustion processes, with and without combustion modification, are needed.

- From the standpoint of mechanisms considerably more work is needed on heterogeneous SO_2 oxidation. The evidence indicates such mechanisms are a major source of primary acid aerosol but very little is known about their details. The potential for carbon particles to act as SO_2 oxidation catalyst has been demonstrated but it remains to be shown how much such a mechanism might contribute to either or both primary or secondary acid aerosol.

- As a corollary to the above, more information on the formation of particulates, especially fine, suspended particles, is needed as a function of combustion modification conditions and fuel quality as they relate to speciation and particle size distributions.

- Some further work on homogeneous mechanisms of SO_2 oxidation is desirable. Reactions such as $SO_2 + OH$ under fuel rich conditions, as would apply to staged combustion, and the reaction of SO_2 with vaporized NaCl to form Na_2SO_4 are examples.

- Stack-gas cleanup procedures can influence the rate of SO_2 oxidation in the early plume. This is especially important for those procedures which may alter the pH of the plume. Particular attention should be given to those conditions where excess base, e.g., NH_3, might be emitted.

- The question of flue-gas desulfurization systems should perhaps be considered separately from combustion modification. That is, what is the potential for FGD to release or remove acid aerosol regardless of combustion modification?

SECTION I

INTRODUCTION, OBJECTIVE, AND SCOPE

In recent years there has been increasing evidence that sulfates in the atmosphere may be of more concern as a health and environmental hazard than sulfur dioxide. Part of this concern is reflected in the fact that SO_2 levels in the atmosphere have been on the decline, while sulfate levels remain unchanged (Altshuller, 1976) (Squires, 1975). For these reasons this study was undertaken for the Combustion Research Branch of the Environmental Protection Agency. The overall purpose of this study was to survey, compile, and evaluate data on the generation and emission of acid aerosols formed within stationary combustion devices. The basic questions being addressed in this study are:

- What is the effect of combustion modification (CM) on the formation and emission of primary acid aerosols in stationary source combustion?
- What is the potential for CM to control the formation and emission of primary acid aerosol?
- What are the research and development gaps requiring further effort to answer properly the first two questions?

It generally is considered that the acidic sulfates, such as sulfuric acid and ferric sulfate, are of greater concern as health hazards than the natural or basic sulfates. When speaking of "acid aerosols" in this study the term is used in the broadest sense. Acid aerosols in this study refer to any and all liquid and solid particles containing sulfates, nitrates, chlorides, and fluorides, as well as sulfates and nitrites of sodium, calcium, ammonia, etc., and all are of equal concern to this study and are included under the umbrella of "acid aerosols". The study is concerned not only with total acid aerosol emission but also their speciation and size

distribution. It is important to be so all inclusive in terminology at this point in time (1) because of limitations to specific relationships between health effects and specific sulfates, nitrates, etc., and (2) because of a lack of specificity in current chemical characterization of particulate emissions.

Although an attempt has been made in this study to examine the production and emission of sulfates, nitrates, chlorides, and fluorides in combustion, by far the greatest emphasis is on the sulfates. This comes about quite naturally due to the instability of nitrates under combustion temperatures and the dearth of information on chlorides and fluorides in combustion processes. As regards the formation and emission of sulfates as primary aerosols, we have arbitrarily defined as primary aerosol any particulate emitted from the stack and/or produced within the first half-mile in the plume. In essence, then, any particulate resulting from rapid reaction (an unanticipated phenomena) on entering the plume or from condensation, nucleation, or agglomeration processes as gases and particulate are mixed and diluted with the ambient environment are considered primary aerosol. The need for this definition of primary aerosol is apparent since the chemistry of SO_2 oxidation in plumes is specifically avoided in this study. The slow, secondary oxidation of SO_2 in plumes is covered by numerous other studies. The reader is referred to a recent analysis of SO_2 oxidation in plumes carried out for EPA (Levy, 1976) for this aspect of the acid aerosol problem.

One final comment by way of introduction: sulfates, nitrates, acid precipitation products and the like observed in the ambient are generally referred to as "second generation pollutants", i.e., pollutants formed by secondary reaction of SO_2 and NO_2 as referred to above. These reactions are well recognized, and it is important in the context of the study at hand to recognize at the outset that the emission of primary sulfates, nitrates, etc., is small relative to other pollutants or relative to second generation acid aerosols. To repeat, the objective of this study is to evaluate the significance of primary acid aerosols as combustion-generated pollutants and to consider how these may be effected by fuel and combustion modifications.

Due to the lack of definitive field test data, it has been necessary to approach the problem from a fundamental point of view and make appropriate speculative extrapolations. First considered are equilibria and its implications for speciation, then the fundamental mechanisms of acid aerosol formation are reviewed. Available field data have been collected and interpreted in light of these principals and research gaps identified.

SECTION II

REGIMES OF FORMATION

In evaluating the effect of various combustion modifications on acid aerosol formation, it must be kept in mind that various contributors to the aerosol may be formed in different parts of the total system under quite different conditions. For this reason, we have divided the combustion system into regimes starting with the flame or combustion region and proceeding through the system to the near plume. In the combustion zone, temperatures are maximum and most of the pertinent reactions are expected to be homogeneous gas phase and fairly rapid. A rapid temperature quench may allow a frozen equilibrium to be attained among sulfur species. Perhaps as much as half the primary acid could be formed in this region.

A second regime, at somewhat lower or intermediate temperatures, is the region of the convective passes. Here the rapid decrease in temperature slows many of the homogeneous reactions to the point that they contribute little to the formation of acids or their precursors. In this and following regions the system is not at thermodynamic equilibrium. In this regime, heterogeneous reactions may be most important. Oxidation of SO_2, for instance, may occur by adsorption and reaction on suspended particulate matter or by adsorption and reaction on heat transfer surfaces or the deposits building up on those surfaces. Since the deposits remain in the boiler environment for a long time compared to a quantity of gas passing through the region, there is time for considerable chemistry to occur within the deposit. When such deposits become dislodged they carry reaction products into the atmosphere. Most of the rest of the primary acid aerosol material is probably formed in this region.

The third regime is the region of the stack where the temperature has dropped significantly. As a practical matter, temperatures are kept as low as possible to maximize economy and high enough that moisture and acid do not condense. Due to the lowered temperature, not much chemistry leading to acid formation occurs here although particulates may be agglomerating and some gas-solid reactions could occur.

The final regime considered in this report is the near plume at close to ambient temperature. Little acid formation is expected in this region although moisture will be condensing and picking up already formed acid. In the case where something changes the plume pH significantly, i.e., NH_3 injection, more reaction may occur.

For the most part, there is insufficient information to quantify or even rigorously define the chemistry occurring in these various regimes. However, it is possible for combustion modification to influence the reactions in all regimes since what occurs in the combustion zone can modify reaction conditions in all succeeding regimes. The data shown in Figure 1 denotes, in a qualitative manner, which reaction mechanisms are likely to be important in each of the temperature regimes discussed above. The importance of high temperature homogeneous reactions is shown in Curve A; that of gas-solid reactions in Curves B and B'; that of reactions involving solution chemistry in Curve C; and the importance of photochemical reactions in Curve D. The area under these curves represents the possible total sulfates formed by the pertinent reaction. The role of gas-solid reactions is shown two ways, B and B', since the extent and temperature range is uncertain. It is clear that solution chemistry (Curve C) and photochemical mechanisms (Curve D) are not likely to be applicable to primary acid sulfate formation, although they are important as far as secondary sulfates are concerned.

In the following sections of this report possible reactions in the first four temperature regimes are discussed, relating field test data to them where such data exist. Equilibrium considerations at temperatures characteristic of the first two regimes are discussed first. At lower temperature frozen equilibrium is assumed. The following section considers basic mechanisms. High temperature homogeneous reactions (the first regime)

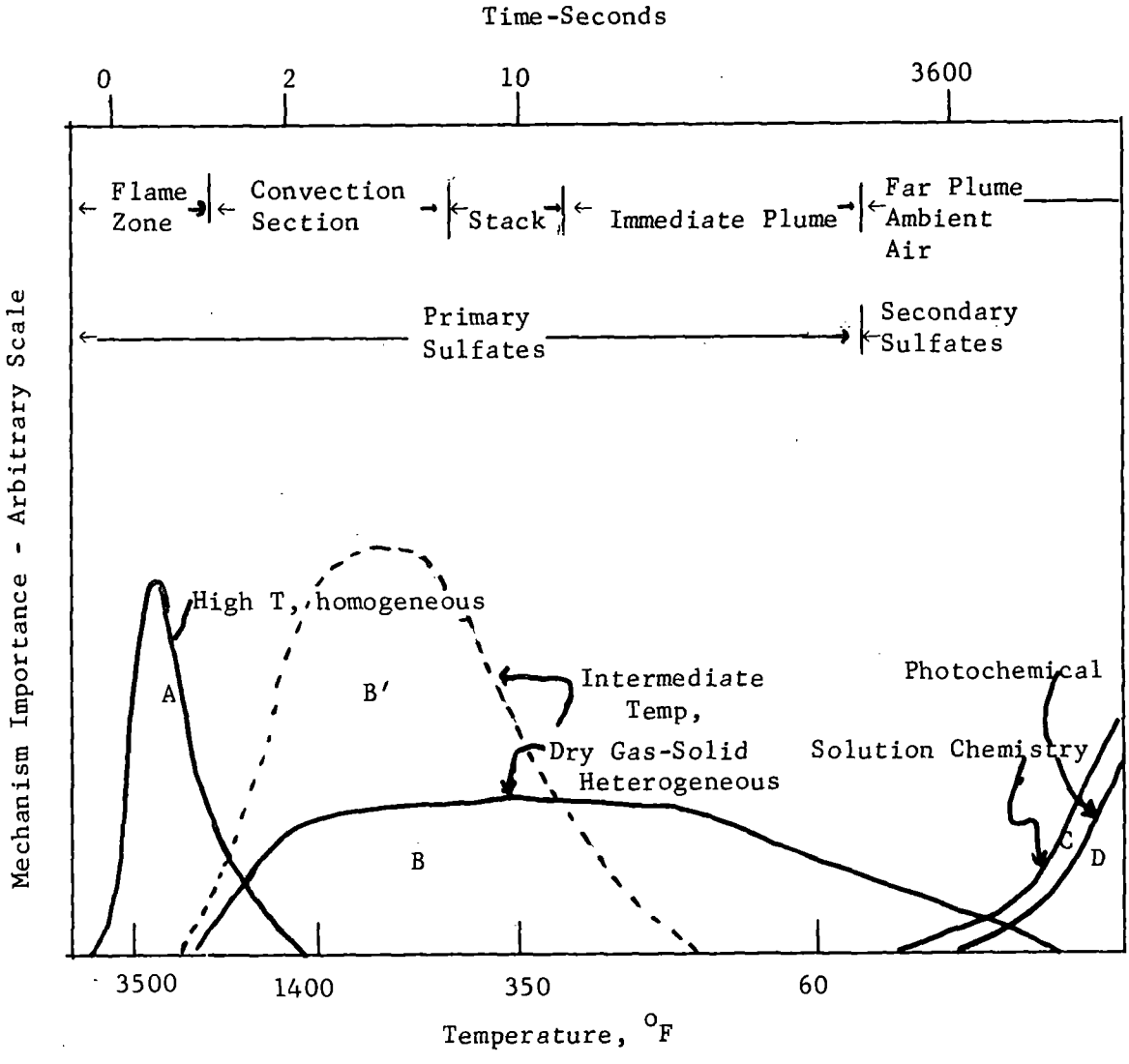

Figure 1. Regimes of Mechanism Importance

are considered first followed by heterogeneous reactions which probably occur at somewhat lower temperatures characteristic of the second regime. Possible reactions in the near plume (the fourth regime) are considered last.

The next section of the report summarizes findings from pilot and field studies. This data cannot be directly tied to the regimes, as defined, but where possible inferences are drawn based on basic data developed in the various regimes.

The next section discusses the possible influence of combustion modification on flue gas desulfurization processes. Although such processes are not a primary subject of this report, they can contribute to acid aerosol emissions and therefore some discussion is warranted.

SECTION III

SAMPLING AND ANALYSIS

Before examining the available field sulfate data some discussion of sampling and analytical practices is in order. Possibly the most serious gap in attacking this problem of acid aerosols lies in the data itself and this deficiency permeates this entire study. It has generally been recognized that sulfate particulate analyses are strongly affected by sampling procedures, i.e., the effect of substrate, SO_2, humidity, etc. As a consequence, most sulfate (and similarly nitrate) particulate data reported must be considered suspect to some degree. The various analytical procedures have recently been critically reviewed by Tanner and Newman (1976).

Throughout the course of this study difficulty was encountered not only because of a general lack of data on primary acid aerosol emissions but also because of uncertainty arising in the methods of analysis and reporting data. It is not always clear whether sulfate refers just to the SO_3 (i.e., H_2SO_4) from flue gas or $SO_4^=$ in the solids or, as in a few cases, the sum of the two. Total $SO_4^=$ in a particle is not necessarily indicative of the acidity of the particle. However, as mentioned at the beginning of this report we are including all sulfate in drops and particles under the term acid aerosol. Speciation of the sulfate is difficult to determine and almost never defined. One is left to infer, for instance, that if a particle is high in sodium and magnesium and also high in sulfate, then the likely species present are sodium sulfate and magnesium sulfate.

Accurate specification of acid aerosol speciation and concentrations in combustion products is critically dependent on a number of parameters that can involve both combustion system variables and sampling and analysis methodology. One commonly used procedure is to attempt to achieve a mass balance between the input rates of components of the fuel/ air mixture and apparent output rates of the individual components as a means for specifying

sampling and analysis efficiency. Often, the inherent range of the input variables is not recognized explicity, and erroneous conclusions concerning the significance of the sampling and analysis results can easily be made. For example, the expected output rate of sulfur species is determined not only by the input rate of sulfur in the fuel but by the detailed (C, H, N, S, O, ash, H_2O) composition of the fuel. The net range expected in the output rate of sulfur species is thus a composite of the effects of the uncertainties of 6-7 separate analyses plus the variations due to changes in firing rate. This aspect of the overall problem is compounded in a coal-fired system by the inherently heterogeneous nature of the fuel, and the absence of continuous representative sampling of the fuel.

Sources of error also exist in the commonly used sampling methods. Ideally, the sampling method should achieve separation and stabilization of each of the species of interest, while maintaining a consistently high level of collection efficiency. Acid aerosols, and their precursors, are characteristically reactive species. Hence care must be taken to avoid contact of the sample with surfaces that may react in such a way as to obscure differences between the identities of the species of interest. For example, the use of unlined metal probes can result in the formation of solid sulfates because of wall reactions with sulfuric acid in the flue gas. Glass fiber filter media commonly used in sampling trains frequently contains appreciable amounts of basic substances. These substances can react with acidic components, especially SO_2, of the flue gas. In stack gas sampling, the amount of sulfur trapped by this type of reaction is probably insignificant with respect to the total solid sulfate trapped on the filter. However, removal of sulfuric acid from the gas stream by this type of reaction can interfere with accurate collection of sulfuric acid at a later point in the sampling train. In the case of sampling of the plume, or even the near plume, filter interactions can be a major source of error. Under plume conditions, the absorption of SO_2 by the basic filter components can lead to apparently high levels of sulfate in the trapped particulate. Impingers used in stack gas sampling trains also can be source of error in specification of flue gas sulfate. Absorption of SO_2 in impinger solutions and subsequent oxidation of the resulting sulfite to sulfate during sampling

and storage prior to analysis has been demonstrated and will, of course, lead to erroneously high acid values.

These chemical sources of error inherent in the sampling methodology have been characterized, and alternative procedures have been recommended (Hillenbrand, 1972) (Coutant, 1976). In brief, these recommendations include the use of fused-silica or Vycor-lined probes, use of high purity fused-silica filters, and the use of the Goksøyr-Ross procedure for sulfuric acid. In spite of the errors involved, however, the Method 6 and Method 8 procedures continue to be used on a wide basis.

SECTION IV

EQUILIBRIUM CONSIDERATIONS

On investigating reactions and mechanisms which can lead to oxides of sulfur and those of nitrogen, and thence to acid aerosols, it appears that the same nonequilibrium factors, particularly superequilibrium oxygen atom concentrations, need to be considered for both groups of compounds in the high temperature, flame region. The reaction products, as determined by many investigators of practical systems, are indicative of a chemical system which has not reached thermodynamic equilibrium. That is, the observed species concentrations are characteristic of the system at equilibrium at a temperature different from that measured. In industrial combustion systems this generally means that the product distribution of pollutants is characteristic of the systems at relatively high temperatures, e.g., at the fire box exit, even though the measurements were made at relatively low temperatures, e.g., in the stack. Thus, the composition is kinetically controlled. This is most striking in the case of SO_2/SO_3 where SO_3 is generally observed to be only a few percent of SO_2 in the flue gas. At high temperatures most of the sulfur would be in the form of SO_2 at equilibrium. But as the equilibrium system cools SO_3 becomes the predominant gaseous sulfur compound. The predicted equilibrium distribution between SO_2 and SO_3, and considering only these species, is shown in Table 1 for various levels of excess air at a number of temperatures (Schwartz and Dietz, 1975). That the predicted result is not observed means simply that as the temperature drops the rate of SO_2 oxidation slows and the gases pass through the system before they reach equilibrium, i.e., the chemistry is kinetically controlled. This is a gross oversimplification of the many factors involved, of course.

TABLE 1. THEORETICAL CONVERSION OF SO_2 TO SO_3 IN FLUE GASES AT DIFFERENT TEMPERATURES AND EXCESS AIR LEVELS

Temperature		$\frac{P_{SO_3}}{P_{SO_2} + P_{SO_3}} \times 100$ for excess air			
°F	°C	10%	5%	1%	0.1%
800	427	97.1	96.1	91.7	77.9
980	527	81.2	75.8	58.7	31.1
1460	627	47.0	39.1	22.6	8.5
1340	727	20.0	15.3	7.6	2.55
1520	827	8.2	6.1	2.87	0.93
1700	927	3.7	2.7	1.25	0.40
1880	1027	1.34	1.33	0.61	0.20
2060	1127	1.01	0.73	0.33	0.11
2240	1227	0.60	0.43	0.20	0.06

P = partial pressure of indicated species.

Consideration of the thermodynamic equilibrium chemistry can be instructive since it describes the direction the reactions are moving. Figures 2 and 3 are the result of calculations based on combustion of coal of an average composition (Ruch, 1974), containing 3.2% sulfur. The elemental distribution is shown in Table 2. The formation of both gaseous and condensed species are included in the calculations. They are based on burning with 2% and 10% excess air. The figures show the distribution of sulfur among a variety of compounds. The various compounds considered in this analysis are given in Table 3. The calculated values for each computation are given in the Appendix. At high temperatures the sulfur appears almost entirely as SO_2. As the temperature decreases, the system at equilibrium, SO_2 is converted to SO_3 and the two become almost equal at about 800 K (980 F). However, the formation of solid sulfates also increases and as the temperature continues to decrease the solids become the predominant sulfur species and sulfur in the gas phase falls to very low values. It will be noted that there is little difference, at equilibrium, between 2% and 10% excess air. That is, almost any excess oxygen determines the main direction of the reactions from the standpoint of equilibrium. There are small differences, of course, as in the SO_2/SO_3 ratio.

Various gaseous species may contribute to acid aerosol formation, particularly sulfates, and these are indicated in Figures 4 and 5, again for the same coal composition with 10% and 2% excess combustion air. These are indicative of the expected equilibrium flue gas compositions. It will be noted that sulfur compounds dominate the situation from the standpoint of acid or acid precursors until the temperature drops below about 700 K (801 F). Below this HCl becomes the predominant species because at equilibrium the formation of solid sulfates removes almost all sulfur from the gas stream. That is, at low temperature equilibrium, one would expect most of the sulfur in the system in the solid phase (ash) and most of the chlorine in the gas phase.

TABLE 2. MEAN ANALYTICAL VALUES FOR CONSTITUENTS IN 101 DIFFERENT COALS ON WHOLE-COAL BASIS

Constituent	Mean	Standard Deviation	Minimum	Maximum
As	14.02 ppm	17.70	0.50	93.00
B	102.21 ppm	54.65	5.00	224.00
Be	1.61 ppm	0.82	0.20	4.00
Br	15.42 ppm	5.92	4.00	52.00
Cd	2.52 ppm	7.60	0.10	65.00
Co	.57	7.26	1.00	43.00
Cr	13.75 ppm	7.26	4.00	54.00
Cu	15.16 ppm	8.16	5.00	61.00
F	60.94 ppm	20.99	25.00	143.00
Ga	3.12 ppm	1.06	1.10	7.50
Ge	6.59 ppm	6.71	1.00	43.00
Hg	0.20 ppm	0.20	0.02	1.60
Mn	49.40 ppm	40.15	6.00	181.00
Mo	7.54 ppm	5.96	1.00	30.00
Ni	21.07 ppm	12.35	3.00	80.00
P	71.10 ppm	72.81	5.00	400.00
Pb	34.78 ppm	43.69	4.00	218.00
Sb	1.26 ppm	1.32	0.20	8.90
Se	2.08 ppm	1.10	0.45	7.70
Sn	4.79 ppm	6.15	1.00	51.00
V	32.71 ppm	12.03	11.00	78.00
Zn	272.29 ppm	694.23	6.00	5,350.00
Zr	72.46 ppm	57.78	8.00	133.00
Al	1.29%	0.45	0.43	3.04
Ca	0.77%	0.55	0.05	2.67
Cl	0.14%	0.14	0.01	0.54
Fe	1.92%	0.79	0.34	4.32
K	0.16%	0.06	0.02	0.43
Mg	0.05%	0.04	0.01	0.25
Na	0.05%	0.04	0.00	0.20
Si	2.49%	0.80	0.58	6.09
Ti	0.07%	0.02	0.02	0.15
Org. S[a]	1.41%	0.65	0.31	3.09
Pyr. S	1.76%	0.86	0.06	3.78
Sul. S	0.10%	0.19	0.01	1.06
Tot. S	3.27%	1.35	0.42	6.47
SXRF	2.91%	1.24	0.54	5.40
Ash	11.44%	2.89	2.20	25.80
Btu	21,748.91	464.50	11,562.00	14,362.00
C	70.28%	3.87	55.23	80.14
H	4.95%	0.31	4.03	5.79
N	1.30%	0.22	0.78	1.84
O	8.68%	2.44	4.15	16.03

Footnote appear on the following page

(a) Abbreviations other than standard chemical symbols: organic sulfur (Pyr. S), sulfate sulfur (Sul. S), total sulfur (Tot. S), sulfur by X-ray fluorescence (SXRF), air-dry loss (ADL), moisture (Mois.), volatile matter (Vol.), fixed carbon (Fix. C), high-temperature (HTA), low-temperature ash (LTA).

TABLE 3. PRODUCT SPECIES CONSIDERED IN COAL COMBUSTION EQUILIBRIUM CALCULATIONS

AlF_3	MgO	ZnO
$AlCl_3$	$Mg(NO_3)_2$	$Zn(NO_3)_2$
Al_2SO_4	MgF_2	ZnF_2
Al_2O_3	$MgCl_2$	$ZnCl_2$
$Al(NO_3)_3$	$MgSO_4$	$ZnCO_3$
B_2O_3	Na_2O	$ZnSO_4$
BF_3	Na_2CO_3	S_2
BCl_3	$NaNO_2$	SO_2
BeO	$NaNO_3$	SO_3
$Be(NO_3)_2$	NaF	H_2SO_3
BeF_2	$NaCl$	H_2SO_4
$BeCl_2$	Na_2SO_3	CO
$BeSO_4$	Na_2SO_4	CO_2
F_2	$NaHSO_4$	H_2O
HF	$NaOH$	H_2
$CaCO_3$	PCl_3	CH_4
CaO	PCl_5	COS
$Ca(OH)_2$	$POCl_3$	O_2
$Ca(NO_2)_2$	HPO_3	N_2
$Ca(NO_3)_2$	H_3PO_4	NO
CaF_2	P_4O_{10}	NO_2
$CaCl_2$	$Pb(NO_3)_2$	N_2O_4
$CaSO_4$	PbO	N_2O
Cl_2	$PbCl_2$	N_2O_5
HCl	$PbSO_4$	HNO_3
Fe_2O_3	SiO_2	$NOCl$
$Fe(NO_3)_2$	VO	
$FeCl_2$	V_2O_4	
$FeCl_3$	V_2O_5	
$FeSO_4$	VCl	

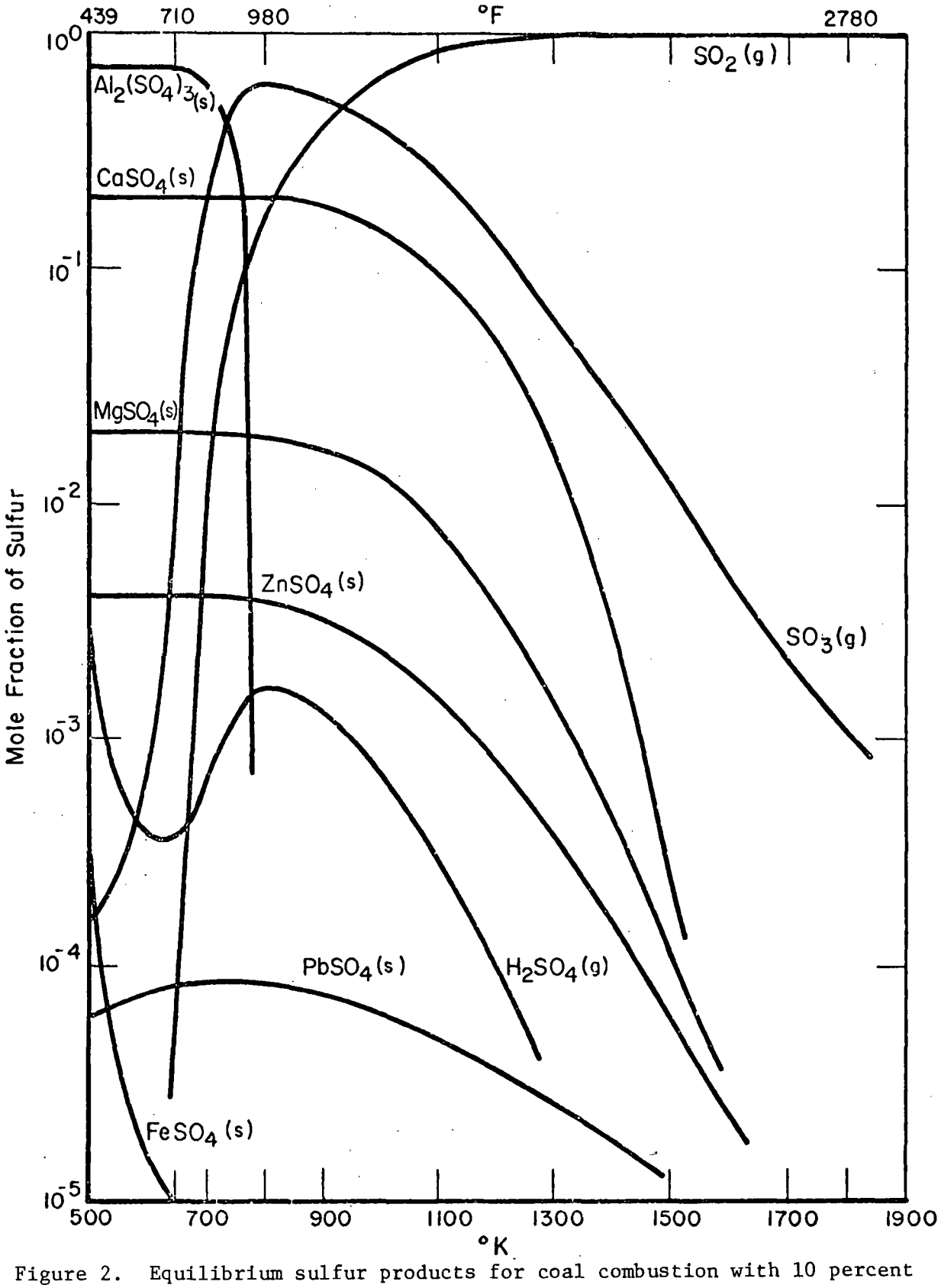

Figure 2. Equilibrium sulfur products for coal combustion with 10 percent excess air, 3.27 percent sulfur

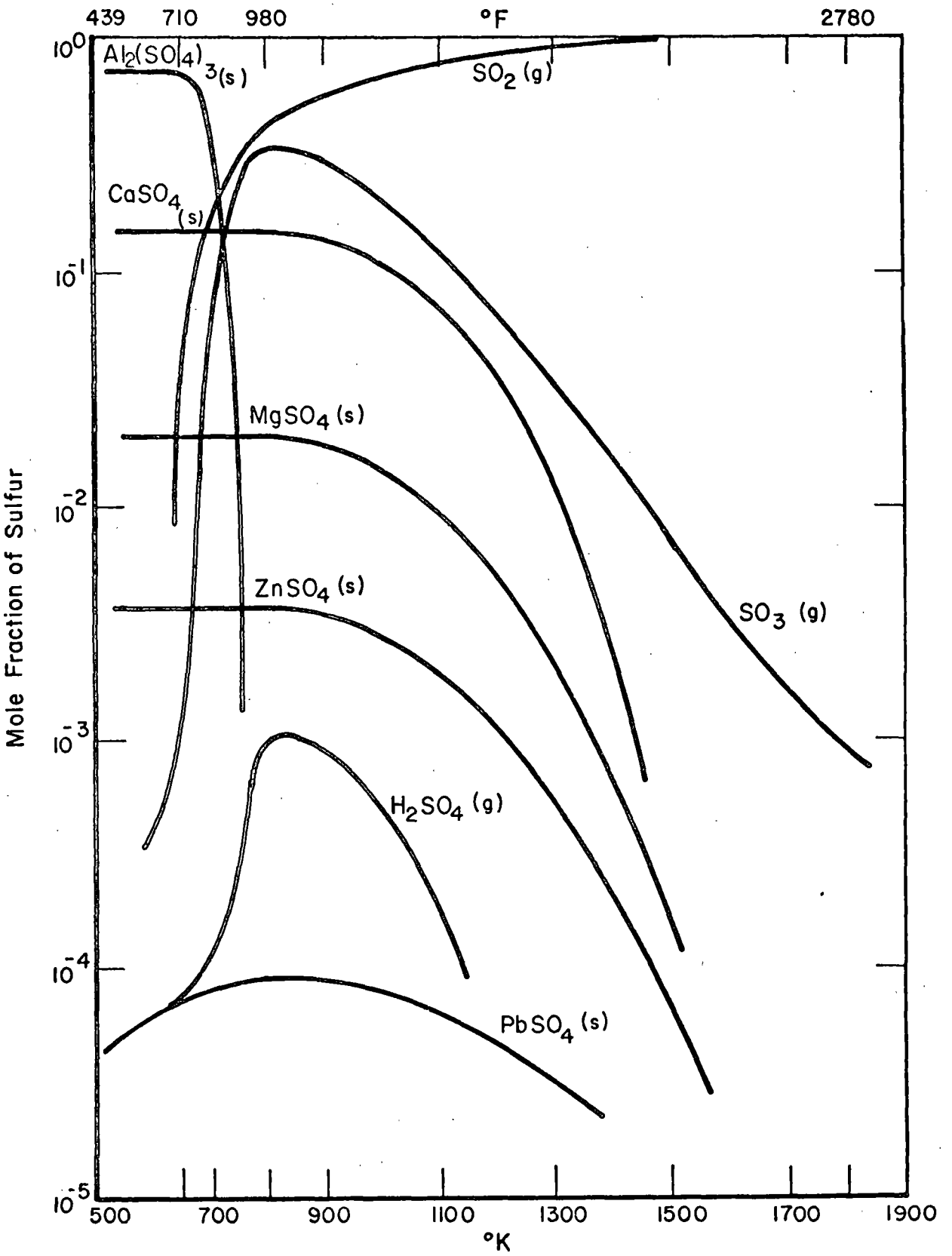

Figure 3. Equilibrium sulfur products for coal combustion with 2 percent excess air, 3.27 percent sulfur

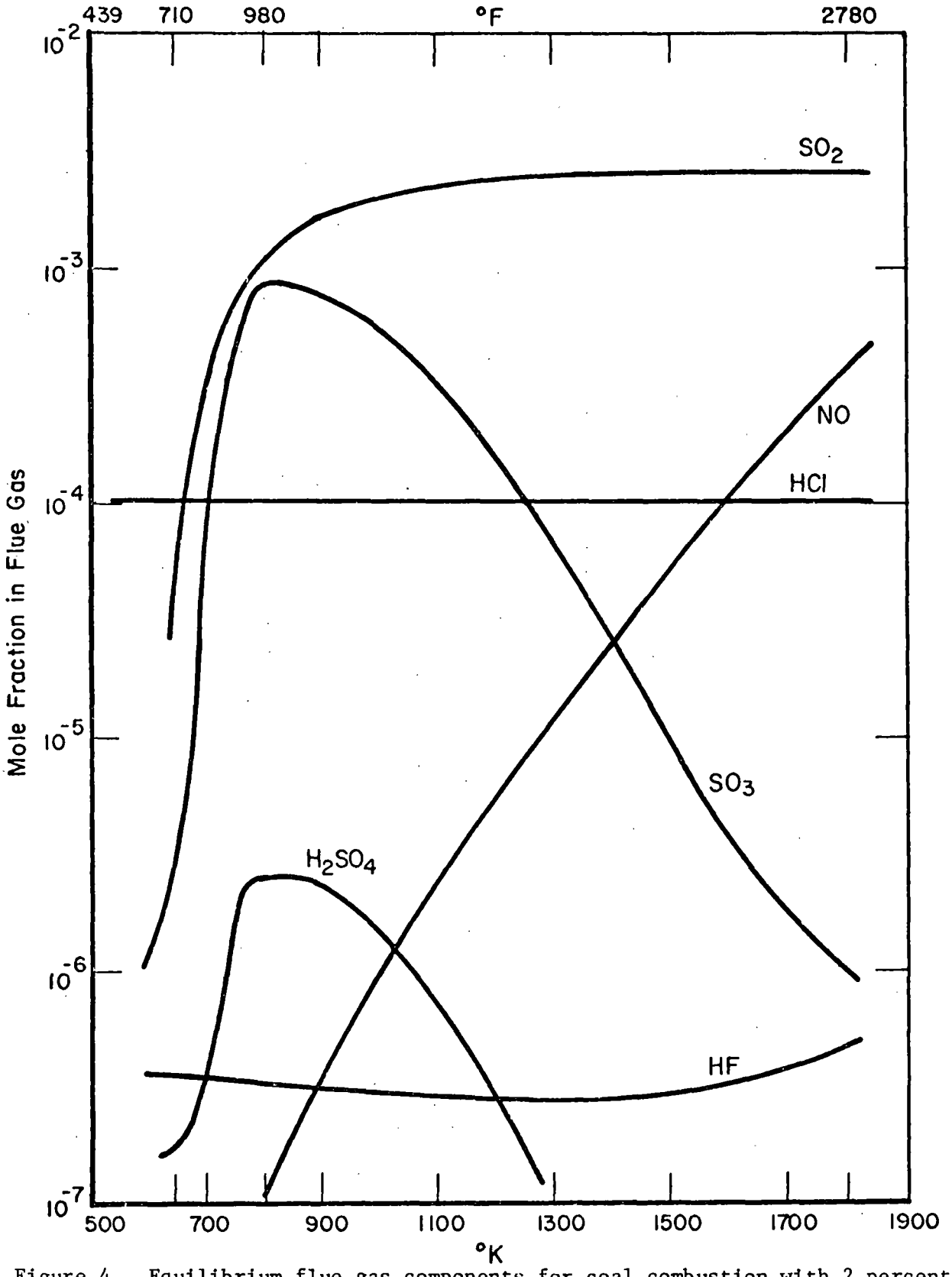

Figure 4. Equilibrium flue gas components for coal combustion with 2 percent excess air, 3.27 percent sulfur

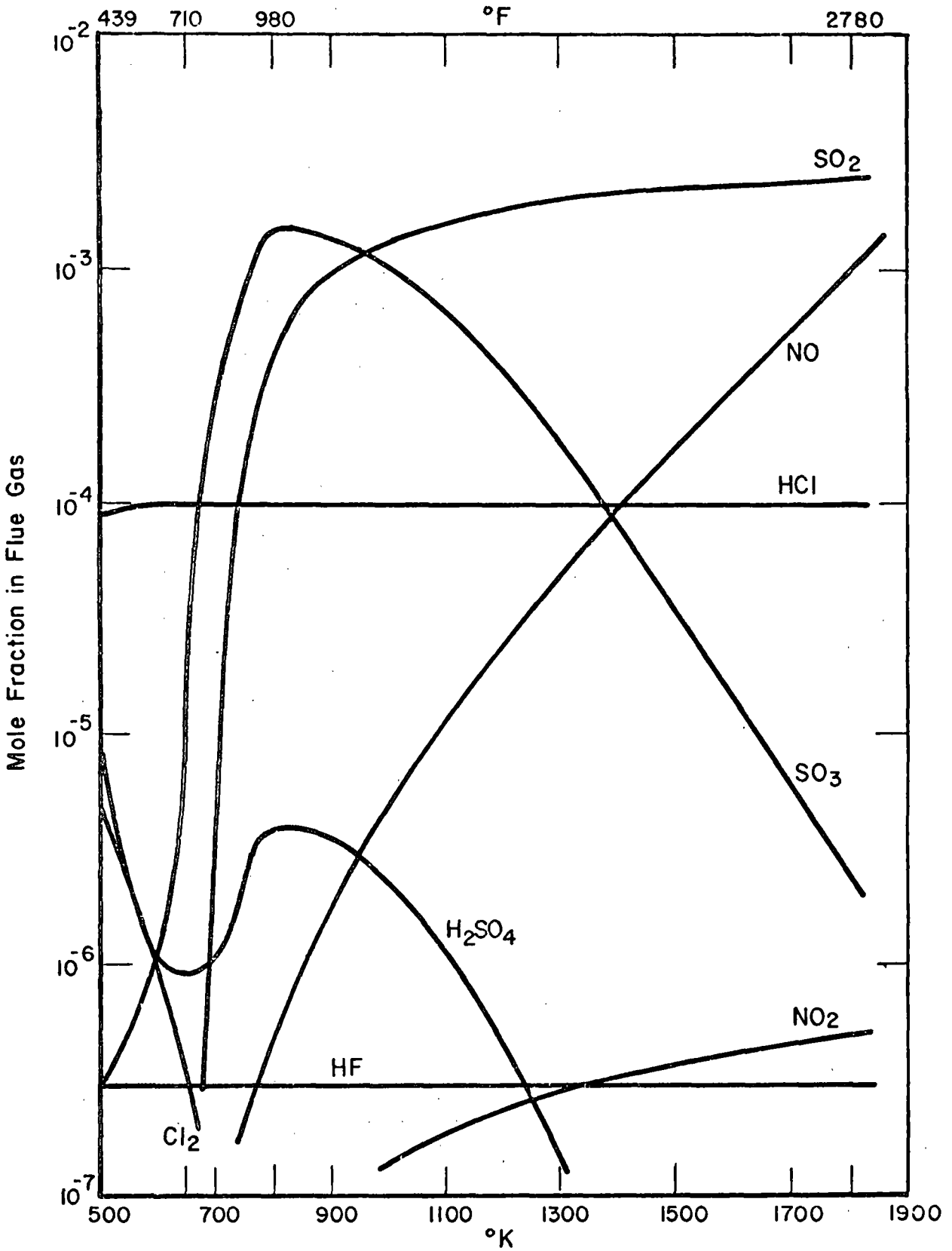

Figure 5. Equilibrium flue gas components for coal combustion with 10 percent excess air, 3.27 percent sulfur

In the solid at equilibrium at about 800 K (980 F) the distribution of sulfates, nitrates, chlorides, etc., is dominated by $CaSO_4$. On the basis of mole fraction in the solid the distribution of $SO_4^{=}$ is

$CaSO_4$	1.4×10^{-1}
$MgSO_4$	1.4×10^{-2}
Na_2SO_4	6.9×10^{-3}
$ZnSO_4$	2.6×10^{-3}
$PbSO_4$	6.2×10^{-5}

All other sulfates and sulfites are at the level of 10^{-6}. The sum of all such species would be about 2×10^{-5} and include

$$FeSO_4 > Na_2SO_3 > NaHSO_3 > Al_2(SO_4)_3 > BeSO_4 \quad .$$

A variety of chlorides also would be expected and together they would total about 4×10^{-5} mole fraction. The compounds, all in the range of 10^{-6}, include $AlCl_3$, $FeCl_2$, $ZnCl_2$, NaCl, VCl_2, $MgCl_2$, $CaCl_2$, and $BeCl_2$, in descending order.

It is interesting to note that very little nitrate or nitrite appear as products in these calculations. They total about 2×10^{-5} mole fraction and include

$$NaNO_2 > Mg(NO_3)2 > NaNO_3 > Al(NO_3)_3 > Ca(NO_3)_2 = Ca(NO_2)_2 > Be(NO_3)_2.$$

Fluorides also are present in the same concentration range and the total of various compounds is about 2×10^{-5} mole fraction. The compounds expected to be present include $AlF_3 > CaF_2 > MgF > NaF > BeF_2$.

Two phosphorous acids also are expected, phosphoric (H_3PO_4) and metaphosphoric (HPO_3), and their total concentration would be about 9×10^{-6} mole fraction.

There is essentially no difference between the 10% and 2% excess combustion air cases for all of these various compounds except some slight general decrease with decreasing excess air, but the change is hardly significant. At still lower temperatures than considered above (< 800 K), there is little change among the species except for $Al_2(SO_4)_3$ which at equilibrium would be the major species. This would occur at the expense of gas phase sulfur (SO_2 and SO_3), but may not happen in practice because the kinetics become too slow. The rest of the species mentioned above are essentially unchanged.

Based on many observations in a wide variety of combustion systems, the composition observed at the stack is more characteristic of equilibrium at higher temperature than the exit temperature. That is, the composition appears to be "frozen" at the higher temperature distribution. If it is assumed that above 1300 K (1800 F) the reaction system is at equilibrium and below it the composition is unchanging, then flue gas compositions can be estimated. On a molar basis for coal with 3.27% S and 10% excess combustion air, the distribution of potential acid aerosol components would be:

SO_2 ∿ 2000 ppm
SO_3 ∿ 200 ppm
HCl ∿ 100 ppm
NO ∿ 50 ppm
NO_2, H_2SO_2, HF ∿ 0.3 ppm

If the same coal burned with only 2% excess combustion air, then the expected distribution would show an increase in SO_2/SO_3 ratio and a decrease in both NO and NO_2. The expected distribution would be:

SO_2 ∿ 2400 ppm
SO_3 ∿ 70 ppm
HCl ∿ 100 ppm
NO ∿ 10 ppm
H_2SO_4, HF ∿ 0.3 ppm
NO_2 ∿ <0.1 ppm

If we made the same assumptions about rates for the solid components and further, that the fly ash would contain about the same distribution of compounds as the total solids, then we would expect in the fly ash, on a molar basis

$CaSO_4$ ∿ 1%
$MgSO_4$ ∿ 0.1%
$ZnSO_4$ ∿ 100 ppm

The various other sulfates, chlorides, etc., mentioned previously would appear at about the ppm level.

In a similar manner, the equilibrium predictions can be compared for fuel oil combustion. Since we are still burning a hydrocarbon fuel, the basic combustion parameters, particularly the temperature range, remain the same. The major difference results from the changed distribution of impurities which can lead to acid aerosols. A distillate fuel will generally have relatively low levels of sulfur, for instance, and very low levels of ash, i.e., the metallic constituents which can lead to a wide variety of inorganic sulfates as in the coal case. A residual oil, on the other hand, will have comparable levels of sulfur, fuel nitrogen, and possibly ash. Therefore the results of equilibrium calculations are similar to those for coal.

Figures 6 through 9 summarize the results for a typical No. 6 and No. 2 fuel oil composition (Levy, 1971) (Cato, 1974). The distribution of elements for the two oils is given in Table 4 and the products included in the computations are the same as those used in the coal computation (Table 2) except, of course, that those compounds involving elements not included in the fuel are not included in the calculation. The complete results of the calculations are given in the Appendix. It should be pointed out that chlorine is not included although it is recognized it may be present in some oils. However, the oil analyses available did not include chlorine. The No. 6 oil contains about an order of magnitude more sulfur than the No. 2 fuel and relatively large amounts of vanadium, iron, and aluminum, as well as smaller amounts of a number of other metals. Although calculations were performed for both 10% and 2% excess air, only the 2% cases are shown since the results were nearly the same.

The distribution of potential acid aerosol species in the flue gas is shown in Figures 6 and 7. The distribution of products in the flue gas for the two oils is about the same, the major difference being the magnitude of the various species. The magnitude of the sulfur species is, of course, directly proportional to the amount of sulfur initially in the fuel. The major difference between the fuel oil cases and that of coal, for equilibrium conditions, is that more of the initial sulfur in the fuel oils remains in the flue gas at low temperature. This results from the lesser ash and hence less formation of solid sulfates. As a result of more sulfur in the flue gas at low temperatures oxidation proceeds further and at the lowest

TABLE 4. TYPICAL FUEL OIL COMPOSITIONS

Species	Weight Percent	
	No. 6	No. 2
C	85.1	87.0
H_2	11.2	12.8
N_2	0.44	0.025
S_2	2.80	0.20
	ppm	
V	225	< 0.1
Ni	40	< 0.1
Na	18	< 0.8
Fe	262	
Al	251	
Si	188	
Mg	20	
Cr	16	
Ca	13	
Co	12	
Ti	6	

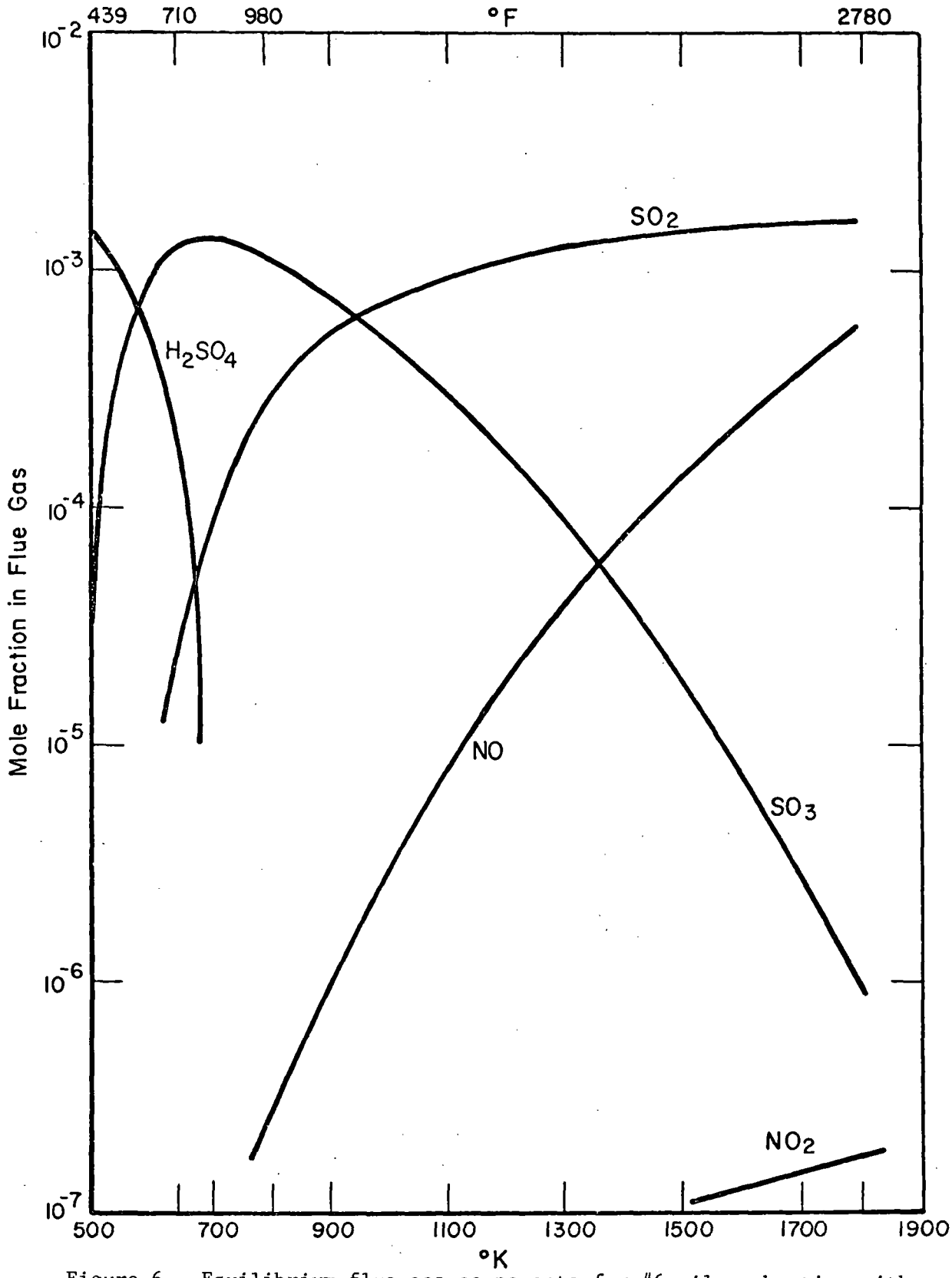

Figure 6. Equilibrium flue gas components for #6 oil combustion with 2 percent excess air, 2.80 percent sulfur

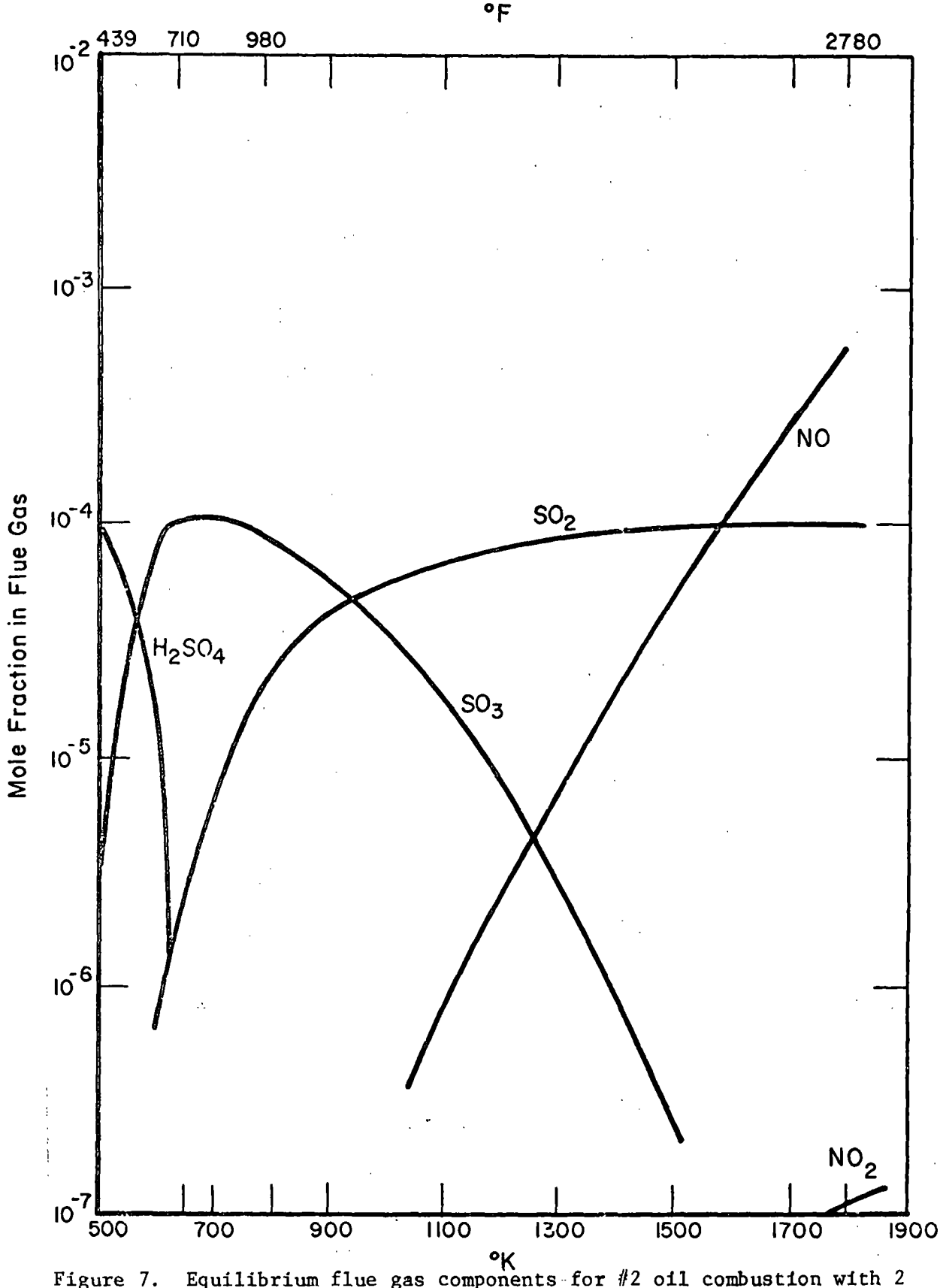

Figure 7. Equilibrium flue gas components for #2 oil combustion with 2 oil combustion with 2 percent excess air, 0.20 percent sulfur

temperature sulfuric acid becomes the major gas phase sulfur species. For the No. 6 oil this could amount to about 0.1 percent of the flue gas at equilibrium, Figure 6. As mentioned previously, however, the system does not come to equilibrium and the calculation represents the potential for sulfuric acid formation, not a prediction of the amount actually formed.

As noted in the coal case discussed previously, there is little effect due to differences in excess air. From the standpoint of combustion modifications, the maximum difference would be expected from the situation in various types of staged combustion wherein less than stoichiometric air is initially utilized. A summary of effects on potential contributors to acid aerosols is shown in Table 5 where 2% less than stoichiometric combustion air is compared to 10% excess. It will be seen that at equilibrium at maximum temperature almost all of the sulfur is in the form of SO_2. There is a large increase in SO_3 in all cases when the air is increased but even so the SO_2/SO_3 ratio remains approximately 1000. The main effect in going from less than to more than stoichiometric air is the increase in NO and NO_2. However, the ratio of NO/NO_2 is again about 1000. In staged combustion, additional air is added in some manner to complete combustion at a reduced temperature. For equilibrium calculations, the results at the reduced temperature and increased air are the same regardless of the distribution of products at the higher temperature so that the calculated combustion system effluent is unaffected by considerations of staged combustion.

The distribution of sulfur in the solid phase at low temperature is what one would expect from the combustion of oil. For residual fuel oils where the total metal content and the number of different metals are both relatively high, the solids will contain a variety of sulfates. For the No. 6 fuel oil used in this example, at low temperature equilibrium, one would find aluminum, iron, magnesium, and nickel sulfates and sodium bisulfate. However, in contrast to the coal case where total ash was much higher, the solids in this example contain only a couple of percent of the total sulfur available in the fuel as shown in Figure 9. Almost all of the sulfur is present as uncondensed sulfuric acid. In the case of the No. 2 oil the contrast with coal is more striking because there is even less ash. As shown in Figure 8 only a very small fraction, 10^{-4}, of the fuel sulfur

TABLE 5. EFFECT OF EXCESS AIR AT A TEMPERATURE OF 1800 K (2780 F)

Percent of Stoichiometric Air	SO_2	SO_3	NO	NO_2	HCl
		Coal (3.27% S)			
-2	2.7×10^{-3}	7.0×10^{-8}	2.4×10^{-5}	-- *	1.0×10^{-4}
+10	2.4×10^{-3}	2.8×10^{-6}	1.0×10^{-3}	5.8×10^{-7}	9.7×10^{-5}
		No. 6 Oil (2.80% S)			
-2	1.7×10^{-3}	7.3×10^{-8}	3.9×10^{-5}	--	--
+10	1.5×10^{-3}	2.1×10^{-6}	1.2×10^{-3}	8.2×10^{-7}	--
		No. 2 Oil (0.20% S)			
-2	1.1×10^{-4}	4.7×10^{-8}	3.8×10^{-5}	--	--
+10	9.8×10^{-5}	1.3×10^{-7}	1.2×10^{-3}	7.6×10^{-7}	--

* These values are all very low.

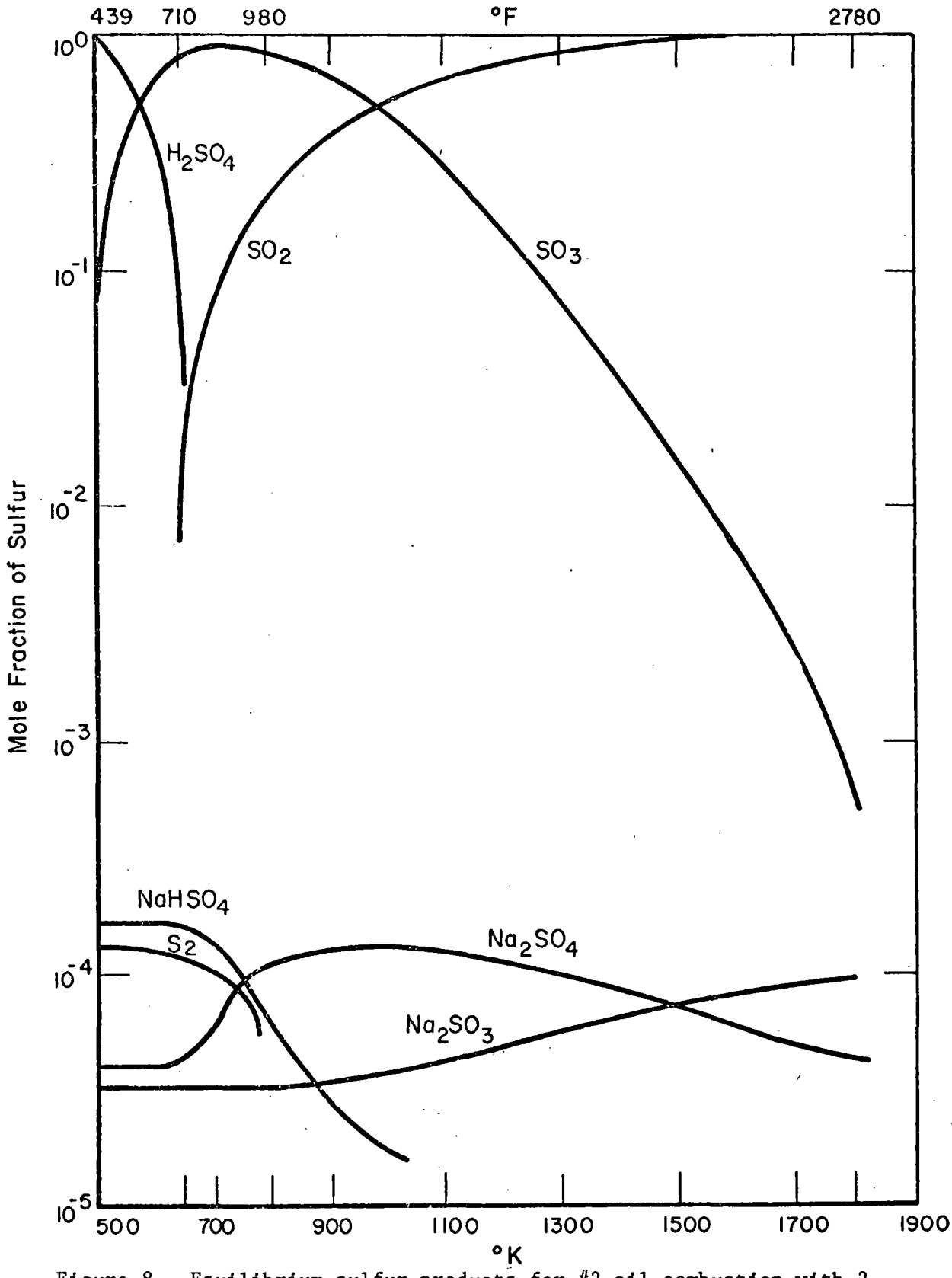

Figure 8. Equilibrium sulfur products for #2 oil combustion with 2 percent excess air, 0.20 percent sulfur

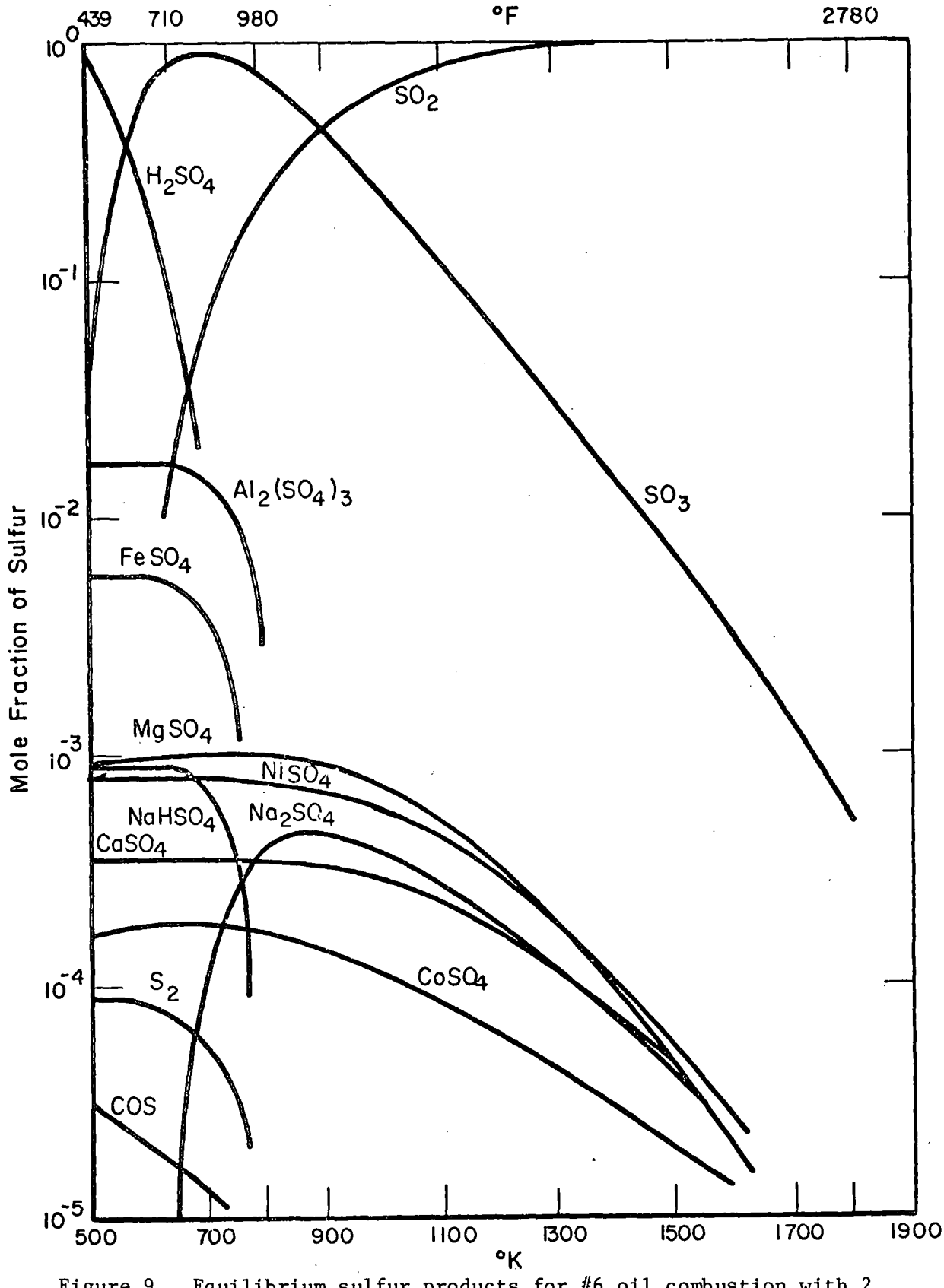

Figure 9. Equilibrium sulfur products for #6 oil combustion with 2 percent excess air, 2.80 percent sulfur

would appear as free sulfur and sodium bisulfate in the small amount of ash expected from a distillate fuel.

As in the previous discussion of coal combustion, it is instructive to assume the system is at equilibrium above some temperature where kinetics are fast, and that composition is unchanging below that temperature in order to get some idea of what flue gas and ash compositions might be. Making the same assumptions of frozen compositions below 1300 K (1800 F) as in the coal case, the expected concentration of acid aerosol precursors in the flue gas for the No. 6 oil with 2 percent excess air and containing 2.8 weight percent sulfur are:

$$SO_2 \sim 1500 \text{ ppm}$$
$$SO_3 \sim 100 \text{ ppm}$$
$$NO \sim 20 \text{ ppm}$$

The fly ash would be expected to contain about equal amounts of magnesium, nickel, sodium, and calcium sulfates amounting to a total of a few mole percent.

The No. 2 oil, containing 0.2 weight percent sulfur would be expected to produce in the flue gas, based on the same assumptions:

$$SO_2 \sim 90 \text{ ppm}$$
$$SO_3 \sim 4 \text{ ppm}$$
$$NO \sim 20 \text{ ppm}$$

In this case there would be much less fly ash but what there was could contain as much as 10 to 20 mole percent Na_2SO_4 plus Na_2SO_3.

A comparison of equilibrium considerations as they relate to observed SO_3 production in practical boiler systems has been given by Hedley (Hedley, 1967) and is shown in Figure 10. The solid lines are theoretical equilibrium calculations for the conversion of SO_2 to SO_3 with either 10% or 0.1% excess air. The dotted line indicates typical actual values at temperatures characteristic of various parts of the boiler system. The horizontal lines indicate expected temperature ranges for various parts of the system. This is consistent with the overall views of mechanisms and kinetics. At high temperatures, point Y, the formation of SO_3, is controlled by superequilibrium oxygen atom concentration. As the gas moves away from the flame and begins to cool the oxygen atoms recombine or react and SO_3 concentration

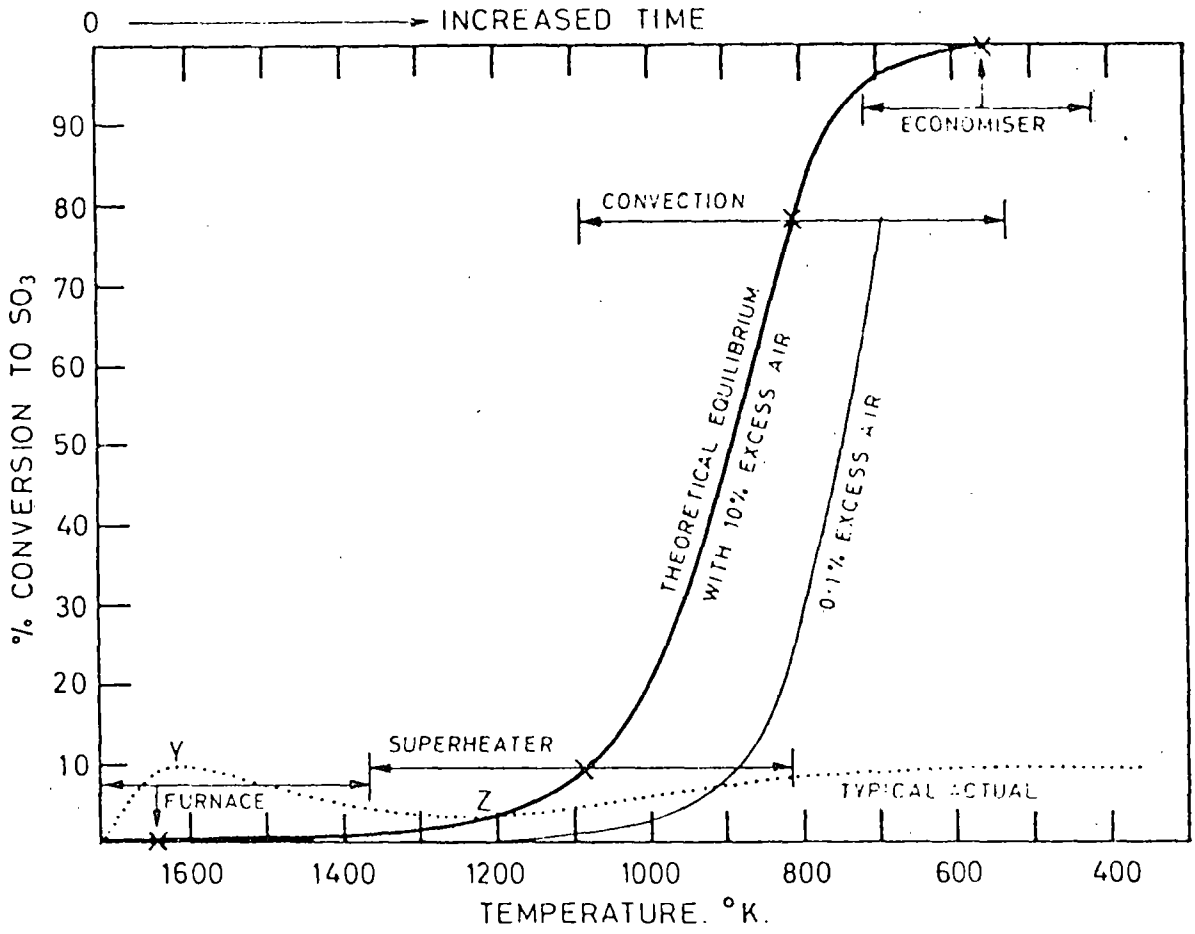

Figure 10. The variation of the theoretical equilibrium yield and possible actual yield of SO_3 with time in a boiler.

falls toward true equilibrium. When the temperature reaches about 1200 K the kinetics become too slow for SO_3 concentration to follow equilibrium as the gases pass rapidly through the boiler system. Though the concentration of SO_3 may rise somewhat it will not reach true equilibrium.

SECTION V

MECHANISMS

From the standpoint of the effect of combustion modification on pollutant formation in general and the potential acid aerosol constituents in particular, most CM schemes are attempts to reduce maximum flame temperatures and minimize the excess oxygen, particularly during the period when temperatures are near maximum. These procedures influence the kinetics of the combustion processes primarily through control of the oxygen atom concentration. Although the mechanisms of NO_x and SO_x formation are not known completely, it appears that the O-atom concentration and that of closely related species, such as OH and HO_2 are critical in oxidizing nitrogen to NO and NO_2 as well as sulfur to SO_2 and SO_3. Since these same radicals are important in the oxidation of carbon, the kinetics of combustion and pollutant formation are inseparable. In addition, CM can influence particulate formation which can further modify possible acid aerosol formation through such processes as adsorption, heterogeneous reactions, and catalysis. Furthermore, these latter reactions will take place at lower temperatures and in parts of the combustion system quite distinct from the aforementioned combustion reactions. The high temperature homogeneous reactions will occur for the most part in the first regime described previously. The heterogeneous processes are expected in the second regime. The final part of this section of the report is concerned with reactions in the forth regime, the near plume. Although the detailed mechanisms are not known well enough to make precise predictions, some generalizations can be made which are useful in considering CM approaches.

HIGH TEMPERATURE HOMOGENEOUS REACTIONS

Formation of SO_2 and SO_3

On combustion of fuels containing sulfur essentially all of the sulfur that leaves the combustion system through the stack will be in the form of SO_2 accompanied by a few percent of SO_3. This situation always pertains in oxidizing systems, which include all industrial boilers, regardless of the initial form of the sulfur. Mechanisms of conversion of sulfur in the fuel to SO_2 and SO_3 have been described (Levy, 1970), (Hedley, 1967), (Cullis, 1972). In the flame, the sulfur is mainly in the form of SO_2 and SO even in a fuel-rich situation. The reactions are in general fast and equilibrium calculations provide a reasonable picture. Results by Johnson et al., (Johnson, 1970) for a propane/air flame containing sulfur are shown in Figure 11 where it is seen that species other than SO and SO_2 do not become significant until the air drops below 80 percent of stoichiometric. The SO results from oxidation of a variety of sulfur species such as S, H_2S, COS, etc., by various processes which for H_2S probably proceeds as

$$O + H_2S \rightarrow OH + SH \quad (1)$$

$$O + SH \rightarrow SO + H \quad (2)$$

$$H + H_2S \rightarrow H_2 + SH \; . \quad (3)$$

O atoms and SO are then chain carriers for further oxidation. Although the details of the process are not fully elucidated, the mechanism probably includes

$$SO + O_2 \rightarrow SO_2 + O \quad (4)$$

$$O + SO + M \rightarrow SO_2 + M \quad (5)$$

Oxygen atoms also are the key to SO_3 formation and, as pointed out by Hedley (Hedley, 1967), the fact that SO_3 produced in flames is generally greater than equilibrium amounts at flame temperature is consistent with superequilibrium oxygen atom concentrations in flames. The pertinent reaction controlling the SO_3 and approach to steady state are thought to be (Merryman, 1971)

$$SO_2 + O + M \rightarrow SO_3 + M \quad (6)$$

$$SO_3 + O \rightarrow SO_2 + O_2 \; . \quad (7)$$

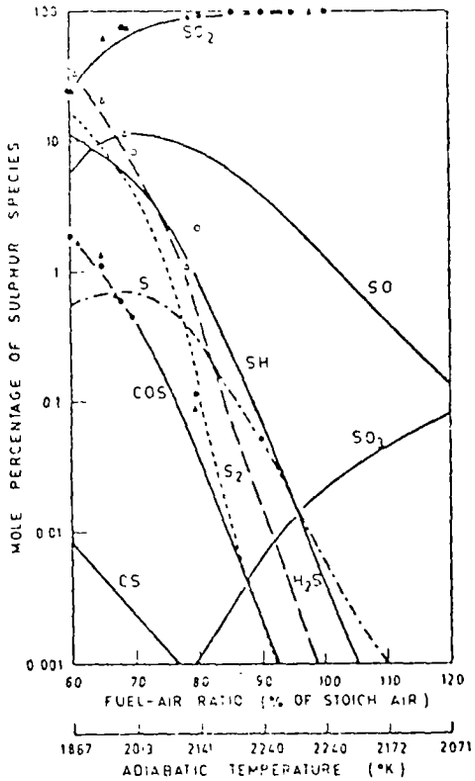

Figure 11. Equilibrium distribution of sulfur-containing species in propane air flames with unburnt gases initially containing 1 percent SO_2 - points represent experimental measurements normalized at 60 percent stoichiometric air: o or ● gas chromatography, ∇ or ▼ mass spectrometry

The importance of oxygen to the formation of SO_3 in practical combustion systems has been recognized for many years and was well illustrated by the work of Barrett, et al., (Barrett, 1966) summarized in Figure 12. When oxygen is at or below stoichiometric there is virtually no SO_3 formed but the first percent increase in excess oxygen greatly increases the formation of the trioxide.

Particularly important to CM considerations, and possible effects of staged combustion, is the pilot scale work of Hedley (Hedley, 1967). He observed that adding oxygen to hot incompletely combusted fuel containing sulfur produced more SO_3 than burning with the same amount of oxygen added to the original combustion air. This effect is attributed to the relatively high concentration of CO in the incomplete combustion mixture. When combustion was completed by adding oxygen, the O atom concentration was greatly increased, presumably by

$$CO + OH = CO_2 + H \tag{8}$$

$$H + O_2 = O + OH \tag{9}$$

which in turn significantly increased SO_3 production.

The homogeneous catalysis of SO_2 to SO_3 by NO_2 is well known and has been discussed by Hedley (Hedley, 1967) and Cullis and Mulcahy (Cullis, 1972). The overall reaction can be described as

$$NO + 1/2\ O_2 = NO_2 \tag{10}$$

$$NO_2 + SO_2 = NO + SO_3 \tag{11}$$

The rate of Reaction 11 has been measured (Armitage, 1971) up to about 920 C (1688 F). It appears that the rate of SO_2 oxidation is limited by the rate of formation of NO_2, i.e., the former reaction above is rate limiting. The significance of such reactions is not clear in practical combustion situations but the homogeneous catalysis could contribute to the formation of SO_3 at low temperature where the reaction of SO_2 with oxygen is quite slow. On the other hand, such reactions may play a part in flames as shown by the work of Levy and Merryman (Levy, 1965). In developing the microstructure of H_2S flames, they demonstrated an increase in SO_3 when the oxidant was switched from O_2 - Ar to O_2 - N_2.

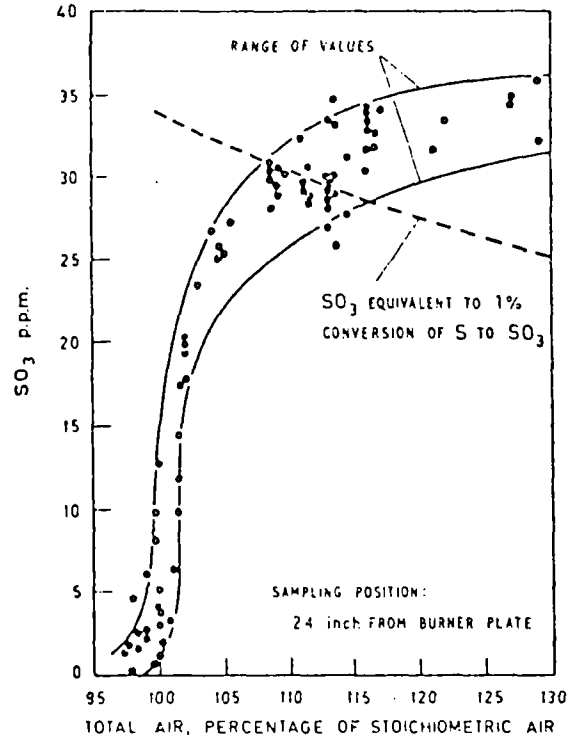

Figure 12. Effect of excess air on the formation of sulfur trioxide in a hydrocarbon flame

The effect of NO at high temperatures has been investigated by Wendt and Ekmann (Wendt, 1975) and found to be quite different. At flame temperatures they found the presence of SO_2 decreased the formation of NO in a methane/air flame. H_2S as a fuel additive also decreased NO formation. In each case, the decrease was as much as 36 percent. The mechanism of these high temperature reactions is largely unresolved but SO_2 is known to promote the recombination of free radicals such as H and OH (Webster, 1965) which are important to the formation of NO in flame environments. In any event, the implication of these results is important to the practical utilization of sulfur bearing fuels. As pointed out by Wendt and Ekmann, the results suggest that fuel desulfurization may lead to increased thermal NO_x production; but the effect on fuel NO_x, if any, remains unresolved.

Formation of NO_2 and Nitrate

Even though most of the available data indicate that nitric acid and nitrates do not contribute significantly to primary acid aerosol, it is thought that some brief review of the mechanisms of formation of the important precursors, NO and NO_2, should be included in this report. This is particularly so since most combustion modifications being used or considered are for the purpose of controlling NO and NO_2 formation. Further, it is inherent in the combustion processes that when sulfur and nitrogen are both present, factors influencing formation of oxides of nitrogen and oxides of sulfur cannot be treated entirely independently.

The formation of oxides of nitrogen results from oxidation during combustion of nitrogen from two sources; nitrogen chemically bound in the fuel, and nitrogen from the combustion air. The mechanisms by which nitrogen from these two sources is oxidized are different. Most attempts to explain NO formation from thermal fixation of combustion air generally start with the Zeldovitch mechanism

$$O + N_2 = NO + N \tag{12}$$

$$N + O_2 = NO + O \quad . \tag{13}$$

This mechanism, however, fails to predict NO concentration in and close to the flame front where the concentration is higher than equilibrium. The high NO concentration in this region is generally attributed to the super-equilibrium concentration of H, OH, and O all of which reach maximum

concentration in the vicinity of the flame front. The hydroxyl radical, through the reaction,

$$OH + N = NO + H \tag{14}$$

is thought to be particularly important in fuel rich situations (Ay, 1976), Bowman, 1972), (Williams, 1972).

Fenimore (Fenimore, 1971) suggested that other routes to NO which whould be considered to account for the initial "quickly formed" NO, which he called "prompt NO", include

$$1/2\ C_2 + N_2 = CN + N \tag{15}$$

$$CH + N_2 = CHN + N \tag{16}$$

which would be followed by (13). Still other routes have been suggested, for instance, Merryman and Levy (Merryman, 1975). Such reactions provide an alternate path for breaking the strong N_2 bond.

Knowledge of the kinetics of these reactions and of combustion radical concentrations allow a qualitative understanding of NO observations in and close to flames and the thermal formation of NO, at least for fuel-lean situations. Under equilibrium conditions, the Zeldovich mechanism predicts NO fairly well. However, there are still many unanswered questions, particularly for fuel rich conditions and our ability to predict NO and NO_2 formation under these conditions needs to be improved.

In the case of fuel-bound nitrogen knowledge of mechanisms and kinetics is incomplete. The mechanisms of oxidation of fuel nitrogen and molecular nitrogen are distinctly different but not necessarily independent. For combustion modifications then, the implication is that the effectiveness of a given CM in reducing NO formation will depend on the fuel. It has been well established that CM can reduce NO in the case of natural gas, propane, or distillate oil combustion but is less effective in the case of coal or residual oil combustion because of the fuel-bound nitrogen in the latter fuels. Although the mechanisms are not clear, several general features are established:

- A large part of the fuel-bound nitrogen can be converted to NO during combustion
- The fraction converted to NO increases with excess air and decreases as the fuel-N concentration increases

- Conversion of fuel-N is not as sensitive to temperature as the thermal nitrogen mechanism

- The conversion to NO is not very dependent on the nature of the N-compound as shown by various basic studies.

The mechanisms which have been proffered for the conversion of fuel-N to NO are all rather speculative. Early studies of ammonia/oxygen flames (Maclean, 1967) (Wolfhard, 1952) demonstrated that pyrolysis led to NH_2 and then NH radicals before reaching the flame front and that NO began to increase rapidly when NH reached its peak concentration. Fine (Fine, 1974) and Sarofim (Sarofim, 1975) and coworkers have suggested a sequence of events which may be represented as

$$RNH_2 \rightleftharpoons NH_2 \rightleftharpoons NH \rightleftharpoons N$$

$$NH \rightarrow NO,\ N_2 \qquad N \rightarrow NO,\ N_2$$

Ammonia, a pyrolysis product of coal, can be converted essentially quantitatively to NO (Sarofim, 1975). However, the conversion drops dramatically when the reaction system is fuel rich, Figure 13, where the product is presumably N_2. Such results have clear implications for CM such as staged combustion. Initial combustion with less than stoichiometric air would be expected to lead to N_2 rather than NO. The removal of some heat prior to completing combustion with some excess air would tend to lower the conversion of N_2 to NO by the "thermal" mechanism discussed earlier. Thus, the total conversion to NO would be decreased.

Pyrolysis studies of model compounds for fuel-N, e.g., pyridines, quinolines, etc., have shown that HCN can be the major pyrolysis product at temperatures above 1000 C (1832 F) in the absence of oxygen (Axworthy, 1975). Pyrolysis of No. 6 fuel oil, a crude, and a coal sample under similar conditions produced fuel-N conversions to HCN in the range 30 to 50 percent and much less ammonia. This suggests HCN could be an important intermediate to NO formation than fuel-N.

Axworthy, in premixed flat flam experiments, compared the rate of formation of NO from NH_3 and HCN (Axworhty, 1975). The results indicate that NO is formed mostly just downstream from the luminous flame zone. The rate of conversion to NO from NH_3 appears greater than for HCN and conversion is suppressed in rich flames.

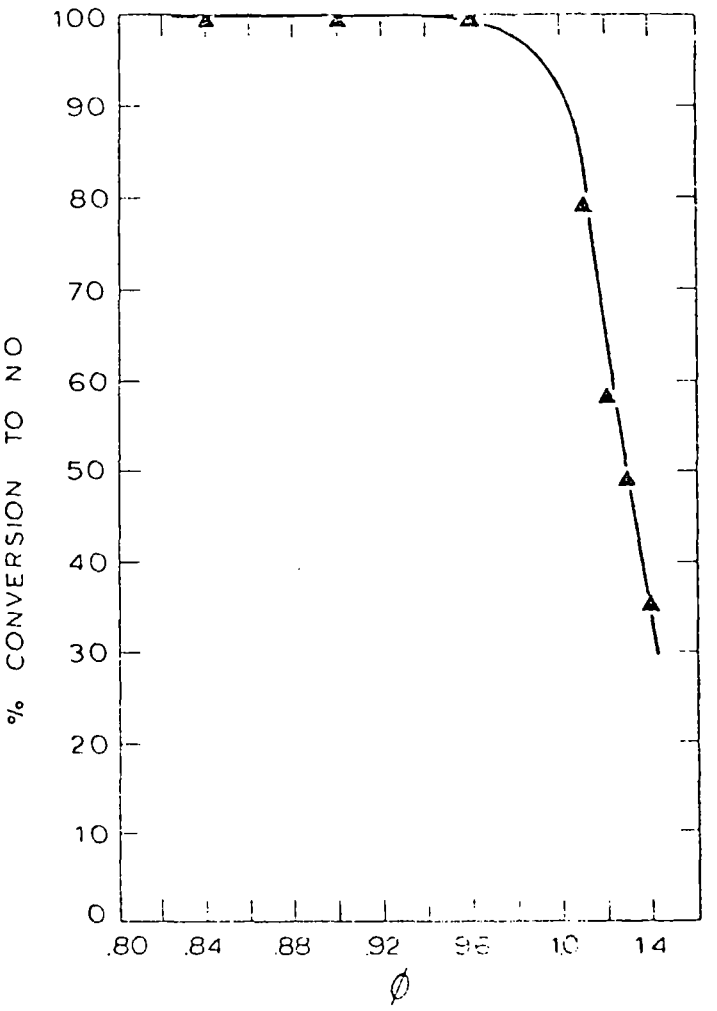

Figure 13. Effect of equivalence ratio on conversion efficiency for an ammonia additive (0.5 percent by weight)

It is recognized that heterogeneous reactions could also play a significant part in conversion of fuel-N to NO. Pyrolyses experiments with fuels and model compounds demonstrate the tendency to form nitrogen containing carbonaceous residues (Axworthy, 1973). Even the volatile N-heterocyclics have a strong tendency to form solids which at lower temperatures may contain most of the original nitrogen. Thus, one could expect some nitrogen containing soot which could lead to heterogeneous formation of NO during burn-out. Wendt and Schultz (Wendt, 1976) have molded coal char burn-out and their results are in agreement with the observed weak temperature dependence of fuel-NO formation and predict an effect of particle size. Also, the results suggest that free stream CO may be more important than O_2 in determining the effect of excess air on heterogeneous formation of fuel-NO. This is an area which warrants further investigation particularly since an effect of some CM techniques such as low excess air firing and staged combustion may lead to increases in particulate formation and hence increased heterogeneous oxidation of nitrogen.

HETEROGENEOUS GAS-SOLID REACTIONS

Catalytic Oxidation of SO_2 by Metals and Metal Oxides (Suspended Phase)

The question often has been raised as to how much of the SO_3 produced in boilers is the result of the catalytic oxidation of SO_2 in contrast to the previously discussed homogeneous reactions. In the temperature range characteristic of the second regime of the combustion system, heterogeneous reactions leading to increased oxidation of SO_2 can occur and are the subject of this section of the report. Several investigations have been made of the catalytic activity of fly ash components in this regard. Fletcher and Gibson (Fletcher, 1954) showed that for temperatures above 600 C (1112 F), Fe_2O_3 greatly increased the formation of sodium sulfate from sodium chloride and SO_2, while at temperatures below 600 C, the sulfate was formed only from SO_3 already present. Thus Fe_2O_3 is a strong catalyst in the oxidation of SO_2. These findings were confirmed in the fundamental work of Vogel, et al, who found that high relative humidity helped promote this fly ash catalysis.

That materials other than Fe_2O_3 in a boiler system can be effective catalysts for the oxidation of SO_2 to SO_3 was demonstrated by Wickert (Wickert, 1957). He found that although Fe_2O_3 was the most active of the materials that he tried, a sample of fly ash brought about a maximum of 36 percent conversion of SO_2 to SO_3 at about 760 C (1400 F). On the other hand, SiO_2 and Al_2O_3 were only weak catalysts in this system. What is most significant, however, was the observation that these catalytic reactions were highly temperature dependent as shown in Figure 14. The catalytic effect of the Fe_2O_3 is greatest at superheater metal temperatures while that of the fly ash goes through a maximum at a slightly higher temperature. The broader peak with Fe_2O_3 indicates the greater importance of this compound as a catalyst for the formation of SO_3, as it operates through a wider temperature range. Obviously the surface area available and length of time for fly ash to spend inside the catalytically active temperature window are of paramount importance in determining the importance of fly ash catalysis.

Manganese dioxide is a powerful convertor of SO_2 to sulfate over a wide range of temperatures, from room temperature (Corn and Cheng, 1972) to at least 340 C (644 F) (Vogel, 1974) and so may play a role throughout the entire convection and stack zone of a power plant. High relative humidities (without condensation) are necessary for the catalysis to proceed.

One of the best catalysts for the conversion of SO_2 to SO_3 is V_2O_5. In the contact process for the manufacture of sulfuric acid SO_2 is passed over V_2O_5 catalysts at a temperature of 427 to 621 C (800 to 1150 F). With a contact time of 2 to 4 seconds, the conversion of SO_2 to SO_3 is 90 percent or greater. Residual fuel oils from the Middle East and from Venezuela contain significant amounts of vanadium and in the combustion process this is converted to V_2O_5. As a consequence, the potential for SO_3 formation by heterogeneous catalytic reaction with V_2O_5 in the combustion of these oils is great. Wickert also investigated the effect of V_2O_5 and mixtures containing V_2O_5 and other boiler deposit components on the oxidation of SO_2 (Wickert, 1959). His results are shown in Figure 15 in which the temperature dependence of the catalytic reaction is again apparent. In this case V_2O_5 was a better catalyst for the reaction than was Fe_2O_3. A mixture containing 90 percent V_2O_5 and 10 percent Na_2SO_4 was just as good a catalyst as was the

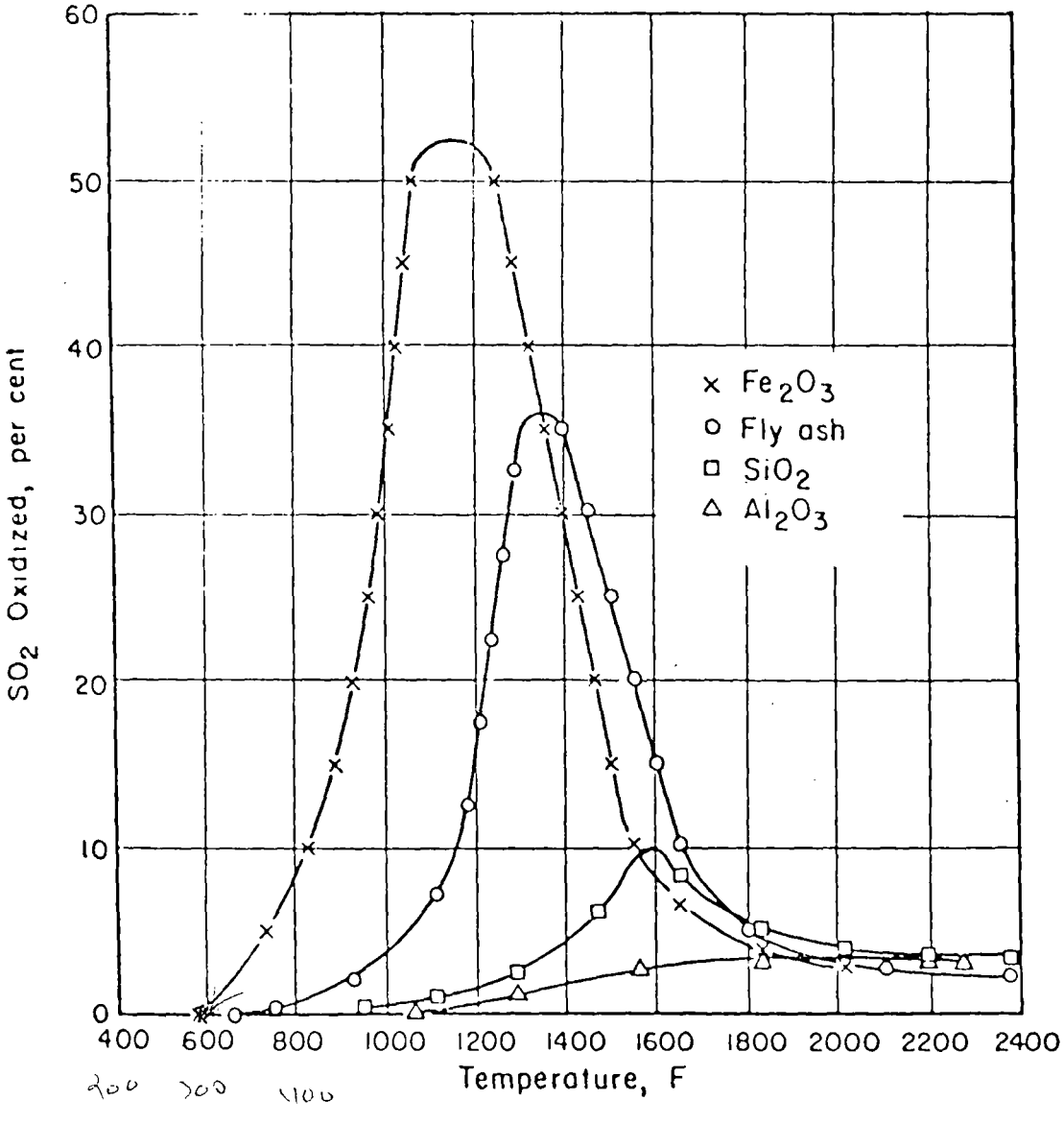

Figure 14. Catalytic oxidation on SO_2 to SO_3 by various materials

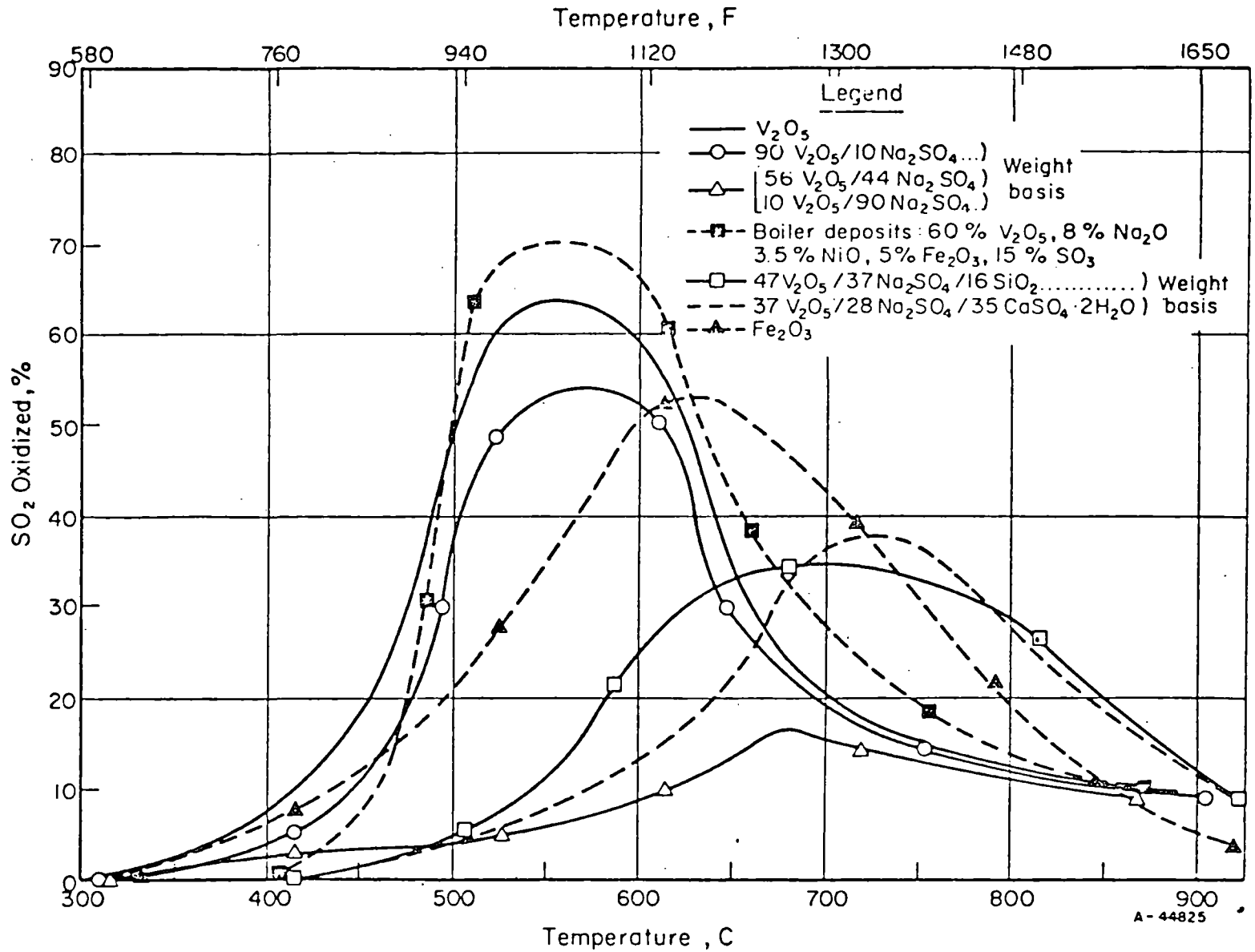

Figure 15. Catalytic oxidation of SO_2 to SO_3 by various materials

Fe_2O_3. However, the boiler deposit from the burning of residual oil containing vanadium was the best catalyst of all, causing a 90 percent conversion of SO_2 to SO_3. Several materials were at their greatest effectiveness in the 900 to 1100 F temperature range of typical boiler tubes. Catalysis by V_2O_5 also was examined by Napier and Stone using short contact times with typical flue gas compositions (Napier and Stone, 1958). The catalyst consisted of V_2O_5 and K_2SO_4 on a silica support. With 1000 ppm SO_2 in the gas stream and the catalyst at 430 C (806 F), from 94 to 98 percent conversiton of the SO_2 to SO_3 was achieved with contact times ranging from 90 to 430 milliseconds. When the contact time was held constant at 170 milliseconds, SO_2 conversions ranging from 92 to 98 percent were obtained when the SO_2 content in the gas stream was varied from 340 to 2700 ppm. It was concluded that the required contact time for catalytic oxidation at low SO_2 concentrations is much lower than that used in the contact process for sulfuric acid. In addition it was noted that the presence of water vapor and CO_2 in the gases had no adverse effect on the catalyst. Hence, heterogeneous catalysis by V_2O_5 in flue gases can well be an important source of SO_3. However, V_2O_5 is effective only in a high temperature "window", and this again poses the question of how combustion conditions affect the available surface area and time that fly ash particles spend in this catalytically effective high temperature window. Furthermore, V_2O_5 is ineffective at room temperatures, and so probably does not contribute to secondary sulfates. Unoxidized vanadium on an Al_2O_3 support is not effective, at least at 340 C (644 F) as shown by Vogel, et al.

Catalytic Oxidation of SO_2 by Soot and/or Carbon

The role of carbon as a catalyst to oxidize SO_2 to SO_4 is reported primarily by Novokov (Novokov, 1974). He found that freshly generated soot or graphite convert SO_2 to SO_4 which is bound to the particles. Evidence that soot was also catalytically active, especially in the present of water vapor was also found. Furthermore, soot was active at only a specified distance down stream from a flame. This distance may imply the existence of a temperature "window" or limitations of capacity to adsorb and react SO_2. The data shows that the decrease of SO_2 across a sooty filter is independent

of SO_2 inlet concentration, a fact which Novokov explains by hypotesizing that the number of active sites on soot particles is controlling rather than inlet species concentrations. Novokov also states that increases in SO_2 oxidation occur at higher O_2/C_3H_8 ratios, although none of these data lie in the fuel lean regime. He attributes this to an increase in the number of "ultrafine, high surface area particles" although it may be due simply to increased O_2 availability. In all his experiments there was a pronounced saturation effect, implying a finite capacity for this process.

However, Novokov's work is not quantitative and so it is not known how much conversion is possible through this mechanism. It is not clear whether particle age or temperature is the determining factor for catalytic activity. There is at present no demonstration that this carbon mechanism is not important, and so it seems reasonable to conclude that the mechanism might account for significant primary $SO_4^=$ formation, especially when fresh carbon particles or soot are formed. Clearly further work is required to quantify this effect and to determine its practical significant.

Combustion and Particulate Characteristics

There is considerable evidence that particulates from coal combustion may contain catalytically active materials. Therefore, the particle size and surface area provided by fly ash will affect the overall uptake and conversion of SO_2 to SO_4. In this section we address the problem of how combustion conditions affect the size distribution of potentially catalytic fly ash particles.

An extensive analysis of a variety of major and minor elemental constituents in 101 different coals from around the United States is illustrated in Table 2 (Equilibrium Considerations, page 24). The various elements as such are shown in Table 2; they in fact occur in complex arrays of molecules which to date have defied complete chemical description.

The most important coal constituents determining the amount and composition of particulates formed in combustion are those contained in the mineral matter. Generally, mineral matter can be classed as inherent and extraneous although exact definitions are difficult because the same ash constituent may be present in both classes. Inherent mineral matter is made up of chemical elements such as iron, calcium, magnesium, phosphorus,

potassium, and sulfur that were combined organically with the plant tissues when the coal was formed. Inherent mineral matter seldom exceeds 2 percent of the weight of the coal (Reid, 1971) and the rest of the ash component is comprised of extraneous mineral matter which consists of minerals mixed in with the coal seams during formation but not actually part of the coal itself.

About 95 percent of the mineral matter is coal is made up of kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), pyrites ($FeS_2$), and calcite ($CaCO_3$) (Reid, 1971). Other elements listed in Table 2 exist in a variety of forms that have not been definitely determined at this time.

The fate of the various coal constituents during combustion is a deeply involved process depending on the original chemical form of the elements and the time-temperature history of the combustion process. For instance, pyrite (FeS) begins to oxidize at only 260 C (500 F) but rapid heating in a pulverized coal fired furnace can cause pyrite to melt before the sulfur has been driven off or the iron oxidized to Fe_2O_3. Hence, moderate to high heating rates will result in the formation of a liquid phase of FeS, whereas slower heating rates will result in the formation of SO_2 and Fe_2O_3 which will also flux the silicates in the ash.

The formation of ash or particulate matter in the flue gases resulting from coal combustion occurs generally by two mechanisms. The first involves formation of larger particles comprised of the low volatile mineral constituents in the coal. These particles consist of cenosphere or hollow, blown-out sections resulting from ashing of the coal. The second mechanism involves the formation of very small particles resulting from the condensation of the more volatile mineral constituents (e.g., Se, As, Pb, Cd, and V).

Abel and Rancitelli have shown that certain selected refractory constituents (Eu, Hf, Sc, Ta, Th, La) are converted nearly quantitatively from the coal to fly ash during the combustion process (Abel, 1975), whereas for the more volatile Se and Sb only 30 percent and 20 percent of each element, respectively, could be detected in the fly ash. Schultz, et al have indicated that the amount of various trace elements ending up in the fly ash is a function of the vapor pressure of that element at the combustion temperature of the process with the higher vapor pressure constituents being retained to a lesser extent (Schultz, 1975).

Elements with higher vapor pressure or high volatility have shown a tendency to preferentially concentrate in the smaller fly ash particles due to condensation. In airborne coal fly ash the elements Pb, Tl, Sb, Cd, Se, Zn, As, Ni, Cr, S, and Be showed higher concentrations in finer particles (Natusch, 1974). Rancitelli has also shown this trend for three fly ash samples from different coal-fired boilers (Rancitelli, 1974). In this case there were significantly higher concentrations of As, Mn, Sb, and V in particles less than 10 micrometers whereas there was a trend to higher concentrations of Fe in particles over 10 micrometers. About the same concentrations of Al, Se, and La were present in particles of all sizes. Cowherd, et al (1975) have also shown that more volatile constituents concentrate in the finer particles.

The major constituents in coal fly ash consist of the major mineral elements in the coal itself: Si, Al, Na, Mg, K, Fe, and Ca. Fly ash analyses generally report ash constituents as the oxide form or in the elemental form although it is usually assumed that in all cases the compounds are in the oxide form.

Analyses of ranges of the major fly ash components in a variety of coal samples as compiled by the Bureau of Mines (Fieldner, 1942) are presented in Table 6. Large variations exist in all components but generally SiO_2 is the major constituent making up about 1/3 to over 1/2 of the ash sample. Aluminum oxide (Al_2O_3) is usually the second most prominent compound comprising about 1/10 to just less than 1/2 of the sample. Iron compounds, which are reported in a variety of forms (Fe, FeO, Fe_2O_3, Fe_3O_4), are about equal in order of magnitude with aluminum. The alkali metals (Na, K) and alkaline earth metals (Mg, Ca) along with Ti comprise the remainder of the primary mineral constituents in the ash.

Catalysis of SO_2 Oxidation by Ash Deposits

Fly ash is deposited on boiler tubes and is available for catalysis of SO_2 to $SO_4^=$ over a long period of time. One would expect that the metals and metal oxides shown to be catalytically active would contribute to catalysis of SO_2 oxidation, when deposited on boiler tubes, provided the temperatures remained in the correct range. In this section we highlight some of the differences between fly ash catalysis in the dispersed mode and in the deposit mode.

TABLE 6. COAL ASH ANALYSIS LIMITS AS GIVEN BY BUREAU OF MINES

Constituent	Percent
Silica	30-60
Aluminum Oxide	10-40
Ferric Oxide	5-30
Calcium Oxide	2-20
Magnesium Oxide	0.5-4
Titanium Oxide	0.5-3
Alkalies	1-4

The potential catalytic effect of deposits has been shown by the work of Glebov, et al (1973). He demonstrated that SO_4 could be oxidized to SO_3 by molecular oxygen in the presence of boiler deposits over the temperature range of 900 to 400 C (1670 to 752 F), the range of a boiler's convective heating surfaces. The most active catalyst powder was found to be a deposit from the convective bundles of oil-fired boilers. The deposit showed catalytic activity comparable to a vanadium pentoxide powder in the experiments. Maximum conversion occurred at a catalyst temperature of 560 C (1040 F). Further, effective catalysts were prepared from mixtures of V_2O_5 + Na_2SO_4 + Fe_2O_3 which had a maximum conversion at 640 C (1184 F).

Using empirical coefficients in conjunction with a simple model of a boiler system, Glebov predicted SO_3 in flue gas as a function of deposit thickness, convective bundle surface area and temperature, and excess air. The predicted values were compared to measured values from a boiler burning a high sulfur oil and good agreement was found. These results indicate that when deposits which may contain vanadium pentoxide are allowed to build up, it is possible that catalysis by the deposits could control the SO_3 effluent.

As the simple sulfates remain in the deposits for extended periods of time, they are gradually converted to complex sulfates by the action of the sulfur oxides in the flue gas stream. The formation of alkali-iron trisulfates such as $Na_3Fe(SO_4)_3$ from the reactions of sulfur oxides with Na_2SO_4 and Fe_2O_3 was studied using radioactive tracer techniques by Krause, et al (1968). The experiments were performed at 600 C (1112 F) and with 2500 ppm SO_2 and 30 ppm SO_3 in a gas stream containing 3 percent O_2. It was demonstrated that the reaction rate of SO_3 to form the trisulfate was 970 times as that with SO_2. A similar compound is formed with potassium and in this case the reaction rate of SO_3 exceeded that of SO_2 plus oxygen by a factor of 1260. Experience with trisulfate formation in an operating boiler was reported by Anderson and Diehel, who placed a probe in front of the superheater tubes (Anderson, 1955). Gas temperatures in the region of the probe were 982 to 1094 C (1800 to 2000 F) and the metal surface temperature of the specimens was maintained at 566 C (1050 F). In this case the fly ash collected from the boiler was found to contain 10.3 percent of sulfate expressed as SO_3. The initial deposit collected on the probe after a week's

exposure contained 15.7 percent SO_3, and after several weeks time, the SO_3 concentration reached 35 percent.

The significance of the formation of sulfates in deposits and the build-up of high concentrations of sulfates stems from the fact that portions of these deposits are removed periodically from the boiler tubes by soot blowing. This operation is carried out at least once a shift and by its nature creates a large amount of particulate in the boiler in a short period of time. As a consequence the capacity of the electrostatic precipitators is taxed during this period and it is quite likely that a significant portion of particulate sulfate passes through the precipitator and is emitted from the stack. Unfortunately, no data are available yet on these overload conditions which are potential sources of particulate sulfate in the atmosphere.

Capacity Considerations

Of paramount importance in determining the overall conversion of SO_2 to $SO_4^=$ by fly ash catalysis is to address the question of capacity of available surface. Fundamental studies on the catalytic activity of V_2O_5 indicate conversions of 90 percent, yet these have never been observed in combustion units. The difference is probably due to the fact that the catalytic activity of V_2O_5 in combustion units is constrained by capacity limitations brought on by available active surface area constraints. Combustion modifications, by altering size distributions of certain metallic species, may alter the capacity of these species to convert SO_2 to $SO_4^=$. Capacity considerations may be applicable both to fly ash catalysis in the disperse phase, fly ash deposit catalysis and catalysis by carbon. Capacity considerations will also affect the amount of H_2SO_4, formed prior to contacting metal, which reacts to form metal sulfates.

EARLY PLUME REACTIONS

The final regime where chemical reactions might be expected to influence primary acid aerosol emissions is the near plume. For the purpose of this study we have arbitrarily defined aerosol observed in the early plume as primary aerosol. Technically this is an arguable point. The primary basis of this definition is to separate the roles of particulate, i.e., SO_3 and H_2SO_4 condensation, formed very rapidly in leaving the stack,

from the typically slow plume chemistry, i.e., SO_2 oxidation process over periods of minutes to hours downwind in a plume.

In the early stages of plume development, say in the first half mile of travel, pollutants are subjected to a rapidly changing environment. Both the temperature and composition of the plume change rapidly in this area because of mixing of the hot flue gas with the relatively cool ambient air. Accurate measurements of reactions in this early plume are nonexistent because of the difficulties of aerial sampling in the narrow early plume. Extrapolations of rates of chemical reactions occurring well downstream of the plume origin can be made, but these are not expected to be very accurate unless some accounting is made of the effects of the early cooling and mixing processes.

There are many processes that can contribute to the overall pollutant changes in the early plume. These processes are indicated in Figure 16. In this figure, the physical processes of cooling, dilution, and condensation (the rapid processes) are segregated from the possible (and slower) chemical interactions for purposes of presentation; ultimately physical processes must be considered in concert with the chemical processes. The chemical interactions are then further broken down into homogeneous and heterogeneous categories.

Physical Processes

A detailed discussion of plume modeling is beyond the scope of this study. Rather, it will suffice here to consider the qualitative manner of change of parameters important to the chemical interactions, namely, temperature and relative humidity, as a function of dilution.

Typical stack gas temperatures for coal- and oil-fired power plants are 135 C (275 F) and 437 C (819 F), respectively. Choice of these operating temperatures reflect differences of sulfuric acid dew points in the two types of systems. As a first approximation, it can be assumed that the ambient air mixes uniformly with the stack gas, and that the heat capacity of the stack gas is about the same as that of air. The temperature of the plume of any point T_p, then is related linearly to dilution, i.e.,

$$T_p = fT_s + (1-f)T_a \tag{17}$$

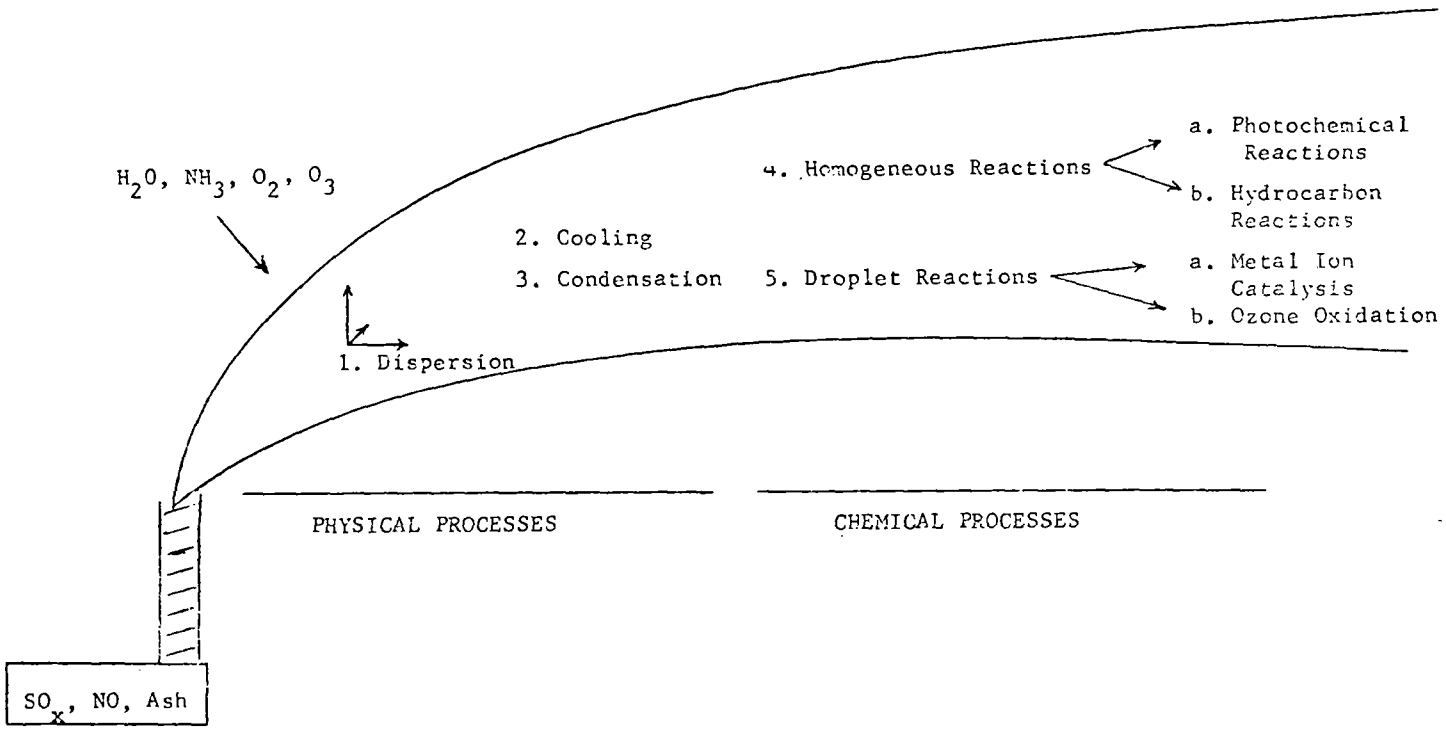

Figure 16. Plume dispersion and reaction processes

where T_s is the stack gas temperature, T_a is the ambient temperature, and f is the fraction of stack gas in a unit volume of plume at any point.

The relative humidity of the plume depends on the plume temperature as well as on the fuel composition and the relative humidity and temperature of the ambient air. At the stack exit, the water content of the stack gas is high, but the temperature is also high. The result is a low relative humitity. As dilution proceeds, both temperatures and average water concentration decrease. However, the relative humidity is linearly dependent on the water concentration and exponentially dependent on the inverse of the absolute temperature. The relative humidity can be given by

$$RH_p = RH_a \left[(fN^p_{H_2O}/N^a_{H_2O}) + (1-f) \left(10^{8.9116} e^{-5174} \left(\frac{1}{T_a} - \frac{1}{T_p}\right)\right)\right] \qquad (18)$$

where $N^p_{H_2O}$ and $N^a_{H_2O}$ are the mole fractions of water in the flue gas and ambient air, respectively. Results of application of Equation 18 to several operating conditions with coal and oil firing are shown in Figures 17 and 18. It is obvious from these figures that appreciable dilution must occur before the plume RH begins to rise significantly. Under some conditions, the plume RH can go through a maximum. These maxima occur when the ambient air is relatively cool and at values of (1-f) in the neighborhood of 0.9. Beyond this point, the RH of the plume approaches that of the ambient air. It is generally agreed that the oxidation of SO_2 to sulfate occurs most readily at RH values greater than 50-70 percent. The approximate relationships between f and distance for a 10 mph wind is shown in Figure 19. Figures 17-19 thus serve as a **guide to estimation of the lag time that may be required** for chemical reactions that are dependent on the relative humidity.

Chemical Processes

Sulfate Formation. The oxidation of SO_2 to sulfate in plumes has been studied extensively in recent years because of the impact of this process on environmental health questions (Gartrell, 1963) (Dennis, 1969) (Coutant, 1972)(Stevens, 1971)(Huser, 1976) (Weber, 1970) (Newman, 1975)(Utah, 1975). In spite of this extensive study, conclusions have only been in qualitative agreement, at best. The basic problem of specification of plume chemistry and kinetics has been tied to the difficulties of aerial sampling combined with the variability of meteorological conditions (Beilke, 1975). Only recently has an attempt been made to coordinate well-characterized chemistry

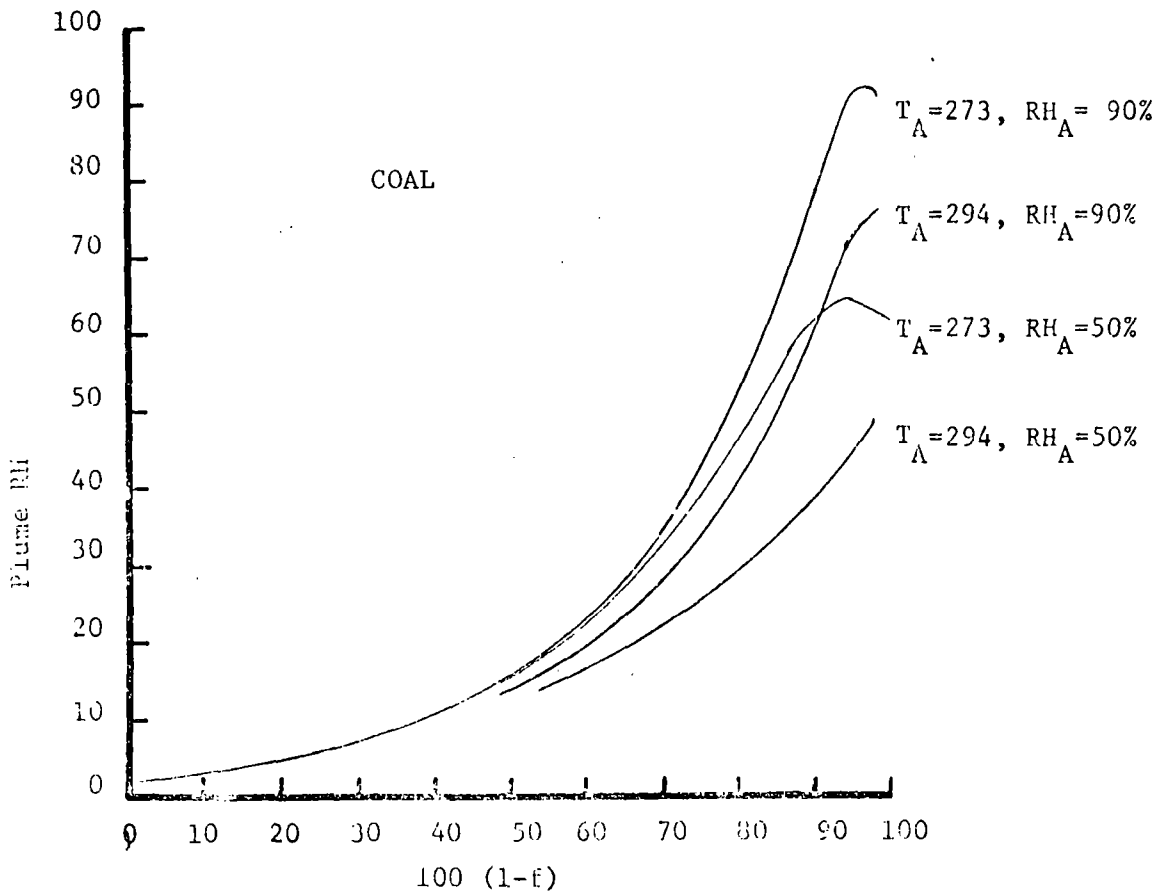

Figure 17. Dependence of plume relative humidity on dilution

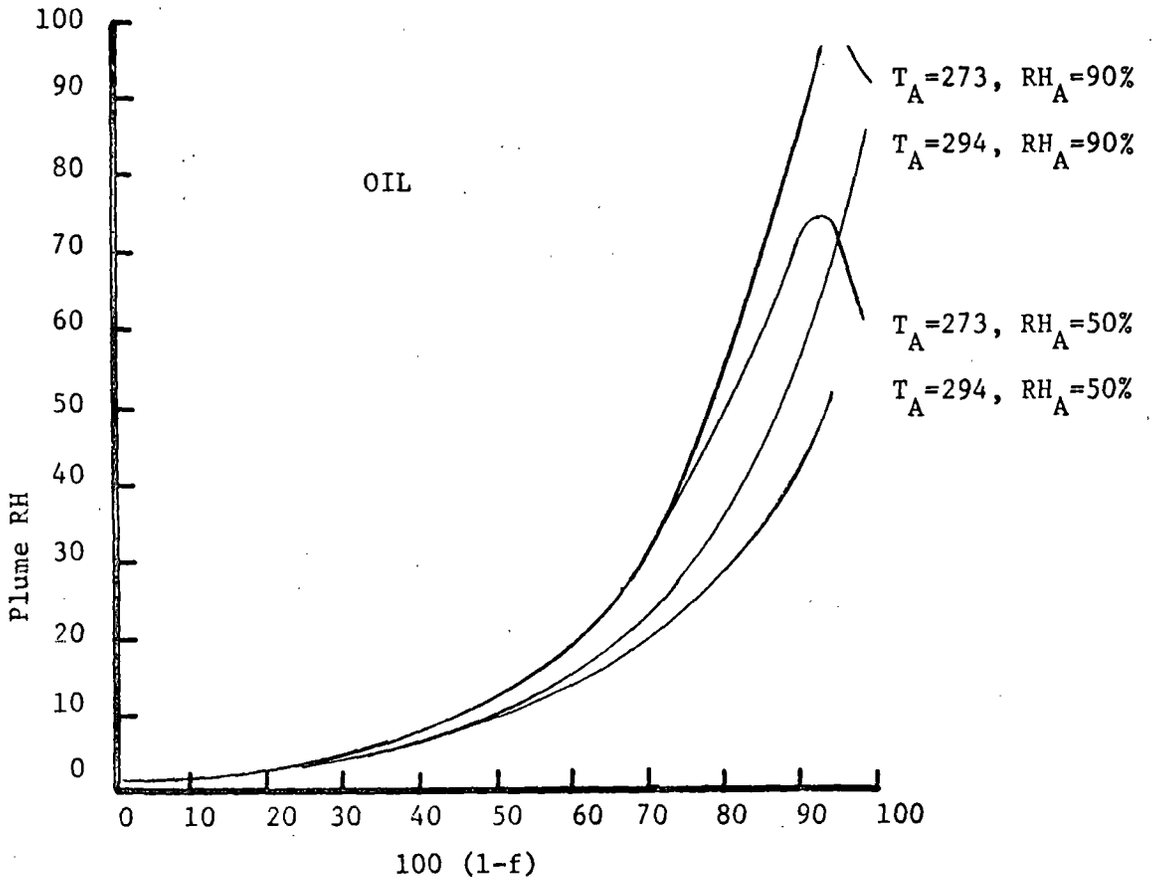

Figure 18. Dependence of plume relative humidity on dilution

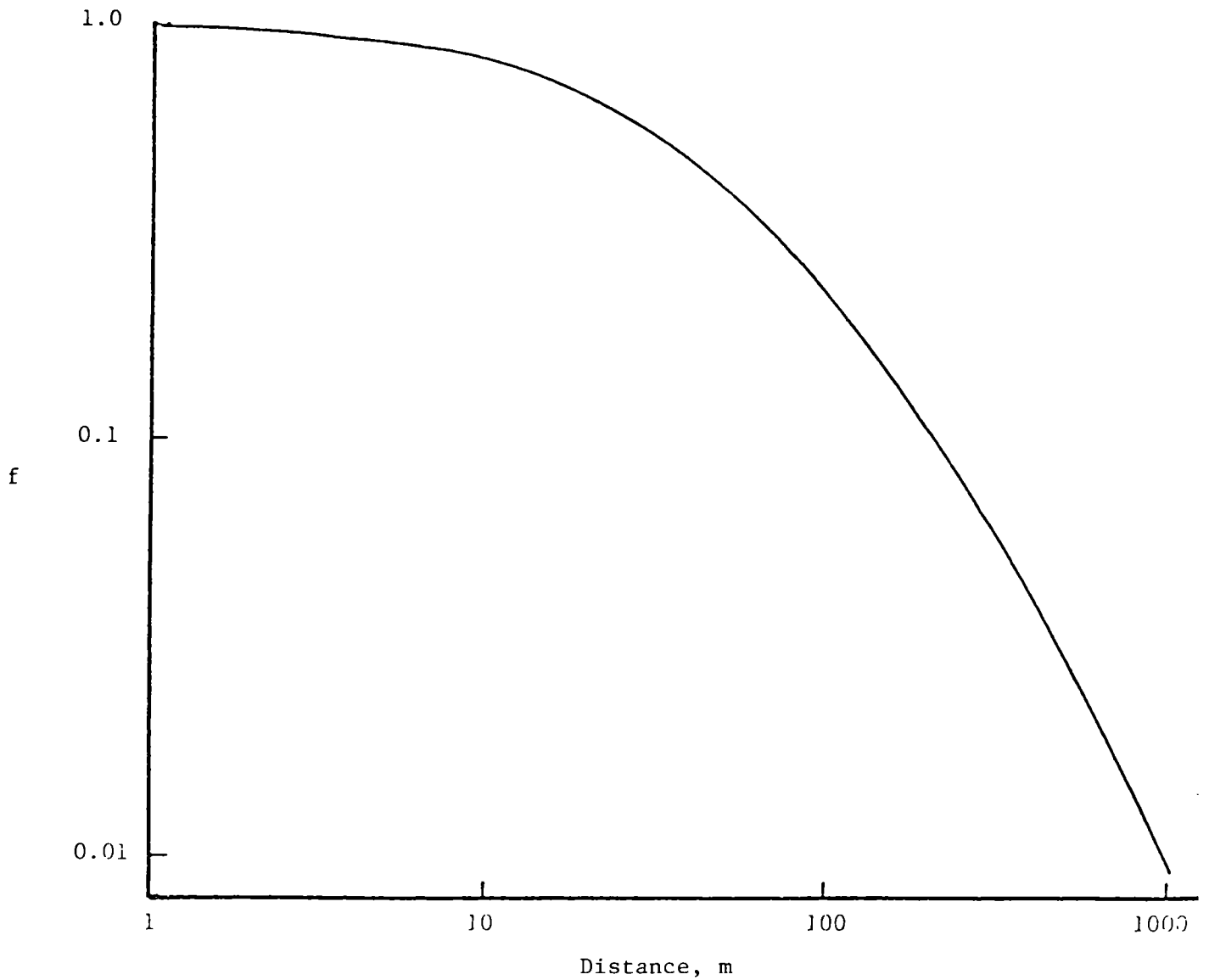

Figure 19. Dilution in early plume

with the variables inherent in plume dispersion to develop a reasonable model of SO_2 oxidation (Freiberg, 1976). Even so, this model has incorporated only one aspect of the possible plume chemistry, namely the iron-catalyzed oxidation of SO_2 in aqueous droplets, and it ignores some aspects of early plume mixing.

It has been argued that many other processes including ozone oxidation, active hydrocarbon reactions, homogeneous oxidant reaction, and nonaqueous heterogeneous catalysis can contribute to the oxidation of SO_2 to sulfate in a plume (Davis, 1975) (Cox, 1974, (Cox, 1972) (Smith, 1974) (Wilson, 1970) (Esponson, 1965) (Penkett, 1972) (Novokov, 1974).

The general status of knowledge on plume oxidation of SO_2 has been reviewed recently by Levy, Drewes, and Hales (Levy, 1976). The preliminary conclusions of Levy, et al, can be summarized as follows:

(1) Plume measurements indicate a range of half-lives for SO_2 of the order of 0.5-10 hrs, depending on meteorological conditions. Ambient temperatures and relative humidity appear to be the most significant variables.

(2) Ozone oxidation of SO_2 in droplets may be important in the downstream portion of the plume, but is probably not important in the early plume where the principal reaction of ozone is with NO.

(3) A lag time in SO_2 oxidation may occur near the stack, but this has not yet been well characterized, there being data both confirming and denying this hypothesis.

(4) Hydrocarbons may promote SO_2 oxidation via photochemical smog reactions.

(5) Considerations of homogeneous gas phase reactions indicates that oxidation by OH could be fast enough to account for some observations, but OH concentrations in a plume are not well-characterized.

(6) Aqueous phase reactions with catalysis by various metal-ion flyash components and NH_3 are known to be fast enough to account for plume observations, and observed relative humidity dependencies suggest these reactions as the principal source of secondary sulfate.

(7) The sorption and oxidation of SO_2 on dry iron oxide or carbon is a capacity-limited phenomenon. Inasmuch as this interaction is said not to be dependent on relative humidity, it may be significant in the early plume, but there exist no data to confirm this hypothesis.

The conclusion that the aqueous phase reactions are most important in the plume oxidation of SO_2 implies that the time lag suggested in Figures 17-19 may be an important factor in limiting the oxidation in the early plume. Also, it should be noted that studies of aqueous phase oxidation of SO_2 indicate a strong inverse relationship between the rate of oxidation and the hydrogen ion concentration in the solution. Various studies yield rates proportional to $[H^+]$.

Droplets formed in the earliest portion of the plume, i.e., near the stack exit are likely to consist primarily of sulfuric acid. This may be partly neutralized by basic components of the fly ash, but it is expected that neutralization of the bulk of the sulfuric acid will occur via reaction with ammonia from the ambient air. Typical concentrations of sulfuric acid in flue gas are of the order of 30 ppm; typical ambient levels of ammonia are of the order of 6 ppb. Thus, a considerable amount of mixing and dilution of the plume with the ambient air is required for neutralization of the sulfuric acid. This too implies the existence of a lag time before appreciable oxidation of SO_2 can occur in the plume. For example, droplets formed near the plume origin are estimated to have a pH of about 3. At a range of about 2.5 km, enough ammonia will have mixed with the plume to form ammonium bisulfate, but the pH at this point will have risen only to about 3.3. Thus, the pH is effectively 3 throughout the first 0.8 km (0.5 mile) of plume travel. The rate of absorption of SO_2 in droplets having this low pH will be very low.

At wind velocities of 5 to 10 mph, the time required for a plume travel of 0.5 mile is 3 to 6 min. Assuming for the moment that there is no time lag, and that the results of previously referenced studies can be extrapolated back to the stack exit, it is estimated that the conversion of SO_2 to sulfate in the early plume is no more than 4 to 7 percent under high humidity conditions. If, on the other hand, one considers the time lag associated with the development of high relative humidity within the plume and neutralization of the sulfuric acid, the apparent overall rate of conversion is

much less. Using the model of Beilke, et al., (Beilke, 1975), we estimate that these effects would confine conversion of 0.3 to 0.7 percent in the first half mile. The recent data of Wilson, et al., indicate about 1 percent conversion after 40 min. and suggest a maximum of only 0.2 percent conversion within 6 min. Of course, little or no conversion is expected in the early plume if the relative humidity of the ambient air is low (Wilson, 1976).

Nitrate Formation. In contrast to the case of sulfate formation, there has been very little attention paid to the formation of nitrates in power plant plumes. In general, the formation of nitrates in the atmosphere is tied to the photochemical reaction chain. In particular, the reaction of ozone with NO to produce NO_2 followed by reactions of the NO_2 is generally believed to be the major route for nitrate formation. In recent studies under the MISTT program, Wilson, et al., have verified the consumption of ozone by NO in the early plume (Wilson, 1976). Their results show that the mass flow of NO_2 in the plume is (within an experimental error of 20 percent) equal to the loss of ozone in the air mixed with the plume. Again this reaction depends on mixing of air with the plume. At ambient levels, of say 80 ppb ozone and flue gas concentration of say 200 ppm NO, large volumes of air will be required for appreciable conversion of the NO to NO_2. Assuming instantaneous reaction, only about 3 percent of the NO is converted to NO_2 after one-half mile travel.

Heterogeneous reactions of NO also are possible in the plume. For example, the sorption of NO on various metal oxides including Fe_2O_3 has been documented by a number of investigators (Otto, 1970). In reducing systems, this sorption can be the first step in catalytic reduction of the NO to N_2O and/or N_2. In oxidizing atmospheres, NO is converted largely to nitrates on these surfaces. Unfortunately, there has been little done to determine the significance of these reactions with respect to fly ash surfaces in plume like atmospheres.

The kinetics of NO and NO_2 reactions in the early plume are even less well characterized than in the case of sulfate formation. The work cited above suggests the possibility of formation of nitrates in the early plume in both daylight and nighttime conditions, but current information does not allow estimation of the extent of nitrate formation. Based on thermodynamic

considerations and the low nitrate values of ambient particulate, primary nitrate aerosols and/or early plume nitrates are probably negligible.

SUMMARY

In the high temperature regime, the reactions involving nitrogen and sulfur are largely homogeneous gas phase reactions leading to the formation of NO and SO_2. As the temperature falls, it would be expected based on thermodynamic equilibrium, that further oxidation would occur. However, various kinetic contraints allow this to occur to only a limited extent.

At lower temperatures, on the other hand, catalysis of SO_2 oxidation by certain metal and metal oxide species may be a significant mechanism in the formation of primary sulfate emission. Combustion conditions and metal species volatility will determine the resulting fly ash surface area availble for catalytic action. Capacity considerations, determined by active surface area, may constrain the total amount of SO_2 converted to sulfate. Temperature is an important consideration, and well defined temperature "windows" exist, outside whose range catalytic reactions of SO_2 do not occur rapidly. This is especially true of vanadium which is very active at high temperatures but quite inactive in the near plume or ambient temperature zone.

There is some qualitative evidence that soot and carbon particles may also catalyze SO_2 oxidation. The extent of oxidation possible and the relationship between activity and surface area, temperature and other variables have not been established. However, it seems prudent at this time to assume that carbon may contribute to primary sulfate formation.

Boiler deposits also may form complex sulfates, which, when removed by soot blowing, may overload the precipitator and contribute significantly to primary sulfate emissions.

Based on the foregoing, it seems prudent to speculate that formation of sulfate through fly ash/soot catalysis is at least as important a mechanism for $SO_4^=$ formation as the high temperature homogeneous mechanism. Its magnitude is likely to be a strong function of combustion conditions, and fuel composition.

The formation of sulfates and nitrates in the early plume is strongly limited by mixing and dilution processes. In the case of sulfates, the time

associated with cooling sufficiently to gain high relative humidities, and the relatively long time required for neutralization of the existing sulfuric acid combine to limit the further oxidation of SO_2 to <0.3-0.7 percent in the early plume. In the case of nitrate formation, the reaction between ozone in the ambient air and NO in the plume can be taken as instantaneous, but the mixing rate is slow enough to limit NO conversion to only about 3 percent in the first half mile of plume travel.

However, it is important to keep speculation about mechanisms in perspective with regard to the formation of primary acid aerosols. In general, NO_2 and SO_3, precursors to acid, are found to be only several percent of the NO and SO_2 in the combustion system effluent. Sulfate is found, occasionally at high levels, in fly ash and when gaseous and particulate sulfates are combined , the total may be of the order of 10 percent (Homolya, et. al., 1976). Nitrate is almost never observed. Chlorine in the fuels would be expected to produce some HCl in the effluent but there is virtually no data on this point. However, HCl has been observed (Piper, 1958) and in one case for a power plant burning pulverized coal, it was determined that virtually all the fuel chlorine appeared as HCl in the flue gas (Iapalucci, et. al., 1969) but the fuel chlorine is generally low for most US coals. This observation is in general agreement with the thermodynamic considerations discussed previously. Thus, based on data presently available to us, to the extent that there is a primary acid aerosol problem, it is a problem of SO_3 and sulfate. The situation may be summarized by considering the results of Cato (Cato, 1974) and Sommer (Sommer, 1975) shown in Figure 20. Where the ratio of SO_3 to (SO_2 + SO_3) is shown for a variety of fuels with a range of sulfur contents in a number of different boiler systems. The apparent increase in conversion to SO_3 at low sulfur concentration may be real or it may reflect the uncertainty of current analyses at low concentrations.

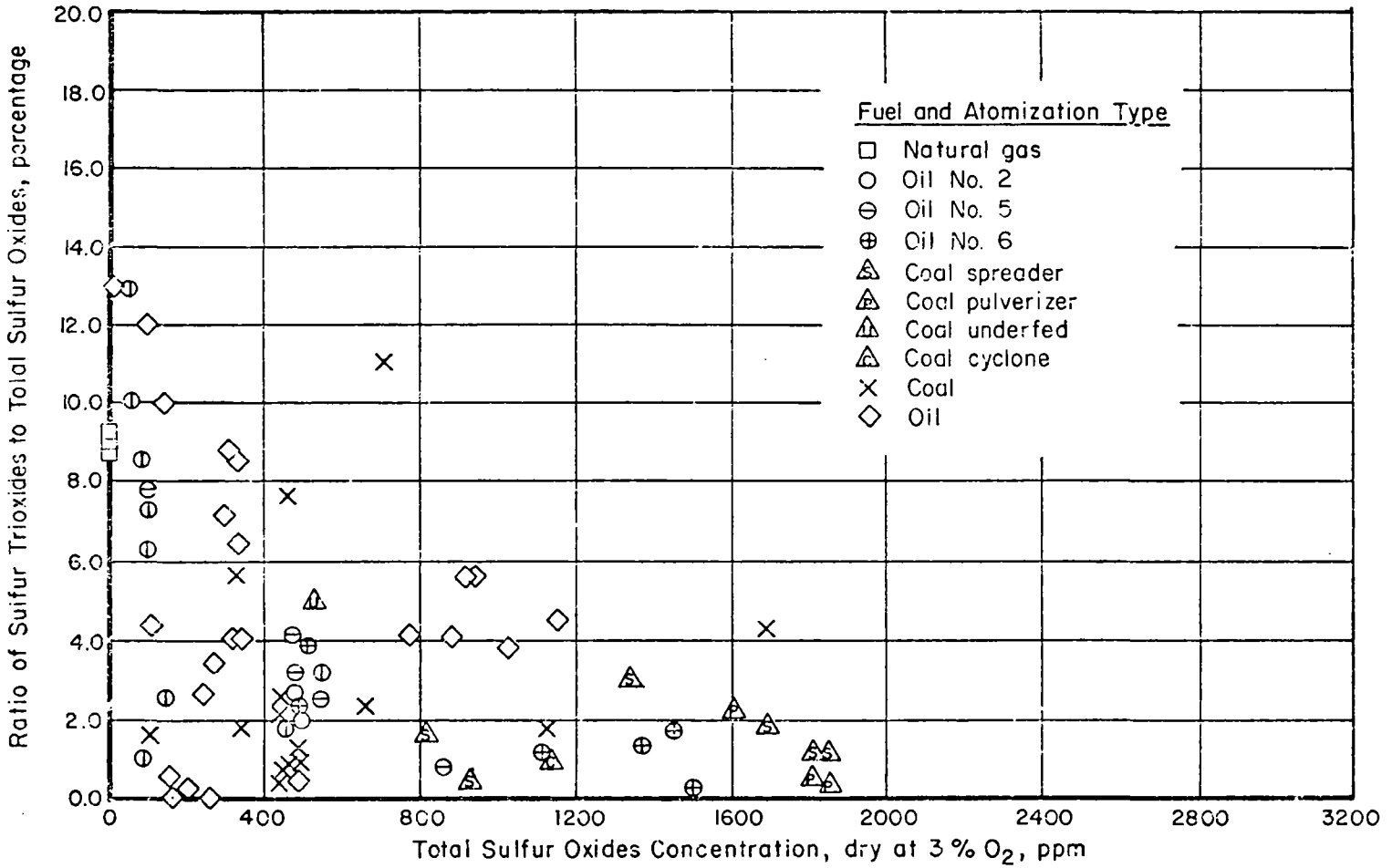

Figure 20. Ratio of Sulfur trioxides to total sulfur oxides as a function of total sulfur oxides measured

SECTION VI

PILOT AND FIELD STUDIES

In this section, and those that follow, the data from field tests and pilot studies of large stationary sources with respect to acid aerosols emitted and the effect of combustion modification (CM) on those aerosols are summarized. Types of combustion modification, which change conditions in the first regime, are described first, followed by a discussion of available data on flue gases. This is followed by a discussion of available pilot and field data on particulates and deposits in light of possible heterogeneous reactions in the second regime. At the outset, it is important to recognize that such data are sparse and, in general, it is difficult to say that a given change in acid aerosol is the result of a specific combustion modification. The following sections, therefore, contain considerable speculation wherein we attempt to predict the effect, if any, of CM on acid aerosol based on meager field data and extrapolation from basic studies.

For the purposes of this program, only a few general types of CM are considered, all of which are currently considered for control of NO/NO_2. At the present time, CM definitions are rather loose and not all authors agree as to what should be considered as CM. The basic approaches and their many variations have been described in detail by others, e.g., Brown (Brown, 1974), Shimizu (Shimizu, 1975), Salooja (Salooja, 1972), and Lachapelle (Lachapelle, 1974). This study is concerned primarily with staged combustion, flue gas recirculation, low excess air and the effects of fuel composition including additives.

In staged combustion, the fuel is burned in what amounts to two steps. In the first stage combustion proceeds with only 90 percent or less air relative to stoichiometric. Too great a deficiency will result in smoke. Heat then is removed from the products. After removal of sufficient heat, the remaining air is added and the combustion process completed in the

second stage with an overall excess of air. There are several terms that are used to designate variations on this method; the terms are not mutually exclusive and are not well defined. However, in general, two-stage combustion (Barnhart, 1960) (Beer, 1973) (Dykema, 1975) (Atkins, 1975) and overfire air jets (Crawford, 1975) are similar. The terms off-stoichiometric firing (Bagwell, 1971) (Breen, 1973) (Jain, 1972), biased firing (Cato, 1974), and BOOS firing (Dykema, 1975) (Burner Out of Service) are applied to the more general cases where, in an array of burners, some will be fired fuel rich and the remainder will be fired fuel lean. In practice, the latter generally seems to mean with no fuel.

Reburning is similar in concept to staged combustion, and is actually a type of staged combustion. The fuel-air mixture is initially burned with large excess air to keep the thermal NO_x production down, some heat is removed, and then additional fuel is added and burned to return the ultimate mixture ratio to an acceptable value.

In flue-gas recirculation, part of the products of combustion, taken from some point in the furnace system after a significant amount of heat has been extracted, are added to the furnace air supply. Thermal NO_x is reduced because of the reduction in peak temperature. For an as yet unexplained reason, particulate production is also decreased. From a thermodynamic point of view, the products at any temperature for a given overall fuel-air ratio are the same for staged combustion and flue-gas recirculation. Flue gas recirculation can be used both in retrofit and new designs but it is more effective in NO_x reduction for gases and light oils than for heavy oils and coal (Shimizu, 1975).

It is well known that the use of as low excess air as possible leads to more effective use of the thermal energy in the gases. Furthermore, NO_x and SO_3 production are reduced because of the lowering of O_2 in the primary flame zone. On the other hand, CO production will increase. Usually, the minimum value of excess air is determined when an acceptable smoke number is exceeded. Better balancing of multiple burner fuel and air supply, and better mixing in each burner aids in reducing the excess air, which is currently routine practice in utility boilers.

SO_3 (H_2SO_4) IN FLUE GAS

Staged Combustion

There is little experimental information from practical-sized equipment on the effect of staged combustion on SO_3. The pilot scale work of Archer, et al., (Archer, 1970) investigated two-stage combustion of a high vanadium residual oil with 2.4% sulfur. They presented the data shown in Figure 21 for the SO_3 concentration leaving the first combustion chamber portion of the furnace. These results demonstrate that SO_3 can be reduced essentially to zero when the first stage is slightly fuel rich. They explain their results by noting from previous work that carbonaceous particles inhibit SO_3 formation, react with SO_3, and physically adsorb it. Such changes do not mean SO_3 is completely eliminated from the boiler, however. When air is added at the second stage to complete combustion SO_3 may well be formed, as demonstrated by Hedley (Hedley, 1967), in excess of that which would have been formed in single-step combustion with the same total air. Also, heterogeneous reactions in the boiler section of the system may produce as much SO_3 in spite of staged combustion. This position was summed up by Schwieger (Schwieger, 1974) "...catalytic oxidation of SO_2 to SO_3 in the superheater and reheater section generally is considered to contribute most of the SO_3. Thus, there might be an unacceptably high level of SO_3 at the air-heater inlet despite an acceptable SO_3 level at the furnace outlet." Pilot scale and more basic studies tend to confirm this expectation, for instance, the previously discussed work of Glebov, et al., (Glebov, 1973), (page 62). However, there is not data from practical systems which substantiate these heterogeneous effects when staged combustion is used.

Flue Gas Recirculation

The situation is quite similar when flue gas recirculation is used. It is well known that thermal NO and NO_2 are reduced by this CM (Tomany, 1971)(Turner, 1972)(Rawdon, 1973)(Muzio, 1974)(Armento, 1974) but there is little direct evidence on SO_2 and SO_3. In one investigation Koizumi, et al., (Koizumi, (1969), in studying the combustion of a 2-1/2 percent sulfur heavy fuel oil in a compact combustor (about 10^7 W/m^3), noted that the variable flame length, for the excess air conditions used, decreased as recirculation

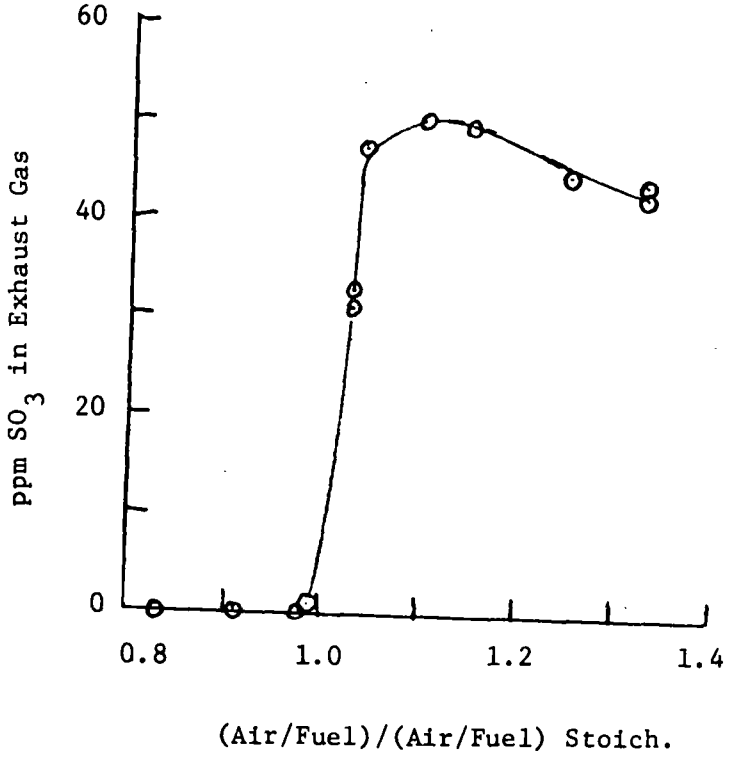

Figure 21. Concentration of SO_3 in exhaust gas of the first stage combustion section for air atomization of residual oil with 2.4% sulfur

increased up to 20 percent, then increased slightly up to 40% recirculation, before starting a final decrease. Furthermore, the acid dewpoint (measured just beyond the combustor) showed a parallel trend. In fact, the acid dewpoint correlated quite well with the flame length. The authors ascribe this effect to improved mixing. Whether this acid decrease would be maintained in view of possible heterogeneous reactions in other parts of the system is questionable. However, at this time there is essentially no data regarding SO_3 from practical systems employing this CM.

Low Excess Air

It is well known that low excess air is effective for reducing NO and NO_2 (Barrett, 1973) (Brown, 1973)(Brown, 1974) and limiting acid in boilers. Basic studies indicates that as excess air approaches zero the ratio SO_3/SO_2 also approaches zero. Csaba (Csaba, 1974) and Macfarland(Macfarland, 1962) compute theoretically the values for various mixture ratios, for specific fuel compositions and a range of product temperatures. They demonstrate the expected increase in ratio of SO_3 to SO_2 as the excess air increases. It should be noted that the effect of mixture ratio on the SO_3/SO_2 ratio persists throughout the furnace in their calculations. These results are consistent with "normal" conversion of SO_2 to SO_3 at this point which Gills reported as 0.2 percent to 2.5 percent. (Gills, 1973)

Koizumi, et al. (Koizumi, 1969), showed for their compact heavy fuel oil combustor that the acid dewpoint, for 2.5 percent sulfur fuel, rose very rapidly from 50 C at 1/2 percent O_2 (the same value as with no sulfur) to about 110 C (230 F) at 1 percent O_2, and 125 C (257 F) at 4 percent O_2.

Experience with oil-fired systems, where low excess air operation is most practical at the present time, has demonstrated that this mode of operation minimizes the formation of sulfates in deposits in the high temperature portion of the boiler, reduces the amount of sulfuric acid formed, and eliminates the emission of acid smuts. Successful operation with low excess air requires that the oxygen in the flue gas be maintained at levels below 0.2 percent. Such operation requires precise control of the fuel-air ratio in all parts of the combustion system to prevent thermal cracking of hydrocarbons and the emission of smoke. Consequently, low excess air operation has been limited to oil-fired systems, because the technology for burning pulverized coal with such little oxygen does not exist.

Normal operation with 12 to 20 percent excess air results in the formation of 25 to 30 ppm SO_3 in the flame with fuels containing 2 to 3 percent sulfur. The excess air must be less than 2 percent to decrease the SO_3 by about half. Further lowering of the excess air results in a rapid drop of the SO_3 level, and at about 0.1 percent oxygen in the flue gas the SO_3 concentration will be reduced essentially to zero.

The first experience with reducing the excess air in boilers occurred at several power stations in England. Crossley reported that at the Marchwood station where the SO_3 content had been about 20 ppm and the sulfuric acid dewpoint was near 150 C (300 F), a reduction in excess oxygen from 3 percent to about 0.5 percent resulted in a reduction in SO_3 to about 3 ppm and a drop in the dewpoint to 121 C (250 F). Similar results were obtained in three other stations as shown in Table 7(Crossley, 1959).

By redesigning the oil burners and exercising very close control on the fuel-air ratio, Glaubitz in Germany was able to lower excess oxygen to 0.2 percent for routine operations. Under these conditions, the surfuric acid was reduced to such an extent that the dewpoint approached that of water, as shown in Figure 22. Glaubitz stated that after 12,000 hours of operation, the boiler still did not have to be shut down for cleaning, indicating that the strongly bonded deposits which build up as a result of the formation of large amounts of sulfates had not developed in this boiler (Glaubitz, 1963). In later work Glaubitz measured the SO_3 concentration as a function of the oxygen in the flue gas in the oil-fired boiler. As shown in Figure 23, the SO_3 concentration drops rapidly as the oxygen in the flue gas becomes less than 1 percent (Glaubitz, 1963).

Low Air Preheat

Lower air preheat is another change of input conditions which lowers the formation of NO and NO_2. There is considerable information regarding the lower preheat effect on the SO_3/SO_2 ratio. However, as Glebov(Glebov, 1973) points out, "data on the influence of flame temperature on process of formation of SO_3 is very inconsistent. It has been firmly established that in pulverized-fuel-fired boilers, the content of SO_3 in the gases decreases --with increasing temperature in the furnace. However, Crumley, et al., (Crumley, 1956) on the basis of experimental data they obtained..." using

TABLE 7. EFFECT OF EXCESS OXYGEN ON SO_3 CONTENT AND DEWPOINT

	Excess O_2, %	SO_3, ppm	Dewpoint, F
Marchwood	3	20	270-320
Marchwood	0.5	2-7	240-255
Poole	<0.6	5	180
Poole	4	45	320
S. Denes	1.7	--	260
Ince	4.5	18	--
Ince	1.0	7	--

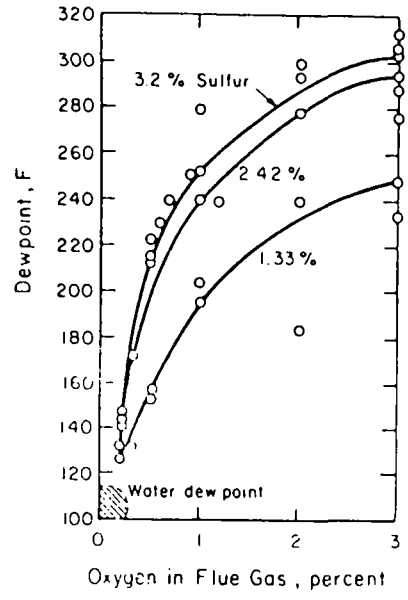

Figure 22. Decrease in dewpoint with low excess air in an oil-fired boiler furnace

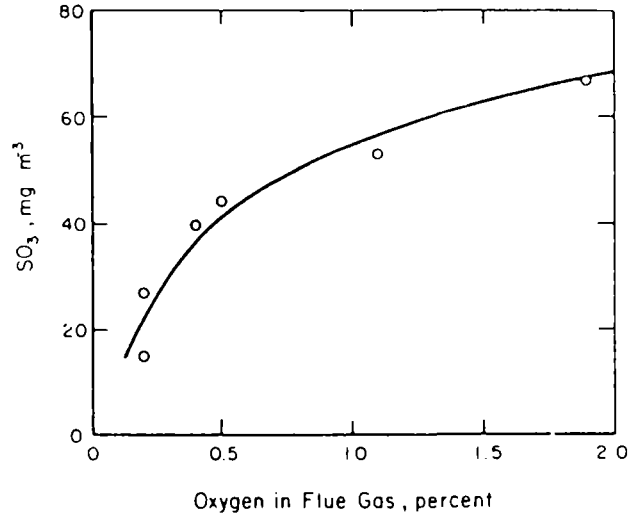

Figure 23. Effect of excess air on SO_3 level in oil-fired boiler furnace

kerosene and distillate show an increase in SO_3 to a flame temperature of 1750 C (3182 F) followed by a leveling off. The difference in the results from the two fuels is considerably less than the difference in 2 percent sulfur in the kerosene and 3 percent in the distillate. At 70 percent excess air with kerosene, about 7 percent of the sulfur was in the form of SO_3; at 28 percent excess air, about 5 percent.

Glebov (Glebov, 1973), in agreement with Macfarland (Macfarland, 1962), Csaba (Csaba, 1974), and Gudzyuk, et al., (Gudzyuk, 1972) shows with thermodynamic calculations that the SO_3/SO_2 ratio decreases with increasing preheat temperature. But Glebov's data on the combustion of high sulfur fuel oil show a constant value of SO_3 from 2100 to 2500 C (3800-4530 F) for two values of excess air. Gudzyuk, et al., (Gudzyuk, 1972) indicate possible effects on SO_3 of high excess air regions near cool walls which might explain some of the contradictory results. As discussed in the section on fly-ash chemistry, SO_3 can be removed from the flue gases by reaction with metal oxides to form solid sulfates, thus reducing the SO_3 concentration in some regions. Or heterogeneous reactions might increase SO_3 under some conditions. Therefore, it is virtually impossible without additional data to predict what the effect of lower air preheat on SO_3 might be in a given system.

Load Reduction

Based on very meager data, it appears that load reduction has no significant effect on SO_3 emissions. Glebov (Glebov, 1973) found no effect of load on SO_3 over a range of 20 percent to 80 percent design load in his study of high sulfur, heavy oil in an experimental furnace. In his theoretical computations he found no change in going from 100 percent to 70 percent load, assuming a catalytic activity of deposits equivalent to that produced by Fe_2O_3, but some increase in SO_3 with decreasing load, assuming catalysis by V_2O_5.

ADDITIVES

Although additives are not generally included in the class title "combustion modification", it was felt that in the special context of this study, referring as it does to acid aerosol production, some comment should be made. Schwieger (Schwieger, 1974) sums up his review of additives by

noting that to control SO_3 the addition should minimize catalytic oxidation of SO_2 to SO_3, react with or absorb SO_3, or neutralize H_2SO_4. The traditional additives for this purpose are MgO and MgO/Al_2O_3. Krause, et al., (Krause, 1976) state that "Significant control of SO_2 or total sulfur emissions by additives does not appear to be possible, although emissions of SO_3 can be controlled."

An early investigation of additives for SO_3 control was conducted by Rendle and Wilsdon who used an experimental furnace which burned 6 to 10 pounds per hour of residual fuel oil (Rendle, 1956). These investigators tried a variety of materials which were fed into the oil-fired furnace at a combustion chamber temperature of 1000 C (1830 F) and 25 percent excess air. The results of their experiments can be summarized as follows:

(1) Powdered SiO_2 gave a maximum of 50 percent reduction in SO_3 concentration, presumably by physical absorption of the sulfuric acid formed.

(2) Carbon blacks did not change SO_3 concentration significantly.

(3) Tars containing pyridine and other organic nitrogen compounds did not change SO_3 levels appreciably.

(4) Oil soluble magnesium and zinc naphthenates completely eliminated SO_3 from the gas stream. The magnesium compound was slightly more effective than the zinc derivative because less material was required for the same effect.

(5) MgO, zinc dust, and dolomite also were capable of removing all of the SO_3 but relatively large amounts of these materials were required.

In each case the amount of additive required was equal to or greater than the stoichiometric amount required to react with the SO_3 in the gas stream. For compounds of the same metal, the oil-soluble materials proved to be more efficient.

Similar success with magnesium and zinc compounds has been reported by other investigators in the laboratory and by actual practice in full-scale boilers. Flint and coworkers, using a small refractory furnace fired with residual oil, also showed that zinc naphthenates could be used to eliminate

SO_3 from the gas stream (Flint, 1953). In their furnace system, 0.07 weight percent of the zinc naphthenate reduced the SO_3 by 75 percent, while twice this amount of the zinc compound completely eliminated the SO_3. In another laboratory-scale study with residual oil, Lewis observed that SO_3 could be completely eliminated by the addition of 0.07 weight percent magnesium in the form of magnesium naphthenate (Lewis, 1955). He also tried an oil soluble zinc compound, but found it to be less effective than the magnesium naphthenate.

In full-scale boiler applications of additives, the Florida Power Corporation found dolomite to be partially effective. Huge and Piotter have reported that at the Inglis Station the addition of 0.1 weight percent of dolomite as a slurry in the fuel oil resulted in about 33 percent reduction in the SO_3 concentration in the flue gas. At the Higgins station, the dolomite was introduced in the combustion air as a dry powder. In this case, 0.1 weight percent of dolomite reduced the SO_3 by 42 percent. However, doubling the amount of dolomite resulted in only a 50 percent reduction in SO_3 (Huge, 1955).

Experience in England at the Marchwood station was reported by Wilkinson and Clarke (Wilkinson, 1959). In this case residual oils containing up to 4.5 percent sulfur constituted the fuel. The addition of dolomite, which was introduced in the vicinity of the burners at a rate of 3 to 4 pounds per ton of fuel, brought about an 80 percent reduction in the SO_3 levels. Magnesium carbonate also was tried, and the 75 percent reduction in SO_3 was achieved with the addition of 1 to 2 pounds of additives per ton of fuel burned. An effort was made to use magnesium oxide similarly as an additive but the fouling and clogging problems which resulted made its use ineffectual in this case.

A combination of the magnesium additive with low excess air operation was reported by Reese, et al (Reese, 1965), who added magnesium metal to the furnace at various locations in a large oil-fired unit which had been experiencing problems with boiler tube corrosion as well as with emissions of acid smuts from the stack. The addition of granular magnesium metal (20 to 59 mesh) to this oil-fired furnace reduced SO_3 in the gases by 60 to 75 percent in different parts of the boiler system. In addition, the emission of acid smuts was stopped. Although low excess air contributed

part of these beneficial results, important benefits were attributed to the MgO which resulted from the combustion of the metallic magnesium. It was suggested that the MgO coated the catalytic tube surfaces and eliminated this mode of formation of SO_3. Evidence that this mechanism was indeed operative was obtained from the fact that 12 pounds of magnesium will neutralize 40 pounds of SO_3, whereas the total SO_3 in the flue gases in this furnace were reduced by 57 pounds per hour when 12 pounds per hour magnesium was added.

The combination of a magnesium oxide additive with low excess air operation also has been reported favorably by Exley of the Long Island Lighting company (Exley, 1966). Four power stations of this company used the additive treatment to reduce acid stack emissions. In addition, magnesium vanadate was recovered from the deposits in the furnace in sufficient quantity to make it worthwhile selling the residue for its vanadium value.

In working with a research boiler fueled with residual oil, Lee and his associates developed an additive which consisted of a mixture of hydrated MgO and Al_2O_3 having a magnesium-to-aluminum ratio of 9 to 1 (Lee, 1969). It was demonstrated that SO_3 can be completely eliminated from the flue gases by the use of this additive in a concentration of 0.1 volume percent in the oil.

There have also been some attempts to use magnesium compounds as fuel or combustion zone additives in coal-fired systems. Michel and Wilcoxson (Michel, 1955) observed that dolomite used at a rate of 7.5 pounds per ton of coal reduced the SO_3 concentration by 50 percent. Doubling the dolomite addition reduced the amount of SO_3 by 90 percent.

Corbett and Fling (Corbett, 1953) added zinc ore concentrate to coal used in stoker-fired boilers at the Brimsdown Power Station. The zinc oxide smoke generated in this fashion eliminated the SO_3 from the flue gases when the additive was used at a concentration of 0.25 weight percent.

The net result of the use of an additive is to form a metal sulfate such as $MgSO_4$ or $ZnSO_4$ instead of sulfuric acid. The formation of these solid particulate compounds will be beneficial to the extent that they are removed by the electrostatic precipitator. Even if they are not removed from the flue gas stream completely and some particulate sulfates are

emitted to the atmosphere, it may still be of benefit to have them in the form of the matal sulfate rather than as a sulfuric acid aerosol. Similar considerations can be applied to the situation with the vanadium in fuel oil because the magnesium vanadate formed by the additive is a high melting compound which will not be held in the tube deposits and passes through the boiler system. As in the case with the sulfates, that portion which is not removed in the electrostatic precipitators will appear in the particulate emitted from the stack. In this case it becomes a question of whether it is better to have vanadium oxides or magnesium vanadate as the particulate material which is distributed through the atmosphere.

SULFATE IN FLY ASH

The composition and characteristics of particulate matter generated in the combustion process depend on a wide variety of variables including fuel composition, firing method, flame temperature, and amount of oxidant or excess air. Coal and No. 5 and No. 6 fuel oil are the two general types of fuels of most interest in generation of particulate emissions because of their significant ash content and also potential for containing significant amounts of sulfur. This results in their being possible generators of acidic particles or particles rich in sulfates. They also contain significant bound nitrogen, but as explained earlier, nitrates are too unstable and it is not surprising that we have uncovered no nitrate particulate information in this study. This part of the report addresses the composition and characteristics of sulfate particulates generated during the combustion process.

Sulfates in Coal Fly Ash

As discussed previously (page 58) most of the mineral matter in coal is made up of kaolinite, calcite, and pyrites. The major elements found in the fly ash are from these minerals and consist of mostly Si, Al, Na, Mg, K, Fe, and Ca. Table 8 illustrates concentration of the major ash constitutents for a variety of coals taken from the general literature. These analyses are in general agreement with those of Table 6 (Catalytic Oxidation, page 61). Table 8 also illustrates some typical measured concentrations of fly ash sulfur compounds, reported as SO_3, which are of major interest in analyzing the impact of fly ash as a primary acid aerosol or sulfate. This

TABLE 8. RANGES OF MAJOR FLY ASH CONSTITUENTS FOR A VARIETY OF COALS

Reference		SiO_2	FeO	Fe_2O_3	Al_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	SO_3	Ignition Loss	Other	Comments
Davis, 1938	Max	49.0	4.3	19.0	30.6	1.5	10.6	1.9	2.2	2.6	2.3	27.9	0.8	Results of 13 different fly ash samples
	Min	30.3	1.3	3.9	16.4	0.8	1.2	0.5	0.4	1.1	0.4	1.5	0.1	
	Average	40.9	2.8	0.2	24.1	1.1	4.3	1.0	0.9	1.6	1.2	11.5	0.4	
Walker, 1974	Max	60.0	18.1		28.1	1.6	28.2	8.1	6.1	2.5	24.2	—	—	13 different fly ashes all with low sulfur western coal
		17.3	3.3		11.2	0.2	8.0	1.5	0.2	0	0.05	—	—	
Bolton, 1975		10.0	23.5		3.5	0.25	0.5	0.9	0.3	—	10.5	—	—	1 test on medium sulfur coal (5.1 percent)
Bickelhaupt, 1974	Max	60.9		5.3	29.2	2.0	23.7	5.4	3.1	1.2	1.8	—	—	6 different fly ashes all with low sulfur western coal
		40.1		3.4	17.8	1.1	6.8	0.9	0.1	0.3	0.3			

data is supplemented by Table 9 showing ranges of fly ash composition given by Walker for 46 coals (Walker, 1974).

Generally, the sulfate level (reported as SO_3) is on the order of less than 1 percent up to about 2 percent. Two cases studied by Walker, however, yielded sulfate contents of over 20 percent with the higher case being 24.2 percent (Walker, 1974). Bolton also recorded an unusually high sulfur content (reported in this case as sulfur instead of SO_3) in one particular coal fly ash sample (Bolton, 1975). It is difficult to say why these high fly ash sulfur contents were recorded. They apparently have no relation to coal sulfur content as the two high readings obtained by Walker were on coal of less than 1 percent sulfur while coal used in the Bolton test has a sulfur level of over 5 percent. Also, of all the 13 coal/boiler combinations analyzed by Walker only 3 had over 6 percent sulfate in the fly ash as SO_3 despite the fact that in all cases coal sulfur content was less than 1 percent. Table 10 shows variations in the ranges of concentrations of Na, Ca, Mg, K, and Fe in Walker's data for the 3 cases with high sulfate compared to average high and low ranges for 7 cases with low sulfate. Na, Ca, and Mg were consistently higher in the high sulfate cases whereas K and Fe exhibited no clear trend.

Additional data on sulfate content in fly ash is shown in Table 11. Three of these cases show sulfate contents for two different locations in the boiler. Where SO_3 is added ahead of the electrostatic precipitator (Oglesby, 1975) to enhance ESP performance, a clear increase in sulfate content is shown at the ESP outlet. Three out of four readings taken at the air heater and stack (Burton, 1973) show a clear increase in sulfate concentration in the stack. A fifth reading taken with soot blowing illustrates a clear increase in sulfate concentration at the air heater but a low reading in the stack.

Photomicrographs of particles collected in the stack of the coal-fired Thomas A. Allen Steam Plant of TVA revealed a "fuzzy" coating on the surface (Bolton, 1974). This fuzzy coating was determined to be a sulfur compound by scanning electron microscope fluorescence analysis combined with ion etching by bombardment with argon ions. This would indicate that sulfur in fly ash is primarily present as a coating on the surface of the fly ash particles.

TABLE 9. CHEMICAL ANALYSIS OF ASH FROM 46 PUBLIC UTILITIES AS GIVEN BY WALKER, 1974

Constituent	Percent
Carbon as C	0.37 - 36.2
Iron as Fe_2O_3 or Fe_3O_4	2.0 - 26.8
Magnesium as MgO	0.06 - 4.77
Calcium as CaO	0.12 - 14.73
Aluminum as Al_2O_3	9.81 - 58.4
Sulfur as SO_3	0.12 - 24.33
Titanium as TiO_2	0.50 - 2.8
Carbonate as CO_3	0.05 - 2.6
Silicon as SiO_2	17.3 - 63.6
Phosphorus as P_2O_5	0.07 - 47.2
Undetermined	0.08 - 18.9

This same sulfate coating effect was also observed for ten fly ash samples. (Burton, 1973). The investigators found that the sulfur was present as a sulfate and that the degree of surface coverage by the sulfate coating varies from 5 to 40 monolayers. A less firm conclusion was that the sulfates may be iron or calcium compounds because a close match was found between the binding energies of the S^2P electrons to those for sulfates of polyvalent cation such as Fe^{+2}, Fe^{+3}, and Ca^{+2}.

In addition to the major ash constitutents discussed, fly ash also contains a long list of minor or trace constituents. The accuracy of determining the concentration of these elements varies considerably and techniques of measurement are still being developed. Nevertheless, certain of these trace elements may be of importance in determining the potential for particulates formed in combustion to affect the emission of acidic aerosols.

The six elements identified as having the most potential for catalytic effects for converting SO_2 to SO_3 in the flue gas are V, Fe, Ni, Pt, Na, Cr, and Cu. The approximate concentrations of these elements as reported in 3 different studies are given in Table 10. The recent results of both Sheibely (Sheibley, 1975) and Abel and Rancitelli (Abel, 1975) are related to an NBS/EPA Standard fly ash sample. The results of Bolton are based on results of fly ash samples taken from the Thomas A. Allen Steam Plant in Memphis, Tennessee (Bolton, 1975). Two numbers are given for the Bolton results indicating measurement by neutron activation analysis (NAA) and by spark source mass spectrometry (SSMS).

As reported earlier in Tables 7-9, iron and sodium are major constituents in fly ash and this also shows in Table 12. Vanadium, chromium, and copper also occur in measurable quantities on the order of several hundred ppm. Platinum and nickel do not appear in these analyses as significant components.

Particle Size in Coal Firing

The size range of particles resulting from coal combustion is an important factor in estimating their pollutant potential. Particle size is important in that it determines the particle surface area available for contact with the flue gases, hence affecting adsorption rates with various

TABLE 10. COMPARISON OF AVERAGE HIGH AND LOW RANGES OF OTHER ASH CONSTITUENTS FOR HIGH AND LOW SULFATES SAMPLES BY WALKER, 1974

Description	Average Concentration Range (percent)					
	Sulfate (SO_3)	Na_2O	CaO	MgO	K_2O	FeO
3 cases high in sulfate	17.6-20.3	0.84-2.82	21.4-23.8	6.0-7.1	0.3 -0.49	7.5 -9.3
7 cases low in sulfate	1.3- 2.6	0.52-0.90	15.2-19.9	2.9-4.4	0.93-1.75	6.76-11.4

TABLE 11. SULFATE CONTENTS IN FLY ASH FROM COAL FIRING

Reference	Test Location	Sulfate Concentration in Fly Ash, percent					Comment
Cuffee, 1964	ESP inlet	0.2					Measured as sulfur
Cowherd, 1975	ESP inlet	7.0					Measured as sulfate
	ESP outlet	5.4					
Oglesby, 1975	ESP inlet	0.26	0.46[a]				Measured as sulfate
	ESP outlet	0.28	1.49				
Burton, 1973	Air heater	5.8	9.3	0.7	2.2	13.7[b]	Measured as SO_3
	Stack	7.6	24.1	15.8	1.6	3.8	

(a) With SO_3 injection ahead of ESP.
(b) With soot blowing.

TABLE 12. TRACE ELEMENTS IN FLY ASH WITH POTENTIAL CATALYTIC EFFECT ON OXIDIZING SO_2 TO SO_3

Reference	Constituent, ppm							
	V	Fe	Ni	Pt	Na	Cr	Cu	Mn
Sheibley, 1975[a]	230	52780	--	--	2658	122	142	466
Abel, 1975[a]	220	65000	--	--	3700	131	<300	489
Bolton, 1975[c]	200/350	93000/100000		(b)	7000/3000	356/70	/400	323/700
Coutant, 1975	91-396	(b)	45-338	(b)	(b)	143-712	50-182	97-200
Burton, 1973	120-440	(b)	500-1000	(b)	(b)	300-500	100-400	300-500

(a) NBS/EPA Standard fly ash.

(b) Values not received.

(c) NAA/SSMS.

gas components, and it also affects the relative ease and efficiency with which the particles can be collected. As described earlier, there is evidence that sulfates occur as a particle coating (Bolton, 1974).

The results of particle size measurements made at the boiler exit on fly ashes from 69 pulverized coal fired boilers (IGCI/ABMA) indicate that for the most probable distribution the mass median diameter of the particles is about 10 micrometers. This agrees well with data by Walker which indicates that for 30 tests on pulverized coal fired boilers the mass median diameter of the particles was from 5 to 15 micrometers (Walker, 1974).

Walker also presented results on 2 cyclone fired units which yielded particle size ranges within the limits for pulverized firing.

Stoker fired boilers tend to produce fewer small particles than pulverized or cyclone fired units resulting in an overall larger size distribution. This is due to the lower combustion intensity or heat release rate per unit volume and also to the fact that the coal is burned in larger lumps or pieces. Data on a particular traveling grate stoker fired unit indicates that in 21 tests the mass median diameter ranged from 12.5 to 37 micrometers (Bradway, 1975).

Oil Combustion

Particulate emissions from oil fired units result in much the same manner as those from coal combustion. Ash or non-combustible constituents in the oil form particulates both by ashing of refractory components and by condensation of more volatile constituents. Also, there is the possibility of forming condensed carbon particles or soot depending on the combustion conditions and degree of fuel atomization.

Just as in coal, ash in crude oil exists in basically two forms inherent and extraneous. Inherent ash is that bound up in the structure of the oil itself and consists of complex organic compounds. Extraneous ash constituents are compounds such as salt and other chlorides, fine particles of sand, corrosion products from ships bunkers and pipelines and, in residual fuel oil, wastes from refinery processes.

Whereas coal ash typically can be at least 5 percent or more by weight of fuel, ash in oil seldom exceeds 0.1 percent. Sulfur contents of oil are also usually lower than those in coal but in the case of residual oil

can range up to 5 percent by weight of fuel. Based on analysis of up to 150 samples of residual oil over the 3 year period from 1955 to 1957 (Orr, 1960) sulfur ranged from a low of 0.29 to a high of 5.25 percent and ash ranged in content from 0.004 to 1.9 percent (only one-tenth of the samples contained more than 0.1 percent).

Typical ranges of compositions of oil ashes for oils from different regions of the United States and from overseas are shown in Table 13. Also shown is the range of concentration of ash constituent in residual fuel oil. As can be seen, ash constituents vary widely even more so than those reported for coal in Tables 7-9. Sulfates occur in oil ash in much higher concentrations than in coal ash (values of over 40 percent shown in Table 13). It is noteworthy that oils can contain significant amounts of V and Ni, elements that have been identified as having a potential catalytic effect on oxidizing SO_2 to SO_3 thus having a potential effect on sulfate emissions. This differs from coal ash where V and Ni are present in ash at only a few hundred parts per million. Also the nature of vanadium compounds in crude oil is such that they are stable up to 800 F. Hence they are not destroyed by refinery operations and as a result they concentrate in the residual (Reid, 1971).

A complete analysis of two different oil ashes after combustion (Negherbon, 1966) is presented in Table 14. This analysis yielded sulfate concentrations (as SO_3) of about 17 and 25 percent. Small amounts of nitrate (NO_3) and chloride were also detected in one sample.

Carbon is also shown as a significant constituent in these two samples accounting for over half of the ash content in one case. According to Novakov carbon could be an important constituent in allowing fly ash particles to adsorb SO_3 from the flue gas forming acid constituents (Novakov, 1974).

Carbon is usually reported as percent combustible in oil fly ash which also would include small amounts of other combustible constituents such as hydrogen. The amount of combustible constituents or carbon in the fly ash depends on combustion conditions and firing method. McGarry reports percent combustibles in oil ash as 99.3 percent for mechanical atomization, 80 percent for steam atomization, and 40 percent for air atomization (McGarry, 1972).

TABLE 13. RANGES OF ASH COMPOSITION IN OIL

Reference		Constituent, percent												
		SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	MnO	V_2O_5	NiO	Na_2O	K_2O	SO_3	Cl	
Ellis, 1937[a]	Max	60.0	44.0	39.0	11.0	4.0	0.5	5.0	4.0	12.0	2.0	21.0	0.2	Percent in oil ash
	Min	5.0	8.0	8.0	1.0	1.0	0	0	0	1.0	0	1.0	0	
Thomas, 1938[b]	Max	38.3	97.5[e]		12.6	4.2	0.4	5.1	4.4	30.8	1.0	42.1	4.6	Percent in oil ash
	Min	0.8	8.9		0.7	0.2	0.2	0	0.5	0.1	--	0.9	--	
Huge, 1955[c]	Max	7.4	5.1	0.3	1.2	2.6	--	15.0	3.2	26.4[f]		40.3	--	Percent in oil ash
	Min	19.0	16.8	0.1	4.8	1.7	0.1	1.6	0.9	19.8		34.8	--	
Orr, 1960[d]	Max	86	57	76	10	1.7	--	740	25	35	1.2	--	--	Parts per million in oil
	Min	6	0.9	3	1.4	1.0	--	14	1.3	5	0.2	--	--	

(a) Fourteen Hungarian and one California oil.

(b) Crudes from across the United States.

(c) Values from Florida Power (Top) and Tampa Electric (Bottom).

(d) Residual oil analysis.

(e) Combined Fe_2O_3 and Al_2O_3.

(f) Combined Na_2O and K_2O as Na_2O.

TABLE 14. ELEMENTAL ANALYSES OF TOTAL PARTICULATES
(Data in percent, Negherbon, 1966)

Elements	Test A Total solids from burning PS[a] 400 oil (collected in a laboratory electrical precipitator at 230° F)	Test B Total solids from burning 4° API oil (collected in a glass filter sock at 300° F)
Carbon	58.1[b]	18.1[b]
Ether, soluble	2.3	4.4
Hydrogen	-	-
Ash (900° C)	17.4	51.2
Sulfates as SO_3 (incl H_2SO_4)	17.5	25.0
Chlorides as Cl	-	.5
Nitrogen as NO_3	-	.3
Iron as Fe_2O_3	3.1	3.7
Chromium as CrO_2	.06	.3
Nickel as NiO	1.8	13.2
Vanadium as V_2O_3	2.5	4.7
Cobalt as Co_2O_3	.08	.3
Silicon as SiO_2	.6	9.7
Aluminum as Al_2O_3	1.6	14.9
Barium as BaO	.4	.1
Magnesium as MgO	.2	.7
Lead as PbO	.1	.2
Calcium as CaO	.2	.4
Sodium as Na_2O	.9	3.0
Copper as CuO	.01	.25
Titanium as TiO_2	-	.004

a Pacific Standard.

b Value probably includes minor amount of hydrogen.

TABLE 14. (Continued)

Elements	Test A Total solids from burning PS 400 oil (collected in a laboratory electrical precipitator at 230° F)	Test B Total solids from burning 4° API oil (collected in a glass filter sock at 300° F)
Molybdenum as MoO_2	.02	.03
Boron as B_2O_3	.01	.1
Manganese as MnO_2	.04	.04
Zinc as ZnO	-	.06
Phosphorus as P_2O_5	.9	-
Strontium as SrO	.04	-
Titanium as TiO	.03	-

Negherbon indicates that the amount of particulate emissions from oil firing depend mostly on combustion efficiency and rate of deposits buildup in the furnace. Combustion efficiency in this case refers to the amount of combustible or unburnt carbon remaining in the ash after combustion. No correlation was found between particulate emissions and the ash content of the oil. Particulate loadings from oil combustion from a variety of sources were found to range from 0.005 to 0.205 gr/scf with the bulk of the values from 0.025 to 0.06 gr/scf (Negherbon, 1966).

Negherbon also found that through high pressure atomization particulate emissions could be reduced by 66 percent over low pressure atomization. He also found that increasing the temperature of residual oil to the burner from 116 C (240 F) to around 315 C (600 F) could reduce particulate emissions by 15 to 17 percent. These reductions in emissions presumably result from increased combustion efficiency or reduced carbon level in the ash.

Particle Size in Oil Firing

Particle size is also an important parameter in evaluating particle characteristics. As was the case with coal, there is evidence that the more volatile constituents in oil ash tend to concentrate in smaller particles. Tests by Engdahl et al (Engdahl, 1969) indicate that vanadium tended to concentrate on particles greater than 4 micrometers.

The particle size distribution was found to vary considerably among various literature sources (Negherbon, 1966) (McGarry, 1972) (Goldfarb, 1972). Mass mediam diameters from 0.3 to 10 micrometers were reported - somewhat lower than coal ash particle sizes.

Type of atomization is important in determining the particle size range Test of steam, air, and mechanical atomized burners (McGarry, 1972) operating on a utility boiler with heavy fuel oil showed that air atomized burners produced the greatest number of fine particles (28 percent less than 3.3 micrometers) while mechanical atomized burners produced the least on a percentage basis (9 percent less than 3.3 micrometers). Steam atomization was about in the middle with 13.5 percent less than 3.3 micrometers. However, this may be misleading because, due to the higher overall amount of particulate generated in the mechanical atomized unit over air atomized, the

total amount of particulate under 3.3 micrometers generated by the mechanical case was about 8 times that of the air atomized case per megawatt of power produced.

Particle growth by natural agglomeration through an oil fired boiler was assumed negligable by Engdahl where theoretical considerations found that about 10 seconds residence time would be required for particles to grow from an assumed initial size of 0.02 micrometers to a final size of 0.065 micrometers (Engdahl, 1969).

Combustion modification techniques for low NO_x emissions can also affect particulate emissions in oil firing. Muzio, et al (1974) showed NO reductions were limited by increased smoke; the limit being a function of the fuel. Best results for a No. 6 fuel oil were obtained with combined FGR and staging which gave up to 45 percent decrease in NO with a two-unit increase in Bacharach number.

Summary

The characteristics of particles generated during coal combustion are primarily a function of ash composition and combustion conditions. Sulfate contents in coal fly ash are mostly in the range of 1 to 5 percent by weight of ash although some data show values as high as 24 percent. Evidence indicates that the sulfates are present as coatings on the surface of the particle and may be present as mostly iron or calcium sulfate. No significant contents of nitrate or chlorides in fly ash were reported in the literature reviewed. Combustion conditions mostly affect particle size and emission rate. Pulverized and cyclone firing create the smallest particles (mass median diameters from 5 to 15 micrometers) while stoker firing produces larger particles (mass median diameters from 12 to 40 micrometers).

Particulates emitted from oil firing are mostly a function of combustion conditions rather than ash composition. The most important variable appears to be degree of atomization. This has a direct effect on the size and carbon content of particles emitted. The size range of particle emitted in oil combustion varies considerably and mass median diameters from 0.3 to 10 micrometers were found. Carbon content of the fly ash also varies considerably and recorded values of over 50 percent by weight of ash were found. In addition to having higher carbon content than

coal ash, oil ash also typically has higher vanadium, nickel, and magnesium content. This may in part account for oil ash also having higher sulfate levels (over 40 percent in some recorded cases) than coal ash. Small amounts of chlorides and nitrates were found in some ash compositions.

SULFATES IN DEPOSITS

In this section we are concerned with deposits formed on various surfaces of the boiler system as distinguished from suspended particulate described in the previous section. Chemical reactions in the deposits which are formed in fossil fuel combustion play an important role in the formation of sulfates and other aerosols which are emitted from the stack. The metal oxides and in some cases, metal chlorides, which are formed in the flame and the immediate post-flame zone are converted to sulfates by the action of the SO_3, SO_2, and the oxygen in the flue gas stream. In addition, some components of both the fly ash and the boiler deposits formed by it can function as heterogeneous catalysts for the oxidation of SO_2 to SO_3. The SO_3 will then be formed from sulfuric acid by reaction with the moisture in the flue gases or solid sulfates by reaction with the metal oxides. The metal sulfates which accumulate in the deposits on the boiler tubes can also be released into the gas stream by the periodic soot blowing which is required to prevent fouling of the boiler passes. All of these factors contribute to the total sulfate burden of the gas stream which leaves the stack.

There is very little data available in the literature on the rates at which sulfates are formed in boilers but in the boiler deposits it is a relatively slow process.

Most of the sulfur in fossil fuels is volatilized during the combustion process, and very little of the sulfur remains in the ash unless the combustion conditions are poor. The sulfur oxides thus formed then react with the metal oxides and chlorides to form the metal sulfates. The reactions also involve water and oxygen and undoubtedly are very complex, probably proceeding in a series of bimolecular steps to reach the final sulfate product. The overall reaction may be described by the typical equation:

$$2NaCl + H_2O + SO_2 + 1/2\ O_2 = Na_2SO_4 + 2HCl, \qquad (19)$$

Halstead and Raask made equilibrium calculations for the sodium chloride-sodium sulfate system, and the results for a coal containing 1.8 weight percent sulfur and 0.07 weight percent chlorine are shown in Figure 24 (Halstead, 1969). In this figure, the variations of the equilibrium partial pressures of NaCl and Na_2SO_4 in the flue gases are plotted against temperature for three different oxygen levels. The broken lines in the figure show the saturated vapor pressures of NaCl and Na_2SO_4 and the temperatures at which these lines intersect the equilibrium pressure lines are those at which the particular compounds will condense from the flue gases. The important conclusion from this plot is that when coal is burned under normal operating conditions with 3 to 5 percent excess oxygen, Na_2SO_4 and not NaCl will condense from the flue gas if the gas is at chemical equilibrium within the superheaters where the flue gas temperature lies between 927 C (1700 F) and 1125 C (2060 F). In order to test this conclusion, probes were inserted into a 60 megawatt boiler fired with coal containing 2.4 percent sulfur and 0.28 percent chlorine. Analysis of the deposits showed that whereas the buildup of the sulfates on the probe continued steadily, chloride was never present in the deposits in more than trace quantities at all temperatures between 527 C (980 F) and 927 C (1700 F). The results are shown in Figure 25. The traces of chloride which were observed in the deposits were attributed to the absorption of vapor phase NaCl by the condensed sulfates. Similar results were obtained in a 200 megawatt boiler fired with coal having 1.1 percent sulfur and 0.97 percent chlorine. However, when the same coal was burned in a 15 megawatt boiler, it was found that NaCl did condense together with <u>greater</u> amounts of Na_2SO_4 and K_2SO_4. By way of explanation, it was suggested that in the smaller boiler the mixing of the fuel and the combustion air was less efficient and led to a fuel-rich condition at the point where the probe was inserted. It was also suggested that the residence time of the flue gas, which was only 1 to 2 seconds between the burners and the probe, may have been too short for the complete conversion of NaCl to Na_2SO_4. Once NaCl does condense in the deposit, the chloride may well persist for a relatively long period of time.

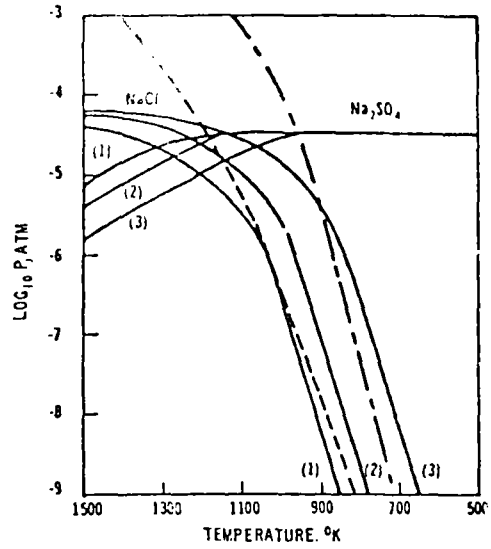

Figure 24. Chloride/sulfate equilibrium coal 3, 1-8 weight percent S, 0.07 weight percent Cl_2. curves: (1) 5 percent O_2 excess (2) Stoichiometric (3) 2 percent O_2

_ _ _ _ _ Saturated vapor pressure NaCl
--------- Saturated vapor pressure Na_2SO_4

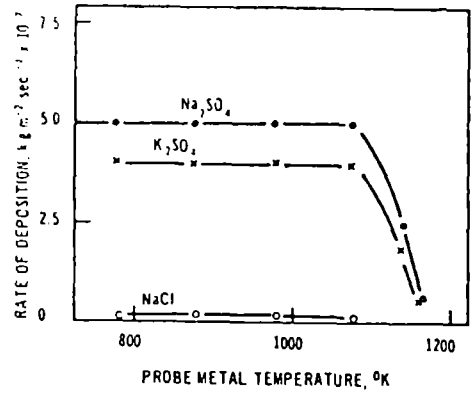

Figure 25. Deposition of sulfates and chloride from flue gas of 60-MW boiler fired with coal of 2.4 percent S and 0.28 percent Cl (3.0 percent excess O_2)

The rate at which NaCl in the deposit is converted into Na_2SO_4 was investigated by Bishop, using a laboratory combustor burning pulverized coal (Bishop, 1968). In the early stages of deposition the chlorine content of the material collected on the probe was substantially greater than the sulfur concentrations. As high as 30 weight percent chlorine were observed while the sulfur expressed as sulfate comprised about 15 percent of the deposit. As the time of exposure to the flue gases continued, the chloride content decreased while the sulfur content increased. It appears that after about 6 hours, a steady state condition was reached at which the chloride concentration was 3 percent while the sulfate amounted to 50 percent of the deposit. X-ray diffraction confirmed the fact that the compounds in the deposit were NaCl and Na_2SO_4. The coal used for these studies was relatively low in sulfur and high in chlorine, there being 0.9 percent of each of these elements in the coal. Consequently with typical American coals in which the chlorine content is relatively low compared to the sulfur, the small amount of chloride formed would be very quickly consumed and converted to sulfate.

The relative effectiveness of SO_2 and SO_3 in transforming NaCl to Na_2SO_4 was investigated by Fletcher and Gibson using radioactive sulfur as a tracer to follow the reactions (Fletcher, 1954). This work demonstrated that on the boiler tube surfaces, which are always at temperatures of 600 C (1112 F) or less, the SO_3 in the flue gases is the primary agent in sulfate formation. However, in the gas-phase reactions occurring in the postflame zone, the sulfate formation would result primarily from the reaction of SO_2 and oxygen with the fly ash particle. The effect of iron oxide on the conversion process was shown to be significant. The rate of sulfate formation from SO_3 was not affected by the presence of the iron oxide catalyst, the rate of sulfate formation from SO_2, on the other hand, was greatly increased (see Figure 14, page 55). Thus, at 500 C (932 F) without Fe_2O_3 in the mixture about one fifth of the Na_2SO_4 was formed from the SO_2. However, in the presence of the Fe_2O_3, 80 percent of the much larger total quantity of sulfate was derived from the SO_2. Even at temperatures as low as 300 C (527 F) 65 percent of the sulfate came from the SO_2. In this case SO_2 was the predominant factor over the whole temperature range.

Because the inorganic content of fuel oil is low, the fly ash formed in oil burning systems is substantially less than that from coal burning systems. At the same time carbonaceous material makes up a greater portion of the fly ash particle resulting from the combustion of oil. Measurements by DuBois and Monkeman on the combustion products of high sulfur residual fuel oil showed that the soot particles which contained a large amount of sulfate were also strongly acidic, indicating the presence of adsorbed sulfuric acid (Dubois, 1973).

Since two-stage combustion requires that the first stage be a fuel-rich zone, combustion is not complete; thus, the oxidation of the sulfur and the carbon will not be complete and the fly ash and deposit chemistry is different from that which occurs in an oxidizing atmosphere.

In an oxygen-deficient atmosphere all of the sulfur from the decomposition of pyrites, FeS_2, will not be oxidized to sulfur dioxide. The first step in the combustion of FeS_2 is a dissociation reaction in which an atom of sulfur is released. An experimental study of the reaction under conditions that would exist in a furnace showed that this sulfur was released in 0.5 seconds at a temperature of 1093 C (2000 F) (Halstead, 1969). The pressure of the sulfur vapor thus formed reaches one atmosphere at 779 C (1435 F). The experiments demonstrated that with the short residence time in the flame, both sulfur and FeS could be deposited on furnace wall tubes.

The presence of FeS in deposits found on badly corroded boiler tubes was reported by W. T. Reid and his colleagues in the early 1940's (Reid, 1945). In seven of the furnaces that they examined, sulfide deposits were found in some areas. Up to 5 percent carbon also was noted in some of these deposits, indicating that the normal oxidation process had not occurred. The cause for these unusual conditions was found to be poor distribution of the coal stream leaving the burners, coupled with coarse pulverization which resulted in deposition of incompletely burned coal on the furnace walls. The problems were corrected by adjustments in the coal distributor pipes and the grinding mill, thus insuring that the carbon and the sulfur would be completely oxidized before reaching the wall tubes. Although this situation was an extreme case, it demonstrates the possibility that with reduced oxygen in the first stage of combustion there will not be sulfate formation on the heat receiving surfaces in this portion of the

boiler. As the fuel mixture is carried into the oxdizing zone, the remainder of the sulfur will be oxidized to SO_2 and SO_3 and sulfate deposits can be formed in the usual manner. However, the deposits in the reducing zone will contain sulfur in the form of FeS. When this FeS is dislodged during the soot blowing process, it is likely that the mass of material being carried through the oxidizing zone will prevent the complete oxidation of the sulfur and particles of FeS will be carried through the boiler with some escaping the precipitator and being emitted from the stack.

SECTION VII

INFLUENCE OF COMBUSTION MODIFICATION ON THE ACID AEROSOL FORMATION POTENTIAL OF FLUE GAS DESULFURIZATION PROCESSES

By their nature, flue gas desulfurization (FGD) systems inevitably emit limited quantities of acid aerosols even without considering combustion modification techniques. Although our primary concern is the effect of CM on acid aerosol emission, since FGD systems can contribute to acid aerosols a brief discussion is included. These emissions occur from FGD systems principally as (1) unremoved molecular and particulate matter, (2) chemicals entrained in scrubbing liquors when wet desulfurization processes are used, and as (3) entrained solid sorbents in the case of dry processes. When combustion modification is used in conjunction with flue gas desulfurization processes, the acid aerosol forming tendencies of the flue gas obviously can be changed. The degree to which the acid aerosol forming tendencies of flue gas are changed by combustion modification techniques depend greatly on the type of flue gas desulfurization process being used. Since there is a myriad of processes currently being developed, the approach used in this study was to:

(1) Review existing flue gas desulfurization technology

(2) Select representative systems from the numerous available processes

(3) Speculate on the acid aerosol forming potential of the flue gas desulfurization process operating normally, and

(4) Speculate on changes in the acid aerosol forming potential of FGD processes when combustion modification techniques are employed.

The path taken by the flue gas to the environment when a stationary power source is equipped with a flue gas desulfurization process is from the flame and convective zones where the combustion modification is occurring, through the air preheater and then through an electrostatic precipitator for ash removal. From the electrostatic precipitator the gas then passes through a desulfurization unit (usually a wet scrubber) where the flue gas is adiabatically saturated to the water dew point. In the desulfurization unit, chemicals are added to promote SO_2 and SO_3 removal. From the desulfurization unit, the gases usually pass to a mist eliminator to remove entrained mist containing the desulfurization chemicals. From there, the gas usually proceeds to a stack gas reheater where heat is added to the gas to give the plume buoyancy and protect the stack against acid corrosion. Following reheat, the gases are emitted to the ambient atmosphere. In the case of oil fired boilers, quite often an electrostatic precipitator is not used. If the desulfurization process utilizes dry sorpiton of SO_2 as the main removal technique, there will be no reheat or mist eliminator sections in the flow train. Likewise, in new plants burning coal, sometimes the ESP will be eliminated from the gas flow train if enough confidence is placed in the wet scrubber to remove fly ash from the gas as well as SO_2/SO_3 in the desulfurization process. Also in industrial boilers, the air preheater and/or the particle collection device may not be found. This section of the report is concerned with acid aerosol formation in the region beginning with the ESP and ending at the reheater.

Typical values of SO_x (SO_2 and SO_3), NO_x (NO and NO_2), and particulate loadings in flue gases going to FGD systems are given in Table 15. The pollutant load will, of course, depend upon the fuel used, i.e., coal, oil, or gas. The SO_x content of the gas will depend upon the sulfur content of the fuel and can vary between wide limits, about 200 to 3000 ppm, depending upon whether low or high sulfur fuel is burned and whether it is oil or coal. The NO_x contents of the flue gas is determined by the method of combustion, the fuel used, and whether combustion modification techniques are used to control the amount of NO and NO_2 produced. Particle loading can range from 3 to 6 grains/scf for coal and about 0.04 to 0.02 grains/scf for oil. In addition, numerous other minor constituents are generated in the combustion process.

TABLE 15. TYPICAL SO_x, NO_x, AND PARTICLE LOADINGS IN FLUE GASES TO FGD SYSTEMS

Boiler Fuel	SO_2/SO_3, ppm	NO/NO_2, ppm	Particulate, grains/scf
Coal	600-3000[a]	225-800	3-6[b]
Oil	200-2000[a]	100-600	0.04-0.2[c]
Gas	Nil	50-375	Nil

(a) Depends on the sulfur content of the fuel.

(b) Mainly fly ash with some unburned carbon.

(c) Mainly unburned carbon.

The scrubbing of SO_2 with reactant liquors requires the intimate contact of SO_2 with the absorbing media. To achieve this gas/liquid contact, numerous types of scrubbers have been developed. For example, in lime/limestone FGD systems, (1) mobile bed, (2) marble bed, (3) spray tower, and (4) venturi scrubbers are used. In most cases, the scrubbing liquor is atomized or sprayed from nozzles countercurrent (mobile bed, marble bed, and spray tower scrubbers) or cocurrent (venturi scrubbers) to the gas stream. Mists of solid and liquid particulates are generated in both the atomization and the turbulent mixing processes of scrubbing. Most mist droplets return to the scrubbing solution because of either particle coalescence (small particle combination to form larger particles) and the force of gravity, or particle collisions with scrubber internals, adhesion, and drainage back into the liquor reservoir. Those not collected are entrained within the scrubber and are directed to the mist eliminator. Several factors, including gas velocity, pressure drop, nozzle design, liquid to gas (L/G) ratio, mixing turbulence, scrubber design, and scrubbing liquor density and viscosity, affect both the number and the size of entrained droplets.

Mist eliminators (ME) were first used in the electric power industry for removing the fine droplets entrained in (or carried with) the humidified air exiting cooling towers. With scrubbers for example, in lime or limestone scrubbing applications, a mist eliminator is a device employed to collect, remove, and return to the scrubbing liquor the liquid and solid particulates which are entrained with desulfurized flue gas exiting the FGD scrubber or absorber. Most ME's employed in flue gas desulfurization applications are based on the principle of inertial impaction. The particles entrained in the gas stream pass through the ME where they are forced to make sudden changes in flow direction. The particles collide and adhere to the ME surfaces where they are collected while the remaining gas stream passes on through the ME. The collected particles combine with other particles until they form a mass of sufficient weight to drain off by gravity. In high solids applications, especially limestone scrubbing, the collected solids tend to form a mud-like deposit over a period of time which must be washed from the collector to keep it free-flowing and operational.

The collection of fine particulates entrained with a gas stream can be accomplished by one or more of the following mechanisms.

(1) Settling,

(2) Inertial impaction,

(3) Diffusion, and

(4) Electrostatic deposition.

Two mist characteristics, the loading and the particle-size distribution, are important in determining the removal efficiency of a ME. At present neither is measured by FGD system operators or vendors. Without these measurements, collection efficiencies cannot be calculated. In addition, the effect of gas velocity, L/G ratio, liquor composition, and other operational variables cannot be adequately evaluated in terms of ME operation. Design features such as scrubber design, degree of turbulence, use of bulk separation devices, and the ME design itself also lack proper evaluation.

A major problem in operating wet flue gas desulfurization systems is the need for stack gas reheat. Reheat is required to avoid downstream condensation and corrosion, to avoid a visible plume, and to enhance plume rise and dispersion of pollutants. With regard to the general effect stack gas reheat has on acid aerosol formation, reheating will cause acid aerosols formed in the FGC system to be dried out, i.e., due to the change in temperature the water dew point will change. This will cause evaporation of water from the mist droplets and hence cause a change in the particle size distrubution of acid aerosols formed in the FGD system. Also due to changes in temperature, chemical changes could take place within the mist particles. For example, increased temperature could lead to the decomposition of stable species present at the normal operating temperature of the wet FGD system (125 to 130 F). This would depend of course on the FGD system in question. Combustion modification techniques per se would <u>not</u> be expected to cause significant changes in the physical-chemical processes occurring normally when a boiler is equipped with an FGD system and the stack gas is being reheated.

POTENTIAL ACID AEROSOLS AND FLUE GAS DESULFURIZATION SYSTEMS

Several FGD processes representative of available technology were selected for analysis and included both wet processes and dry processes.

Wet processes all use a mist eliminator to remove entrained chemicals added to the process to promote SO_2 removal. Thus unremoved mist would seem to be a potential source of acid aerosol emissions. Similarly, dry processes would in general have entrained absorbent fines eluted from the flue gas/solid contacting device used for desulfurization. In general, dry processes do not have a particle removal device analogous to a mist eliminator following the reactor to remove entrained solids. Usually, the contacting device is designed to minimize this problem. Entrained solids from dry processes would consist of sulfates and perhaps nitrates of the sorbent.

Wet processes could involve either slurry scrubbing (for example, the lime/limestone and MgO processes) or clear liquor scrubbing. In the latter case, the scrubbing liquor could have a wide range of pH values--from dilute alkali (either sodium or ammonium ion), to slightly acidic buffered solutions (BOM citrate and Stauffers' phosphates processes), to low pH solution such as the Chiyoda process.

In dry processes, the temperature sequence experienced by the flue gas would be considerably different compared to wet processes because of the adiabatic quenching operation used in the latter type of systems. In both cases, the residence time the gas spends proceeding through the FGD system would be about the same. This should be true even if the boiler were operated using combustion modificaiton techniques.

Boilers equipped with FGD systems have the potential to emit to the environment materials considered as acid aerosols. In a very general sense, potential acid aerosol sources may be classified according to the following "loose" scheme:

Species	Source
1. Sulfur Species	
a. Metal sulfates/sulfites	Entrainment in mist and FGD sorbents
b. Metal bisulfates/bisulfates	Entrainment in mist
c. $H_2SO_4(\ell)/H_2SO_3(\ell)$	Entrainment in scrubber mist and unabsorbed SO_2/SO_3 partition to mist
d. SO_2	Residual SO_2 leaving FGD systems
e. SO_3	Residual SO_3 leaving FGD systems
f. $(NH_4)_2SO_4$	Generated in NH_3 scrubbing
g. $CuSO_4$	Generated in CuO desulfurization
h. Other molecular species such (f) and (g) which are intrinsic to specific FGD systems	
2. Particulate Species	
a. Particulate ash	Ash with sorbed acidic molecular species
b. Carbon particles	Carbon with sorbed acidic molecular species
3. Nitrogen Compounds	
a. Metal nitrates/nitrites	Entrained in mist and on FGD solid sorbents
b. NO	Residual leaving FGD systems
c. NO_2	Residual leaving FGD systems
4. Chlorides	
a. HCl	Residual leaving FGD systems and partitioned to mist
b. Metal chlorides	Entrained in mist
c. NH_4Cl	Generated in NH_3 scrubbing
5. Fluorides (same as chlordies described above)	

As seen in the above classification the main sources of acid aerosols are:

(1) Unremoved molecular species--SO_2, SO_3, NO, NO_2, HCl, HF, etc.

(2) Particulate species formed in the combustion process which can act as sorbents for acidic molecular species

(3) Entrained mist from wet FGD systems

(4) Entrained solids from dry FGD systems

(5) H_2SO_4 used as a scrubbing agent, for example in the Chiyoda process

(6) H_2SO_3 and H_2SO_4 formed by partition of unreacted SO_2 and SO_3 to mist particles.

With few exceptions, FGD systems tend to mitigate and diminish the acid aerosol problem relative to the case of no control. This occurs because there is a finite efficiency for removal of the molecular species and particulate matter contained in the flue gas by the desulfurization processes. For example, SO_2 removal can vary between 70 and 90 percent depending upon the FGD system in question and the sulfur content of the fuel. Likewise some degree of NO_x removal occurs in FGD systems although this is admittedly small, perhaps 10 to 40 percent depending on the FGD systems. For each of the other pollutants, similar numbers for removal efficiencies can be speculated.

Ignoring the inefficiencies in FGD systems which lead to unremoved molecular species and particulate matter, the main source of potential acid aerosols directly attributable to the FGD systems are:

(1) Entrained mist containing chemicals used in wet FGD systems (including mist generated during flue gas quenching)

(2) Entrained solids eluted from dry FGD systems which consist of partially reacted sorbents containing sulfates, sulfites, nitrites, nitrates, etc.

Very few quantitative data exist as to the importance of these sources to the acid aerosol problem and neither the process developers, system operators nor regulatory agencies seem to be collecting such information.

The difficulty of the situation is compounded by the fact that acid aerosol emissions in the form of entrained mist and eluted solid particles depend greatly upon the FGD system in question, i.e., the specific process being used on the combustion source. For example, potential acid aerosol emissions from a boiler equipped with the lime/limestone process would be expected to be considerably different from the Chiyoda CT-101 process which would be different from the Shell CuO process and so on. Additionally, mist carryover would be expected to vary considerably with scrubber type and mist eliminator design. For example spray towers and venturi scurbbers produce heavier mist loadings than a marble bed scrubber which tends to abate

mist formation by the nature of its design. Also droplet size becomes finer and mist loading increases as the pressure drop through the scrubber increases, i.e., for a given liquid flow rate, more mist at a smaller diameter is produced because the gas velocity is increased. Alternately, at a given gas velocity through the scrubber, more mist at a finer size is produced as the liquid rate is increased (higher L/G ratio).

Bascially the same phenomena occurs in dry FGD processes in which the gas is contacted at elevated temperatures in adsorbers of different designs. For example, the grain loading of partially reacted CuO sorbent eluted from the Shell process would be expected to be lower than the grain loading of partially reacted char eluted in the Foster Wheeler-Bergbau Forchung process. This occurs because of difference in reactor design configurations in the two processes and sorbent chemicals and their abrasive properties.

The crux of the above discussion is that it is very difficult to generalize and that each FGD system must be considered in its own right. Although admittedly a compromise when one considers that there are over 50 processes under development, an attempt was made to "qualitatively characterize" the entrained materials eluted from several systems. Such materials would have to be considered as potential acid aerosol formers and directly attributable to the operation of the FGD system. This "best guess" speculative analysis is summarized in Table 16 where it is seen a wide variety of chemical substances can be emitted depending upon the FGD process.

Richards and Gerstle attempted to summarize available quantitative information (actually "best guesses") on the contribution FGD systems make to the acid aerosol problem (Richards, 1974). All of their work was concerned only with "sulfate" emissions and wet FGD processes. No mention was made of dry processes, since in all probability no data were available to them. The data of Richards and Gerstle together with estimates for Unit 6 of Paddy's Run (LG&E) and Unit 1 of Will County (Commonwelath Edison Company) are presented in Table 17. The latter two estimates were obtained from data presented by Rosenberg, et al. (Rosenberg, 1976) All data pertain to mist eliminator entrainment of scrubbing liquors. As seen in Table 18, the data scatter considerably. Consider for instance, estimates for Unit 6 of the Paddy's Run Station of LG&E which uses a lime scrubber. Estimates range from between 0.25 to 3.5 percent of the input sulfur in the coal, i.e.,

TABLE 16. QUALITATIVE LIST OF POTENTIAL ACID AEROSOL FORMERS EMITTED FROM FGD SYSTEMS

Process	Entrained Particles: Wet Process Liquids (Mist)	Entrained Particles: Dry Process Solids	Comments
Lime/Limestone Process	$CaSO_4$ $CaSO_3$ $CaHSO_3$ $CaSO_3 \cdot 1/2\ H_2O$ $CaSO_4 \cdot 2H_2O$ $CaCO_3$	--	Slurry mist with dissolved solids. Also $Ca(OH)_2$ would be present in lime scrubbing.
Magnesium Oxide Process	MgO $MgSO_4$ $MgSO_3$ $MgSO_3 \cdot 3H_2O$ $MgSO_3 \cdot 6H_2O$ $MgSO_4 \cdot 7H_2O$	--	Potential dry sulfate and sulfite emissions occur from calcination step in the process. Also acid mist from H_2SO_4 production.
Double Alkali Process	$NaCO_3$ Na_2SO_3 $NaHSO_3$** Na_2SO_4 $NaOH$	--	Trace quantities of $CaSO_3/CaSO_4/Ca(OH)_2$ recirculated from the reaction tank to the scrubber are undoubtedly also emitted.
Wellman-Lord Process	Na_2SO_3 $NaHSO_3$** Na_2SO_4 $NaOH$	--	Side reactions occur in the evaporator/crystallizer which lead to polythionate compounds, such as $Na_2S_2O_7$, being present in the scrubber liquor.

TABLE 16. (Continued)

Process	Entrained Particles: Wet Process Liquids (Mist)	Entrained Particles: Dry Process Solids	Comments
Catalytic-IFP Process	$(NH_4)_2SO_3$ $(NH_4)_2SO_4$ $(NH_4)HSO_3$ $(NH_4)HSO_4$	--	Fine particles of $(NH_4)_2SO_4$ are formed between the gas phase reaction of SO_2 and NH_3 in the flue gas.
BOM Citrate Process	Na_3Cit NaH_2Cit NaH_2Cit $NaHSO_3$** $NaHSO_4$ Na_2SO_4 H_3Cit	--	pH4 to 5 solution containing a wide variety of sodium citrate/bicitrate and sulfate compounds.
Stauffer Phosphate Process	Na_2SO_4 $NaHSO_3$** Na_3PO_4	--	Very similar to BOM citrate process, pH 4 to 5 scrubbing liquor. Also polythionates due to oxidative side reactions.
Chiyoda CT-101 Process	H_2SO_3 H_2SO_4 $CaSO_4 \cdot 2H_2O$ $Fe_2(SO_4)_3$	--	Strongly acidic (pH ~ 0.3) scrubbing liquor with dissolved ferric sulfate catalyst.
Shell SFGD Process	--	CuO $CuSO_4$ Cu_2S	Eluted solids from acceptor reactors.

TABLE 16. (Continued)

Process	Entrained Particles: Wet Process Liquids (Mist)	Entrained Particles: Dry Process Solids	Comments
Foster Wheeler - Bergbau Forschung Process	--	Char Char/SO_3 Char/H_2SO_4	Solids eluted from char adsorber.

* No attempt was made to list the chemical analogs of absorbed NO, NO_2, HCl, HF, etc., which are contained in small quantities in the flue gas and partially removed by the FGD process.

** Other more complex polythionates are undoubtedly present, for example Na_2S_2O sodium pyposulfate.

TABLE 17. SULFATE EMISSIONS SUMMARY—REPRODUCED IN PART FROM RICHARDS AND GERSTLE (Richards, 1976)

Source	Van Ness	Burchard	Koehler	Smallwood	Westlin	Westlin	Westlin	York	Van Ness[b]	Smyrk[b]
Ident.	L G & E	L G & E	Boston-Mystic	Union Carbide	1	2	3	Lawrence	L G & E	Will County
Control System	Lime scrubber	Lime scrubber	Mag Ox	None	None	None	Lime-stone scrubber	Limestone Injection	Lime scrubber	Limestone scrubber
Fuel	Coal, 3.5% S	Coal, 3.5% S	Oil, 2.5% S	Coal, 1% S	Coal, 0.85% S	Oil, 0.3% S	Oil, 2.5% S	Coal, 3.4% S	Coal, 3.5% S	Coal, 3-4% S
MW	70	70	150	~30	--	--	--	~100	70	165
Sulfate emission as sulfur	1.3[a] lb/min	0.43 lb/min	0.13 lb/min	1 lb/hr				0.4 lb/min	0.11 lb/min	0.078
Percent input sulfur emitted as sulfate	3.3[a]	1.0	0.4	0.3	0.2	2.7	2.4	1.1	0.25	0.1

(a) Based on estimate of maximum moisture carryover through demister; mist was assumed to contain 11 grams $CuSO_4$//100 grams of water.

(b) Estimated from data presented by Rosenberg, et al.

feed to the boiler, is emitted to the environment as $CaSO_4$ and $CaSO_3$ in the form of mist particles.* Likewise at the Will County Station where limestone wet scrubbing is practiced, approximately 0.1 percent of the sulfur input in the fuel is thought to be emitted as aqueous mist entrainment in the form of $CaSO_4/CaSO_3$ slurry (5 to 8 percent suspended solids and 5000 ppm dissolved solids). On Unit 4 of the Lawrence Station of Kansas Power and Light Company, where tail end limestone injection wet scrubbing is practiced, a similar estimate is that about 1.1 percent of the sulfur in the coal is emitted as entrained mist (agina $CaSO_4/CaSO_3$ solution). For the Mystic Station of Boston Edison Company on a 150 MW oil filter boiler employing MgO scrubbing, about 0.4 percent of the sulfur is emitted as a $MgO/MgSO_3MgSO_4$ slurry mist.

It is very difficult to draw conclusions from fragmentary numbers such as those in Table 17. The best that can be done is to conclude that mist eliminator entrainment is probably a small problem compared with the inefficiencies in the FGD systems for sulfur removal, i.e., where perhaps 10 to 30 percent of the input sulfur to the boiler is emitted as SO_2 which has the potential to be an acid aerosol former. Even this conclusion is suspect however, and would depend upon the health effects associated with the relative sources and the eventual composition the acid aerosols assume. Although no data can be cited, the same conclusion probably holds for the dry FGD systems also.

EFFECT OF COMBUSTION MODIFICATION ON ACID AEROSOL FORMATION IN FGD SYSTEMS

All of the combustion modification techniques described in this report will lead to changes in the physical-chemical characteristics of the flue gas. These modifications in character will then manifest themselves in changes in the acid aerosol formation potential of the flue gas as it proceeds through the FGD system relative to the case where no combustion

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* Using the percent sulfur input to the boiler being emitted as sulfate may not be a valid basis for making qualtative judgements since this will depend on the relative health effects of the emitted sulfates.

modification was employed on the combustion source. Succinctly stated, all combustion modification techniques will lead to at least one of the following changes in characteristics of the flue gas:

(1) Decreased gas volume due to either low excess air and/or low firing rate. This would amount to perhaps a 10 to 20 percent change in volume relative to the case of no combustion modification.

(2) Decreased total NO and NO_2 concentration in the flue gas. This would amount to a 25 to 65 percent reduction in the NO and NO_2 content of the flue gas depending upon the type of fuel burned, for example, from about 225-800 ppm to about 100-500 ppm for the case of coal firing.

(3) The total concentration of SO_2 and SO_3 in the flue gas should remain about the same. For example, for coal this would be anywhere from 600 to 3000 ppm total depending upon the coal source (western or eastern bituminous) and its sulfur content.

(4) The ratio of SO_2 to SO_3 should increase slightly due to a slight decrease in SO_3 concentration. This occurs because the formation of SO_3, although thermodynamically favored at low temperatue, will be limited by the kinetic rate of formation which is diminished at low temperature.

(5) Particle formation rates may increase due to combustion modification, especially for carbonaceous materials. Since these materials will probably be submicron in size, this will effectively increase the particle number load on the ESP and flue gas contacting device used in the FGD system. The mass load on the particle removal devices would not be expected to increase significantly.

(6) Fuel additives, especially compounds containing metal and/or metal oxides will increase the particulate load on the ESP and FGD systems. Since particles formed from additives should also be submicron in size, the same comments made under (5) are applicable here.

In a very qualitative sense, introducing combustion modification on an existing boiler equipped with an FGD system leads to several changes. Since the gas volume decreases, less mist will be entrained off the back of the scrubber. However, since the gas velocity through the scrubber will decrease the mist eliminator efficiency will also be decreased. Since any FGD system must be designed to cope with fluctuations in boiler load which result in the wet scrubber or dry adsorber seeing decreased gas flow rate, the net effect will probably be insignificant. FGD systems are usually designed for the maximum flow rate of flue gas generated by the boiler, i.e., when the boiler operates under maximum load and maximum excess air. Also, FGD systems are designed to have good turndown capabilities, i.e., perhaps by a factor of two, or be able to operate at half load on the boiler. Since combustion modifications would result in perhaps a 10 to 20 percent decrease in flow rate, this should be within the turndown capabilities of most FGD systems. For boilers where no FGD system exists, introduction of combustion modification should present no serious problem for the FGD system. This conclusion is reached because designers of the FGD system would simply factor into the design the effect combusiton modification would have on the decreased volumetric flow rate.

Decreased NO and NO_2 concentration in the flue gas would decrease the potential for acid aerosol formation. This results from the obvious decreased emission of NO and NO_2 to the enviornment and the change for partition to mist and/or solid particles escaping the desulfurization unit. Also, since the concentration of NO and NO_2 is decreased in the flue gas, the concentration of nitrates and nitrites in scrubber liquors should be lower. Hence, the concentration in mist particles entrained off the back of mist eliminators will be decreased. In dry desulfurization processes, based upon adsorption theory and typical adsorption isotherms, NO and NO_2 sorbed on entrained solids would also be expected to be less since the gas phase NO and NO_2 concentrations are reduced.

With regard to Item 3, since the SO_2 and SO_3 concentration in the flue gas remains essentially the same under combustion modification, the acid aerosol potential of the flue gas will be essentially the same as for a boiler normally operating with an FGD system. The potential for FGD systems to emit and contribute to the acid aerosol problem has been previously

discussed and those comments apply here. Likewise under Item 4, since the ratio of SO_2 to SO_3 remains essentially constant or increases slightly due to combustion modification, this will have a negligible effect on the operation of the FGD system and the acid aerosol formation of the gas. In actual practice, FGD systems are designed to handle a range of SO_2 concentrations, with an upper limit set on the maximum SO_2 concentration (hence sulfur input) to the process.

The most significant effect on acid aerosol formation results from Items 5 and 6, increased small particle formation due to carbon formation or the addition of fuel additives. Both result in the same synergistic effects when interacting with FGD systems and will be discussed together. The formation of small particles of carbon, active metals, and metal oxides will lead to increased particle surface area. These materials can serve as adsorption sites for potential acid aerosol formers, notably SO_2, SO_3, NO, NO_2, HCl, HF, and other minor constituents of flue gas. Also, these small particles could serve as sites to catalyze oxidative reactions. Since the temperature is elevated to about 150 C (300 to 325 F) at the point in the duct work where the gases leave the ESP, the predominant sorption mechanism would in all probability be chemisorption although some amount of physical adsorption would undoubtedly occur. Some sorption would also occur on the larger fly ash particles. However, since the surface area increases greatly with the small submicron particles, and because of the greater chemical reactivity of carbon, elemental metals, and metal oxides, one would expect greater sorption on the carbonaceous and active metal surfaces formed during combustion than on ash particles. As the flue gases normally pass through the electrostatic precipitator, ash removal of particles down to about 1 micron would occur. Collection efficiency would depend on the age and physical condition of the ESP and would range from about 90 percent for old units on retrofit boilers to 99 percent on new units. However, virtually no removal is afforded submicron particles. Thus, the increased number of small particles formed in combustion modification would aggrevate the acid aerosol problem.

In the demister and reheat sections of the FGD system, virtually no small particle removal will occur. Additionally, particles of a larger size will be added to the gas due to reentrainment from the mist eliminator so

the particle size distribution will change. Also, the reheat section, since mist drying is occurring, contributes to a further change in the particle size distribution. Additionally, the added residence time of the gas in the scrubber removal section, mist eliminator and reheat sections of the FGD system will lead to further adsorption of unremoved molecular species on small submicron particles.

Dry removal processes would give rise to essentially the same scenario described above except that no quenching, mist elimination, or reheat occurs. Little if any removal of submicron particles would occur in dry FGD systems. They would also suffer from the added disadvantage of putting entrained solids into the flue gas. These solids, such as partially reacted char in the Foster Wheeler-BF process or partially reacted CuO in the Shell FGD process, would serve as additional sites for sorption of potential acid aerosols. Solid char particles would also be expected to catalyze the reaciton of SO_2 to SO_3.

SUMMARY

SO_2 removal technology has been reviewed with regard to the formation of acid aerosols under combustion modification conditions. A myriad of FGD processes exist and currently over 50 are in various stages of development. FGD technology was categorized to permit a wide variety of processes to be considered. Ten (10) processes were selected for analysis which represent a cross-section of the current and emerging state of FGD technology. To perform any type of meaningful analysis, two situations must be considered. First the situation where acid aerosols are emitted from boilers equipped with FGD systems but not performing combustion modification. Second, assessing changes is acid aerosol emission from boilers equipped with FGD systems and where combustion modification is being performed. Based upon this analysis, the following conclusions are drawn:

(1) As a general rule, it is felt that FGD system mitigate the acid aerosol problem. The conclusion is based on the fact that FGD processes have finite removal efficiencies for many of the species considered as potential acid aerosol formers. Hence, FGD processes should lead to reduced masses of emissions which could lead to secondary acid aerosols in the environment. However, inefficiencies exist in FGD systems and molecular and

particulate species capable of forming acid aerosols are emitted even when FGD systems are operating normally.

(2) There exists, however, certain emissions which can be considered as potential acid aerosol formers which are directly attributable to the FGD process.

There are

(a) Entrained mist containing chemicals used in the wet FGD processes--including mist generated during the FGD quenching operation

(b) Entrained solids eluted from dry FGD processes which consist of partially reacted sorbents which contain sulfates, sulfites, nitrates, nitrites, chlorides, etc.

(3) Very few data, either qualitative or quantitative, exist as to the importance of these FGD derived sources to the acid aerosol problem. Neither the process vendors, FGD process operators (boiler operators), or regulatory agencies appear to be taking measurements and performing analytical studies to elucidate the importance of these sources.

(4) Acid aerosols emitted as particulate matter (both as liquids in mist and entrained solids) depend greatly on the FGD system in question and each FGD process must be evaluated separately as to its potential for aggravating the acid aerosol problem. Thus, it is difficult, if not impossible, to generalize among FGD systems.

(5) The physical and chemical nature of the particulate emissions from FGD processes will depend for the most part on the process and the hardware used in its operation. A wide range of particle size, pH values, and chemical composition are possible. The particles emitted should have the physical-chemical characteristics of the reactive liquors used in the wet FGD systems and the partially reacted sorbents used in the dry processes. Certain FGD processes by their very nature, for example, the Chiyoda CT-101 and the Foster Wheeler-Bergbau Forschung processes, would appear to have the potential to aggravate the acid aerosol problem more than other processes.

(6) Major variables thought to determine FGD process emissions of acid aerosol particles are

(a) Wet processes - reactor design, chemical nature of the scrubber liquors, removal

efficiencies, scrubber gas velocity, pressure drop, liquid to gas ratio, and mist eliminators efficiency

(b) Dry processes - reactor design or configuration, chemical nature of the solid sorbent, removal efficiencies, gas velocity through the reactor, and pressure drop.

(7) Considering sulfur emissions only (because what few data exist are in this area), quantitative estimates as to the fraction of input sulfur to the boiler emitted as entrained particles vary widely. For coal-fired boilers equipped with FGD processes, it appears that between 0.25 to 3.5 percent of the sulfur input to the boiler is emitted as entrained particles. For data on one oil-fired boiler equipped with a wet FGD system, a similar number would be about 0.4 percent of the available sulfur is emitted as entrained particles. At best, such fragmentary numbers must be considered as speculative guesses.

(8) Because of the scarcity of available data in this area, it is difficult and probably unwise to draw conclusions. The best that appears possible is to conclude that entrained FGD particles are probably a minor contributor to the acid aerosol problem, as compared to the inefficiencies in the FGD processes where perhaps 10 to 30 percent of the input SO_2/SO_3 to the scrubber and much of the NO/NO_2 are emitted to the environment. Even this conclusion is suspect because it would depend on the relative health effects associated with the particles emitted from FGD systems and those of the unabsorbed species which have the potential to form secondary acid aerosols.

(9) As far as FGD processes are concerned, all combustion modification techniques can be represented for purposes of analysis in terms of one or more of the following effects:

(a) Decreased gas volume due to low excess air and/or low firing rate

(b) Decreased total NO and NO_2 concentration in the flue gas

(c) The total concentration of SO_2 and SO_3 in the flue gas remains the same, i.e., the sulfur load on the FGD process remains about the same

(d) The ratio of SO_2 to SO_3 increases slightly due to small decreases in the SO_3 concentration

(e) Increased rates of formation of submicron particles.

(10) As a general rule, combustion modification would not be expected to greatly aggravate the acid aerosol problem associated with a boiler equipped with an FGD process, i.e., relative to the case where the boiler is operrated with an FGD process but no combustion modification. In other words, going to combustion modification on a boiler already equipped with an FGD process should not change greatly the existing acid aerosol emissions.

(11) The most significant effect that combustion modification might have on FGD processes appears to be in the increased number of small submicron particles potentially formed during combustion modification relative to normal boiler operation. These particles could serve as sorption sites for acid gases present in the flue gas. Addiitonally, they could serve as active sites to promote oxidative reactions. The efficiency for removal of submicron particles by the gas/liquid or gas/solid contacting devices used in FGD processes would be minimal. The same conclusion would be true for the electrostatic precipitators found on most large boilers preceding the FGD systems. Consequently, to the degree that combustion modification increases the rate and number of submicron particles, it would aggravate the acid aerosol problem.

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APPENDIX

The tabulated results of the computed equilibrium product concentrations for combustion of coal and two fuel oils are collected in this Appendix. The elemental composition of the coal used in these calculations is given in Table 2, page 24. The compositions of the fuel oils is given in Table 4, page 33. The product species considered in these calculations are given in Table 3, page 26 and the same product species were considered for all the coal and oil calculations except for those situations where the lack of an element, in the case of the oils, precludes the existence of a compound.

COAL RUN AT 1800K, 1 ATM, 2% EXCESS AIR

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	SiO_2	.79998428E-01
0	Al_2O_3	.24998538E-01
0	CaO	.19996590E-01
0	Fe_2O_3	.14999072E-01
0	MgO	.19975115E-02
0	B_2O_3	.49611375E-04
0	V_2O_4	.30993055E-05
4	VO	.99665234E-06
4	Na_2SO_4	.98582292E-06
4	$CaCl_2$	.97619824E-06
4	Na_2SiO_3	.96443119E-06
4	Fe	.94413770E-06
4	$FeSO_4$	.91552747E-06
4	NaCl	.87430543E-06
4	$MgSO_4$	.86703602E-06
4	MgF_2	.86420048E-06
4	C	.85806783E-06
4	Al	.85067910E-06
4	$NaHSO_4$	.80269965E-06
4	NaF	.78679593E-06
4	Na_2O	.78218868E-06
4	PbO	.78137500E-06
4	$ZnSO_4$	.78125781E-06
4	$ZnCO_3$	.78125415E-06
4	B	.78125000E-06
4	V_2O_5	.77986829E-06
4	$Al_2(SO_4)_3$	.74924817E-06
4	ZnO	.73243335E-06
4	$MgCl_2$	.72913525E-06
4	Pb	.72567773E-06
4	CaF_2	.55818045E-06
4	VCl_2	.52500000E-06
4	H_3PO_4	.62506250E-06
4	V	.52500000E-06
4	$Ca(OH)_2$	.51035181E-06
4	Si	.60987589E-06
4	$CaSO_4$	.59321345E-06
4	$AlCl_3$	.58129942E-06
4	$CaCO_3$	.57799041E-06
4	$PbSO_4$	.53722556E-06
4	Na_2CO_3	.53655720E-06
4	HPO_3	.52217342E-06
4	Na_2SO_3	.50204718E-06
0	BeO	.50125000E-06
4	$BeSO_4$	.18887500E-06
4	$BeCl_2$	.12600000E-06

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
4	BeF_2	.12537500E-06
4	Be	.52500000E-07
4	$Mg(NO_3)_2$	.10000000E-08
4	$Be(NO_3)_2$	.10000000E-08
4	$FeCl_2$	.10000000E-08
4	$Fe(NO_3)_2$	.10000000E-08
4	ZnF_2	.10000000E-08
4	$Ca(NO_3)_2$	.10000000E-08
4	$Pb(NO_3)_2$	.10000000E-08
4	$NaNO_3$	.10000000E-08
4	$Ca(NO_2)_2$	.10000000E-08
4	$NaNO_2$	.10000000E-08
4	$Zn(NO_3)_2$	.10000000E-08
4	$Al(NO_3)_3$	.10000000E-08
4	$ZnCl_2$	.10000000E-08
TOTAL CONDENSED		.14207078E+00

COAL RUN AT 800K, 1 ATM, 2%/0 EXCESS AIR

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	SiO_2	.79998419E-01
0	Al_2O_3	.24997967E-01
0	$CaSO_4$	.19995192E-01
0	Fe_2O_3	.14998736E-01
0	$MgSO_4$	.19978544E-02
0	Na_2SO_4	.99346496E-03
0	$ZnSO_4$	.39714859E-03
0	B_2O_3	.49611375E-04
0	$PbSO_4$	.81874968E-05
0	V_2O_5	.31526041E-05
4	$NaNO_2$	.97656641E-06
4	$NaOH$	.97587860E-06
4	Na_2SiO_3	.97274072E-06
4	Na	.97174072E-06
4	Na_2SO_3	.97018903E-06
4	Na_2CO_3	.94767641E-06
4	H_3PO_4	.93548898E-06
4	$Mg(NO_3)_2$	.92957689E-06
4	$FeSO_4$	.89616749E-06
4	$Al(SO_4)_3$	.88588192E-06
4	AlF_3	.86580454E-06
4	Fe	.86331196E-06
4	$AlCl_3$	.86317224E-06
4	$NaNO_3$	.85497009E-06
4	CaF_2	.85141933E-06
4	VO	.85017871E-06
4	$NaHSO_4$	.84548646E-06
4	$NaCl$	.83946636E-06
4	B	.78125000E-06
4	$ZnCl_2$	.77310374E-06
4	$FeCl_2$	.77269235E-06
4	Zn	.76831371E-06
4	$ZnCO_3$	.76682550E-06
4	V_2O_4	.75120007E-06
4	VCl_2	.72321289E-06
4	PbO	.66139069E-06
4	HPO_3	.65788864E-06
4	V	.62500000E-06
4	Pb	.62500000E-06
4	MgF_2	.62371397E-06
4	NaF	.61818750E-06
4	Na_2O	.61128833E-06
4	Si	.61033573E-06
4	Ca	.60914612E-06
4	C	.60145816E-06
4	$CaCO_3$	.59756050E-06

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
4	$MgCl_2$	.59732339E-06
4	$Al(NO_3)_3$	.57247063E-06
4	$Ca(NO_3)_2$	.56199330E-06
4	$Ca(NO_2)_2$	.56199281E-06
4	$Ca(OH)_2$	.56199257E-06
4	CaO	.56199244E-06
4	ZnO	.54817040E-06
4	$PbCl_2$	.52911255E-06
4	$CaCl_2$	.50986646E-06
0	$BeSO_4$	.26662500E-06
4	$Be(NO_3)_2$	.25100000E-06
4	BeO	.18018750E-06
4	$BeCl_2$	.14993750E-06
4	BeF_2	.12600000E-06
4	Be	.31250000E-07
4	$Zn(NO_3)_2$	.10000000E-08
4	$Pb(NO_3)_2$	.10000000E-08
4	$Fe(NO_3)_2$	.10000000E-08
4	MgO	0.
4	ZnF_2	0.
4	Al	0.
4	Mg	0.
TOTAL CONDENSED		.14347422E+00

COAL RUN AT 650K, 1 ATM, 2% EXCESS AIR

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)	C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	SiO_2	.79998777E-01	4	Ca	.60914512E-06
0	$Al(SO_4)_3$	.24605361E-01	4	CaF_2	.60810648E-06
0	$CaSO_4$	.19995121E-01	4	Na_2CO_3	.60580713E-06
0	Fe_2O_3	.14998257E-01	4	Mg	.59725905E-06
0	$MgSO_4$	.19961815E-02	4	$Pb(NO_3)_2$	.58616016E-06
0	$NaHSO_4$	.19883333E-02	4	$Al(NO_3)_3$	.57582389E-06
0	$ZnSO_4$	.39704863E-03	4	NaCl	.55820373E-06
0	Al_2O_3	.39299708E-03	4	$Ca(OH)_2$	.54865768E-06
0	B_2O_3	.49611375E-04	4	MgO	.54563031E-06
0	HFO_3	.39089540E-04	4	$CaCl_2$	.53002042E-06
0	$PbSO_4$	.73210568E-05	4	VO	.52767041E-06
0	V_2O_5	.32991635E-05	4	$Ca(NO_3)_2$	.52557223E-06
4	$NaNO_2$	.97656641E-06	4	$PbCl_2$	.50312842E-06
4	Na	.97174072E-06	0	$BeSO_4$	.38845294E-06
4	$Mg(NO_3)_2$	.96826500E-06	4	NaF	.21783277E-06
4	C	.96796387E-06	4	$BeCl_2$	.19278125E-06
4	$FeCl_2$	.93385350E-06	4	BeO	.19124176E-06
4	$NaNO_3$	.92159039E-06	4	$Be(NO_3)_2$	.14036719E-06
4	H_3PO_4	.91691772E-06	4	BeF_2	.60906860E-07
4	Na_2SO_3	.91147376E-06	4	Be	.31250000E-07
4	$Fe(NO_3)_2$	.90915801E-06	4	$Zn(NO_3)_2$	.10000000E-08
4	Fe	.90466409E-06	4	ZnF_2	0.
4	MgF_2	.87783353E-06	TOTAL CONDENSED		.14450732E+00
4	NaOH	.85195046E-06			
4	$MgCl_2$	.83453016E-06			
4	PbO	.83163586E-06			
4	$AlCl_3$	.82491785E-06			
4	Na_2SO_4	.82288430E-06			
4	V_2O_4	.81471502E-06			
4	B	.78125000E-06			
4	$ZnCl_2$	.77163357E-06			
4	$CaCO_3$	.76774355E-06			
4	$ZnCO_3$	.76531925E-06			
4	AlF_3	.76523863E-06			
4	Pb	.76200879E-06			
4	Zn	.75196289E-06			
4	$FeSO_4$	.74367846E-06			
4	Al	.72417259E-06			
4	CaO	.58625918E-06			
4	ZnO	.55745301E-06			
4	VCl_2	.62556250E-06			
4	V	.62500000E-06			
4	Na_2SiO_3	.61449945E-06			
4	$Ca(NO_2)_2$	.61035205E-06			
4	Si	.61033573E-06			
4	Na_2O	.61022010E-06			

COAL RUN AT 650K, 1 ATM, 2% EXCESS AIR

GASEOUS PRODUCTS

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	N_2	.30199994E+02
0	CO_2	.59999956E+01
0	H_2O	.24969746E+01
0	HCl	.39882057E-02
0	SO_2	.16828616E-02
0	SO_3	.10577982E-03
0	HF	.14408227E-04
0	H_2SO_4	.73397424E-05
1	CH_4	.33463447E-06
1	S_2	.21233984E-06
1	O_2	.13486592E-06
1	Cl_2	.76697016E-08
1	P_4	.51035156E-09
1	NO	.50160262E-09
1	F_2	.26519052E-09
1	PCl_5	.97656250E-12
1	H_2SO_3	.58550104E-12
1	H_2	.32183552E-12
1	NO_2	.15095071E-12
1	BF_3	.14747189E-12
1	CO	.55949159E-13
1	N_2O	.57524579E-13
0	$FeCl_3$	.47581038E-13
1	NOCl	.59970230E-14
0	P_4O_{10}	.47479526E-16
1	HNO_3	.77434462E-18
0	BCl_3	.10382101E-20
0	$POCl_3$	.77961525E-22
1	COS	.72843781E-31
1	N_2O_4	.19282572E-31
1	PCl_3	.88642303E-35
1	N_2O_5	.54729802E-39
TOTAL GASEOUS		.38702765E+02

TOTAL PRESSURE = 1.0000 ATM.

COAL RUN AT [redacted], 1 ATM, 2% EXCESS AIR

GASEOUS PRODUCTS

800K

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	N_2	.30199994E+02
0	CO_2	.59999971E+01
0	H_2O	.24978978E+01
0	SO_2	.42578898E-01
0	SO_3	.33925401E-01
0	O_2	.20446799E-01
0	HCl	.39879143E-02
0	H_2SO_4	.98233589E-04
0	HF	.13598132E-04
0	P_4O_{10}	.96039041E-05
0	NO	.44932470E-05
0	Cl_2	.29158384E-06
0	NO_2	.69138888E-07
0	N_2O	.38599788E-09
0	NOCl	.87721345E-10
1	CH_4	.17282012E-10
0	H_2	.55955449E-11
0	CO	.31671197E-11
0	HNO_3	.16468992E-11
1	P_4	.14459428E-11
0	H_2SO_3	.65577312E-12
0	$FeCl_3$	.29818026E-12
0	BF_3	.13036372E-13
0	$POCl_3$	.52988441E-18
0	BCl_3	.96568373E-19
0	N_2O_4	.64266204E-21
0	N_2O_5	.10096320E-25
0	COS	.69097808E-29
0	PCl_3	.18389653E-29
0	F_2	.18785523E-34
0	S_2	.37607557E-37
0	PCl_5	.12123215E-41
TOTAL GASEOUS		.38798954E+02

1800K

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	N_2	.30192687E+02
0	CO_2	.59589724E+01
0	H_2O	.24936565E+01
0	SO_2	.99950240E-01
0	O_2	.59300872E-01
0	CO	.31024809E-01
0	NO	.14620349E-01
0	HCl	.39765743E-02
0	H_2	.34284435E-02
0	NaOH	.18132719E-02
0	Zn	.39770305E-03
0	Na	.17673517E-03
0	SO_3	.41354842E-04
0	HF	.15931691E-04
0	P_4O_{10}	.97154410E-05
0	$PbCl_2$	.79587207E-05
0	NO_2	.29498894E-05
0	N_2O	.74666124E-06
0	Mg	.32147443E-07
0	Cl_2	.34651824E-08
0	NOCl	.14093228E-08
0	COS	.41300838E-09
0	Ca	.14704153E-09
0	H_2SO_4	.49744307E-10
0	$FeCl_3$	.25613099E-10
0	S_2	.44118781E-11
0	HNO_3	.27540221E-11
0	H_2SO_3	.36832737E-12
0	BCl_3	.58617804E-14
0	$POCl_3$	.33135544E-15
0	BF_3	.12059982E-15
0	PCl_3	.36066876E-17
0	AlF_3	.50543846E-18
0	CH_4	.69309060E-19
0	N_2O_4	.24622900E-19
0	F_2	.38295920E-23
0	N_2O_5	.12370770E-23
0	P_4	.88194525E-31
0	PCl_5	.15242427E-33
TOTAL GASEOUS		.38870094E+02

COAL RUN AT 1800K, 1 ATM, 98% OF STOICHIOMETRIC AIR

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	SiO_2	.79998883E-01
0	Al_2O_3	.24998449E-01
0	CaO	.19996570E-01
0	Fe_2O_3	.14999072E-01
0	MgO	.19969863E-02
0	B_2O_3	.49611375E-04
0	V_2O_4	.30388027E-05
4	VO	.99665234E-06
4	Na_2SO_4	.98644662E-06
4	$CaCl_2$	.97619824E-06
4	$MgSO_4$	.94431327E-06
4	Fe	.94413770E-06
4	$FeSO_4$	.91552747E-06
4	Al	.88174421E-06
4	MgF_2	.86665753E-06
4	V_2O_5	.84037109E-06
4	$NaHSO_4$	.80364037E-06
4	NaCl	.79081423E-06
4	NaF	.78533810E-06
4	Na_2O	.78261295E-06
4	PbO	.78137500E-06
4	$ZnSO_4$	.78125781E-06
4	$ZnCO_3$	.78125415E-06
4	B	.78125000E-06
4	$Al_2(SO_4)_3$	.77894582E-06
4	Pb	.74112672E-06
4	ZnO	.73243335E-06
4	Na_2CO_3	.72921207E-06
4	$MgCl_2$	.72168894E-06
4	$AlCl_3$	.66878644E-06
4	CaF_2	.66473259E-06
4	VCl_2	.52600000E-06
4	H_3PO_4	.62506250E-06
4	V	.62500000E-06
4	$Ca(OH)_2$	.61035181E-06
4	Si	.60987589E-06
4	$CaSO_4$	.59886949E-06
4	$CaCO_3$	.58364645E-06
4	HPO_3	.55780510E-06
4	$PbSO_4$	.53722656E-06
4	Na_2SO_3	.52942979E-06
4	Na_2SiO_3	.50959158E-06
4	C	.50134652E-06
0	BeO	.50125000E-06
4	$BeSO_4$	.18887500E-06
4	$BeCl_2$	.12600000E-06
4	BeF_2	.12537500E-06
4	Be	.62500000E-07
4	$FeCl_2$	.10000000E-08
4	$Fe(NO_3)_2$	.10000000E-08
4	$ZnCl_2$	.10000000E-08
4	$Mg(NO_3)_2$	.10000000E-08
4	$Pb(NO_3)_2$	.10000000E-08
4	ZnF_2	.10000000E-08
4	$Be(NO_3)_2$	.10000000E-08
4	$NaNO_2$	.10000000E-08
4	$Zn(NO_3)_2$	.10000000E-08
4	$Ca(NO_3)_2$	.10000000E-08
4	$Ca(NO_2)_2$	.10000000E-08
4	$NaNO_3$	.10000000E-08
4	$Al(NO_3)_3$	.10000000E-08
TOTAL CONDENSED		.14207022E+00

COAL RUN AT 1800K, 1 ATM, 98% OF STOICHIOMETRIC AIR

C VECTOR	EQUILIBRIUM CONCENTRATION (MOLES)
0 N_2	.28999548E+02
0 CO_2	.55500546E+01
0 H_2O	.24448543E+01
0 CO	.44994126E+00
0 SO_2	.99986595E-01
0 H_2	.52427315E-01
0 HCl	.39764490E-02
0 NaOH	.14399549E-02
0 NO	.90361207E-03
0 Na	.55060470E-03
0 Zn	.39770805E-03
0 O_2	.23584534E-03
0 HF	.15915132E-04
0 P_4O_{10}	.97065331E-05
0 $PbCl_2$	.79432717E-05
0 SO_3	.26525014E-05
0 COS	.15067442E-05
0 Mg	.48506261E-06
0 S_2	.27010727E-06
0 N_2O	.45979989E-07
0 NO_2	.11688890E-07
0 Ca	.22186632E-08
0 Cl_2	.22659726E-09
0 $FeCl_3$	.26821798E-10
0 NOCl	.22644761E-10
0 H_2SO_4	.32334416E-11
0 H_2SO_3	.37342558E-12
0 BCl_3	.71855901E-14
0 CH_4	.39171302E-14
0 HNO_3	.27816925E-14
0 $POCl_3$	.34979574E-15
0 BF_3	.12590951E-15
0 PCl_3	.59382360E-16
0 AlF_3	.63209435E-18
0 P_4	.75076736E-19
0 N_2O_4	.39962426E-24
0 F_2	.24992239E-24
0 N_2O_5	.12872567E-29
0 PCl_5	.16963285E-33
TOTAL GASEOUS	.37604355E+02

TOTAL PRESSURE = 1.0000 ATM.

COAL RUN AT 500K, 1 ATM, 10°/o EXCESS AIR

VECTOR	EQUILIBRIUM CONCENTRATION (MOLES)
0 SiO_2	.79998743E-01
0 $Al_2(SO_4)_3$	.24998290E-01
0 $CaSO_4$	.19995016E-01
0 Fe_2O_3	.14896095E-01
0 $MgSO_4$	.19960038E-02
0 $NaHSO_4$	.19882803E-02
0 $ZnSO_4$	.39582253E-03
0 $FeSO_4$	.20521233E-03
0 B_2O_3	.49611374E-04
0 HPO_3	.39452237E-04
0 $PbSO_4$	.58390898E-05
0 V_2O_5	.34399063E-05
4 $CaCO_3$	.99545887E-06
4 $PbCl_2$	.97694141E-06
4 $NaNO_2$	.97656541E-06
4 $Mg(NO_3)_2$	.97543783E-06
4 $ZnCO_3$	.95961005E-06
4 PbO	.93784375E-06
4 $Ca(NO_3)_2$	.93229009E-06
4 $Ca(NO_2)_2$	.93228911E-06
4 CaF	.92184948E-06
4 Na_2O	.89334575E-06
4 MgO	.89118740E-06
4 $Al(NO_3)_3$	.86621829E-06
4 ZnO	.85070207E-06
4 $ZnCl_2$	.84922458E-06
4 NaCl	.84590620E-06
4 Na_2SO_4	.84590620E-06
4 Mg	.80438539E-06
4 Fe	.79683917E-06
4 $MgCl_2$	.78260786E-06
4 $Zn(NO_3)_2$	.78125781E-06
4 B	.78125000E-06
4 NaF	.76565866E-06
4 Al_2O_3	.74897860E-06
4 Zn	.74267578E-06
4 $FeCl_3$	.73067561E-06
4 Al	.72315534E-06
4 $NaNO_3$	.67513080E-06
4 Na_2CO_3	.67248014E-06
4 Na_2SiO_3	.64881189E-06
4 Na	.64781189E-06
4 VCl_2	.62543750E-06
4 V_2O_4	.62531250E-06
4 VO	.62512500E-06
4 $Pb(NO_3)_2$	.62512500E-06

VECTOR	EQUILIBRIUM CONCENTRATION (MOLES)
4 V	.62500000E-06
4 Pb	.62500000E-06
4 Si	.61034168E-06
4 Ca	.60914512E-06
4 $Ca(OH)_2$	.60128617E-06
4 $Fe(NO_3)_2$	.55868034E-06
4 NaOH	.56823136E-06
4 Na_2SO_3	.55764461E-06
4 C	.56632338E-06
4 H_3PO_4	.55672461E-06
4 MgF_2	.54255970E-06
4 $FeCl_2$	.50743121E-06
0 $BeSO_4$	.40371875E-06
4 BeO	.36264063E-06
4 AlF_3	.33980591E-06
4 BeF_2	.98781250E-07
4 $BeCl_2$	.63500000E-07
4 $Be(NO_3)_2$	.45109375E-07
4 Be	.31250000E-07
4 S_2	.28165527E-09
4 $AlCl_3$	0.
4 CaO	0.
4 ZnF_2	0.
4 $CaCl_2$	0.
TOTAL CONDENSED	.14460856E+00

COAL RUN AT 650K, 1 ATM, 10% EXCESS AIR

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	SiO_2	.79998638E-01
0	$Al_2(SO_4)_3$	.24998203E-01
0	$CaSO_4$	.19995128E-01
0	Fe_2O_3	.14998+45E-01
0	$MgSO_4$	.19963159E-02
0	$NaHSO_4$	.19876723E-02
0	$ZnSO_4$	.39715774E-03
0	B_2O_3	.49611375E-04
0	HPO_3	.39403417E-04
0	$PbSO_4$	.73565020E-05
0	V_2O_5	.32834531E-05
4	$NaNO_2$	.97656541E-06
4	Na	.97174072E-06
4	$Mg(NO_3)_2$	.96826610E-06
4	Na_2SO_3	.95241796E-06
4	$FeCl_2$	.93385325E-06
4	NaCl	.89326169E-06
4	$MgCl_2$	.83453006E-06
4	$AlCl_3$	.82491793E-06
4	$PbCl_2$	.81574756E-06
4	V_2O_4	.78170313E-06
4	B	.78125000E-06
4	$ZnCl_2$	.77807054E-06
4	$ZnCO_3$	.77175605E-06
4	MgF_2	.76906041E-06
4	Zn	.76196289E-06
4	NaOH	.75422507E-06
4	Na_2SiO_3	.75409572E-06
4	Fe	.74902500E-06
4	$FeSO_4$	.74193893E-06
4	Al	.72417259E-06
4	NaF	.71437910E-06
4	PbO	.69850830E-06
4	Na_2SO_4	.59329942E-06
4	$Fe(NO_3)_2$	.59195421E-06
4	$Ca(OH)_2$	.58625931E-06
4	CaO	.58625919E-06
4	$NaNO_3$	.58271771E-06
4	Na_2CO_3	.66536687E-06
4	VCl_2	.52556250E-06
4	VO	.62512500E-06
4	V	.62500000E-06
4	$CaCl_2$	.62271909E-06
4	$Ca(NO_2)_2$	.51035205E-06
4	Si	.61033673E-06
4	Na_2O	.61022010E-06

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
4	Ca	.50914512E-06
4	$CaCO_3$	.50899321E-06
4	H_3PO_4	.50314014E-06
4	Mg	.59725990E-06
4	$Pb(NO_3)_2$	.58616016E-06
4	$Al(NO_3)_3$	.57582862E-06
4	C	.56394288E-06
4	Pb	.54708203E-06
4	ZnO	.53546569E-06
4	CaF_2	.52948181E-06
4	$Ca(NO_3)_2$	.52657582E-06
4	MgO	.52000743E-06
4	Al_2O_3	.50187514E-06
4	AlF_3	.47314326E-06
0	$BeSO_4$	.38204297E-06
4	BeO	.21092969E-06
4	$BeCl_2$	.19278125E-06
4	$Be(NO_3)_2$	.14036719E-06
4	BeF_2	.+7528906E-07
4	Be	.31250000E-07
4	$Zn(NO_3)_2$	.10000000E-08
4	ZnF_2	0.
TOTAL CONDENSED		.14450538E+00

COAL RUN AT 800K, 1 ATM, 10% EXCESS AIR

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	SiO_2	.79998419E-01
0	Al_2O_3	.24338173E-01
0	$CaSO_4$	.19995130E-01
0	Fe_2O_3	.14998706E-01
0	$MgSO_4$	.19978532E-02
0	Na_2SO_4	.39381414E-03
0	$ZnSO_4$	.39669473E-03
0	B_2O_3	.49611375E-04
0	$PbSO_4$	.88488875E-05
0	V_2O_5	.32834531E-05
4	$NaNO_2$	.97656541E-06
4	NaOH	.97587860E-06
4	ZnO	.97290016E-06
4	Na_2SiO_3	.97274072E-06
4	Na	.97174072E-06
4	$AlCl_3$	.96891933E-06
4	Na_2CO_3	.96004305E-06
4	$Mg(NO_3)_2$	.92957785E-06
4	$FeCl_2$	.90266536E-06
4	AlF_3	.86372380E-06
4	Fe	.86332537E-06
4	$NaNO_3$	.85497009E-06
4	CaF_2	.85123527E-06
4	$FeSO_4$	.82644795E-06
4	$ZnCl_2$	.80353810E-06
4	V_2O_4	.78170313E-06
4	B	.78125000E-06
4	$ZnCO_3$	.77176957E-06
4	Zn	.76196289E-06
4	Na_2SO_3	.75539196E-06
4	NaCl	.72929839E-06
4	C	.68849698E-06
4	HPO_3	.65373752E-06
4	$NaHSO_4$	.62158831E-06
4	VCl_2	.62556250E-06
4	VO	.62512500E-06
4	V	.62500000E-06
4	Pb	.62500000E-06
4	MgF_2	.62435470E-06
4	$Al_2(SO_4)_3$	.62253164E-06
4	NaF	.61818750E-06
4	Na_2O	.61128833E-06
4	Si	.61033573E-06
4	$CaCO_3$	.60919194E-06
4	Ca	.60914512E-06
4	H_3PO_4	.60803467E-06

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
4	$MgCl_2$	.58291696E-06
4	$Al(NO_3)_3$	.57247201E-06
4	$Ca(NO_3)_2$	.56199375E-06
4	$Ca(NO_2)_2$	.56199326E-06
4	$Ca(OH)_2$	.56199301E-06
4	CaO	.56199289E-06
4	$CaCl_2$	.56078920E-06
4	$PbCl_2$	.52911255E-06
0	$BeSO_4$	.25662500E-06
4	$Be(NO_3)_2$	.25100000E-06
4	BeO	.18018750E-06
4	$BeCl_2$	.14993750E-06
4	BeF_2	.12600000E-06
4	Be	.31250000E-07
4	$Zn(NO_3)_2$	.10000000E-08
4	$Pb(NO_3)_2$	.10000000E-08
4	$Fe(NO_3)_2$	.10000000E-08
4	ZnF_2	0.
4	Al	0.
4	PbO	0.
4	MgO	0.
4	Mg	0.
TOTAL CONDENSED		.14347376E+00

COAL RUN AT 1800K, 1ATM, 10°/o EXCESS AIR

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	SiO_2	.79998533E-01
0	Al_2O_3	.24998588E-01
0	CaO	.19996584E-01
0	Fe_2O_3	.14999086E-01
0	MgO	.19974689E-02
0	B_2O_3	.49611375E-04
0	V_2O_5	.33614844E-05
4	$CaCl_2$	.97619824E-06
4	$MgCl_2$	.96383972E-06
4	NaCl	.93129847E-06
4	$FeSO_4$	.91552747E-06
4	Fe	.91552734E-06
4	MgF_2	.86070161E-06
4	Na_2SiO_3	.85962373E-06
4	PbO	.78137500E-06
4	$ZnSO_4$	.78125781E-06
4	B	.78125000E-06
4	$NaNO_3$	.74503799E-06
4	$NaHSO_4$	.74503409E-06
4	Al	.74260203E-06
4	Na_2CO_3	.73822575E-06
4	$ZnCO_3$	.71633730E-06
4	C	.71280492E-06
4	$Al_2(SO_4)_3$	.71068741E-06
4	Na_2SO_4	.70919477E-06
4	Na_2SO_3	.70919379E-06
4	V_2O_4	.70345313E-06
4	Na_2O	.70212113E-06
4	$MgSO_4$	.69830141E-06
4	ZnO	.66751650E-06
4	$AlCl_3$	.66660769E-06
4	CaF_2	.64885013E-06
4	HPO_3	.64456694E-06
4	VCl_2	.62600000E-06
4	VO	.62512500E-06
4	H_3PO_4	.62506250E-06
4	Pb	.62500000E-06
4	V	.62500000E-06
4	$Ca(OH)_2$	.61035181E-06
4	Si	.60987589E-06
4	$CaSO_4$	.60077286E-06
4	$CaCO_3$	.58554982E-06
4	$PbSO_4$	.53722656E-06
0	BeO	.50125000E-06
4	$BeSO_4$	.18887500E-06
4	$BeCl_2$	.12600000E-06

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
4	BeF_2	.12537500E-06
4	Be	.62500000E-07
4	$Zn(NO_3)_2$	.10000000E-08
4	$Co(NO_3)_2$	.10000000E-08
4	$Be(NO_3)_2$	.10000000E-08
4	$Co(NO_2)_2$	.10000000E-08
4	$ZnCl_2$	.10000000E-08
4	$Al(NO_3)_3$	.10000000E-08
4	$Pb(NO_3)_3$	.10000000E-08
4	$Mg(NO_3)_3$	.10000000E-08
4	$FeCl_2$	.10000000E-08
4	$Fe(NO_3)_3$	.10000000E-08
4	$NaNO_2$	.10000000E-08
4	ZnF_2	.10000000E-08
4	NaF	0.
TOTAL CONDENSED		.14207035E+00

COAL RUN AT [redacted], 1 ATM, 10% EXCESS AIR

GASEOUS PRODUCTS

500K

VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	N_2	.31999993E+02
0	CO_2	.59999965E+01
0	H_2O	.24967878E+01
0	O_2	.44910177E+00
0	HCl	.35770989E-02
0	H_2SO_4	.39994309E-03
0	Cl_2	.20614488E-03
0	SO_3	.16206916E-04
0	HF	.15104533E-04
1	CH_4	.29660823E-06
0	NO_2	.85087085E-07
0	NO	.52459705E-08
0	SO_2	.59640288E-09
0	HNO_3	.27551053E-09
0	NOCl	.10116688E-09
1	P_4	.95367432E-11
1	F_2	.23279747E-11
0	BF_3	.17089093E-11
0	N_2O	.11543875E-11
1	COS	.64899324E-13
1	PCl_3	.30517578E-13
1	PCl_5	.30517578E-13
0	H_2SO_3	.20770177E-16
0	N_2O_4	.12045340E-18
0	H_2	.31006622E-21
1	N_2O_5	.56601004E-23
0	CO	.54093766E-23
0	BCl_3	.15258519E-24
0	PO	.39676271E-27
0	P_4O_{10}	.41556381E-28
TOTAL GASEOUS		.40950094E+02

650K

VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	N_2	.31999994E+02
0	CO_2	.59999783E+01
0	H_2O	.24969209E+01
0	O_2	.44919065E+00
0	HCl	.39602663E-02
0	SO_3	.57606783E-03
0	H_2SO_4	.37775846E-04
1	CH_4	.19054041E-04
0	HF	.15189318E-04
1	Cl_2	.13397863E-04
0	SO_2	.51648865E-05
1	NO	.94231334E-06
0	NO_2	.50316663E-06
1	P_4	.31035156E-09
0	NOCl	.45813743E-09
1	F_2	.26533580E-09
1	S_2	.17968777E-09
1	N_2O	.10814377E-09
0	HNO_3	.10569503E-09
1	PCl_5	.97656250E-12
1	BF_3	.15798052E-12
1	$FeCl_3$	.45293753E-13
1	COS	.26313295E-14
1	H_2SO_3	.16997526E-14
1	H_2	.18152681E-15
0	P_4O_{10}	.56251339E-16
0	CO	.37195435E-16
1	N_2O_4	.20245342E-18
1	BCl_3	.98829981E-21
0	$POCl_3$	.76344285E-22
1	N_2O_5	.12057817E-22
0	PCl_3	.48992227E-38
		.40950712E+02

COAL RUN AT [redacted], 1 ATM, 10% EXCESS AIR

GASEOUS PRODUCTS

800K			1800K		
C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)	C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	N_2	.31999934E+02	0	N_2	.31978491E+02
0	CO_2	.59999722E+01	0	CO_2	.59887925E+01
0	H_2O	.24977839E+01	0	H_2O	.24958278E+01
0	O_2	.45738973E+00	0	O_2	.48403334E+00
0	SO_3	.50051512E-01	0	SO_2	.99877193E-01
0	SO_2	.15387377E-01	0	NO	.42988757E-01
0	HCl	.39854119E-02	0	CO	.11204800E-01
0	H_2SO_4	.16439384E-03	0	HCl	.39755730E-02
1	CH_4	.24810879E-04	0	NaOH	.18773071E-02
0	NO	.21876741E-04	0	H_2	.12351561E-02
0	HF	.13603441E-04	0	Zn	.39783789E-03
0	P_4O_{10}	.36842379E-05	0	SO_3	.11480595E-03
1	NO_2	.15480409E-05	0	Na	.11284981E-03
1	Cl_2	.13394629E-05	0	NO_2	.24096306E-04
0	N_2O	.18858455E-08	0	HF	.16744147E-04
0	NOCl	.89010990E-09	0	P_4O_{10}	.96848426E-05
1	HNO_3	.76890920E-10	0	$PoCl_2$	.80593984E-05
1	S_2	.27683175E-10	0	N_2O	.21970140E-05
1	P_4	.19073486E-10	0	Mg	.12238014E-07
1	H_2	.12165506E-11	0	Cl_2	.96136215E-08
1	CO	.68861604E-12	0	NOCl	.67115157E-08
0	$FeCl_3$	.28943996E-12	0	H_2SO_4	.13068882E-09
1	H_2SO_3	.23861545E-12	0	Ca	.55976342E-10
0	BF_3	.12692916E-13	0	HNO_3	.36476755E-10
0	$POCl_3$	.50825187E-18	0	$FeCl_3$	.24854702E-10
1	N_2O_4	.30462106E-18	0	COS	.18259921E-10
0	BCl_3	.93733763E-19	0	H_2SO_3	.34833060E-12
1	N_2O_5	.22008931E-22	0	S_2	.69937733E-13
1	PCl_3	.38350121E-30	0	BCl_3	.66586025E-14
1	COS	.25850653E-31	0	$POCl_3$	.31682364E-15
1	F_2	.86471319E-34	0	BF_3	.13596421E-15
0	PCl_5	.10981548E-41	0	N_2O_4	.15534865E-17
TOTAL GASEOUS		.41035792E+02	0	PCl_3	.12412945E-17
			0	AlF_3	.68257121E-18
			0	CH_4	.10455041E-20
			0	N_2O_5	.21680599E-21
			0	F_2	.11741794E-22
			0	PCl_5	.13761346E-33
			0	P_4	.32106879E-35
			TOTAL GASEOUS		.41108990E+02

#2 Fuel Oil, 2% Excess Air, 1 Atm.

1800 K

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
4	C	.86411754E-06
0	Na_2SO_3	.58697607E-06
4	Na_2O	.31396387E-06
4	Na_2SO_4	.29398804E-06
4	Na	.25263770E-06
4	Na_2CO_3	.13024939E-06
4	NaOH	.93363647E-07
0	NiO	.51000000E-07
0	V_2O_5	.39250000E-07
4	$NiSO_4$	.26000000E-07
4	Ni	.25000000E-07
4	V_2O_4	.19375000E-07
4	VO	.19000000E-07
4	V	.18750000E-07
4	$NaNO_3$	.76654053E-08
4	$NaHSO_4$	.69785156E-08
4	$NaNO_2$	.10000000E-08
4	$Ni(NO_3)_2$	.10000000E-08
4	$Ni(OH)_2$	.10000000E-08
TOTAL CONDENSED		.27513152E-05
0	N_2	.42645730E+02
0	CO_2	.72251684E+01
0	H_2O	.63941873E+01
0	Ne	.10000000E+01
0	Ar	.10000000E+01
0	He	.10000000E+01
0	O_2	.20778564E+00
0	NO	.32526267E-01
0	CO	.24830612E-01
0	SO_2	.62551808E-02
0	H_2	.58126466E-02
0	NO_2	.99251610E-05
0	SO_3	.39142497E-05
0	N_2O	.15951168E-05
0	HNO_3	.14743570E-10
0	H_2SO_4	.78813819E-11
0	COS	.59039545E-11
0	H_2SO_3	.38587963E-13
0	S_2	.21560614E-14
0	N_2O_4	.18196704E-18
0	CH_4	.44929536E-19
0	N_2O_5	.13826752E-22
TOTAL GASEOUS		.59542312E+02

800K

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
4	C	.75526560E-06
0	Na_2SO_4	.71807031E-06
4	$NaHSO_4$	.38370313E-06
4	$NaNO_2$	.37600000E-06
4	Na_2SO_3	.21225000E-06
4	Na_2CO_3	.14251563E-06
4	NaOH	.53812500E-07
0	$NiSO_4$	.51500000E-07
0	V_2O_5	.39250000E-07
4	$Ni(OH)_2$	.26250000E-07
4	V_2O_4	.19375000E-07
4	VO	.19000000E-07
4	V	.18750000E-07
4	$NaNO_3$	.17625000E-07
4	NiO	.12750000E-07
4	Ni	.12500000E-07
4	Na_2O	.11734375E-07
4	Na	.11718750E-07
4	$Ni(NO_3)_2$	.10000000E-08
TOTAL CONDENSED		.28830703E-05
0	N_2	.42661991E+02
0	CO_2	.72499921E+01
0	H_2O	.63999858E+01
0	Ne	.10000000E+01
0	He	.10000000E+01
0	Ar	.10000000E+01
0	O_2	.20626210E+00
0	SO_3	.49634470E-02
2	SO_2	.12951010E-02
1	NO	.16961787E-04
1	CH_4	.69641718E-05
0	NO_2	.66930511E-06
1	S_2	.47750700E-07
1	N_2O	.14017618E-08
0	HNO_3	.32972058E-10
0	H_2	.55903577E-11
0	CO	.14922633E-11
1	H_2SO_4	.92455670E-12
0	H_2SO_3	.33308853E-13
1	N_2O_4	.39251047E-19
1	N_2O_5	.15812126E-23
1	COS	.98239301E-32
TOTAL GASEOUS		.59524514E+02

#2 Fuel Oil, 2% Excess Air, 1 Atm

650 K

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	$NaHSO_4$	.96475000E-06
4	C	.85408078E-06
4	S_2	.76401068E-06
4	$NaNO_2$	.37600000E-06
4	Na_2CO_3	.32887500E-06
4	Na_2SO_4	.24118750E-06
4	Na_2SO_3	.21225000E-06
4	NaOH	.53812500E-07
0	$NiSO_4$	.51500000E-07
0	V_2O_5	.39250000E-07
4	$Ni(OH)_2$	.26250000E-07
4	V_2O_4	.19375000E-07
4	VO	.19000000E-07
4	V	.18750000E-07
4	$NaNO_3$	.17625000E-07
4	NiO	.12750000E-07
4	Ni	.12500000E-07
4	Na_2O	.11734375E-07
4	Na	.11719750E-07
4	$Ni(NO_3)_2$	.10000000E-08
TOTAL CONDENSED		.40464196E-05
0	N_2	.42661999E+02
0	CO_2	.72499849E+01
0	H_2O	.63993325E+01
0	Ne	.10000000E+01
0	He	.10000000E+01
0	Ar	.10000000E+01
0	O_2	.20568345E+00
0	SO_3	.55292775E-02
0	H_2SO_4	.63930933E-03
0	SO_2	.88328917E-04
1	CH_4	.13828277E-04
0	NO	.73529984E-06
1	NO_2	.22063612E-06
1	COS	.95501823E-07
0	N_2O	.80927078E-10
1	HNO_3	.46105375E-10
1	H_2SO_3	.51250683E-13
1	H_2	.82888215E-15
1	CO	.80081938E-16
1	N_2O_4	.26785702E-19
1	N_2O_5	.89540244E-24
TOTAL GASEOUS		.59523272E+02

500K

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	$NaHSO_4$	.96475000E-06
4	S_2	.82367159E-06
4	C	.51240753E-06
4	$NaNO_2$	.37500000E-06
4	Na_2CO_3	.32887500E-06
4	Na_2SO_4	.24118750E-06
4	Na_2SO_3	.21225000E-06
4	NaOH	.53812500E-07
0	$NiSO_4$	.38999993E-07
0	V_2O_5	.38968750E-07
4	$Ni(NO_3)_2$	.26000000E-07
4	V_2O_4	.21875000E-07
4	$Ni(OH)_2$	.20000000E-07
4	V	.18750000E-07
4	$NaNO_3$	.17625000E-07
4	VO	.14562500E-07
4	NiO	.12750000E-07
4	Na_2O	.11734375E-07
4	Na	.11718750E-07
4	Ni	.62500000E-08
TOTAL CONDENSED		.37521885E-05
0	N_2	.42662000E+02
0	CO_2	.72499981E+01
0	H_2	.63938817E+01
0	Ne	.10000000E+01
0	He	.10000000E+01
0	Ar	.10000000E+01
0	O_2	.20561387E+00
0	H_2SO_4	.61160447E-02
0	SO_3	.14065809E-03
1	CH_4	.86713686E-06
1	COS	.19249212E-06
0	NO_2	.37310810E-07
0	SO_2	.92222103E-08
0	NO	.48805250E-08
0	HNO_3	.12014025E-09
0	N_2O	.85377081E-12
0	H_2SO_3	.56587566E-15
0	N_2O_4	.15934343E-19
0	H_2	.14146536E-20
0	CO	.11645797E-22
0	N_2O_5	.42028034E-24
TOTAL GASEOUS		.59517751E+02

#2 Fuel Oil, 10% Excess Air, 1 Atm., 1800K

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
4	C	.86412107E-06
0	Na_2SO_3	.58597607E-06
4	Na_2O	.31396387E-06
4	Na_2SO_4	.29398804E-06
4	Na	.25263770E-06
4	Na_2CO_3	.13024939E-06
4	NaOH	.93363647E-07
0	NiO	.51000000E-07
0	V_2O_5	.39250000E-07
4	$NiSO_4$	.26000000E-07
4	Ni	.25000000E-07
4	V_2O_4	.19375000E-07
4	VO	.19000000E-07
4	V	.18750000E-07
4	$NaNO_3$	.76654053E-08
4	$NaHSO_4$	.69785156E-08
4	$NaNO_2$	.10000000E-08
4	$Ni(NO_3)_2$	.10000000E-08
4	$Ni(OH)_2$	.10000000E-08
TOTAL CONDENSED		.27513187E-05

0	N_2	.45970643E+02
0	CO_2	.72383590E+01
0	H_2O	.63972788E+01
0	O_2	.10155366E+01
0	Ne	.10000000E+01
0	Ar	.10000000E+01
0	He	.10000000E+01
0	NO	.74658184E-01
0	CO	.11640027E-01
0	SO_2	.62507357E-02
0	H_2	.27211661E-02
0	NO_2	.48687142E-04
0	SO_3	.83593493E-05
0	N_2O	.36745300E-05
0	HNO_3	.10223127E-09
0	H_2SO_4	.15736444E-10
0	COS	.56585558E-12
0	H_2SO_3	.36050981E-13
0	S_2	.98454726E-16
0	N_2O_4	.40918109E-17
0	CH_4	.18860923E-20
0	N_2O_5	.66446554E-21
TOTAL GASEOUS		.63717148E+02

#2 Fuel Oil, 10% Excess Air, 1 Atm, 800K

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
4	C	.76206806E-06
0	Na_2SO_4	.71807031E-06
4	$NaHSO_4$	.38370313E-06
4	$NaNO_2$	.37600000E-06
4	Na_2SO_3	.21225000E-06
4	Na_2CO_3	.14251563E-06
4	NaOH	.53812500E-07
0	$NiSO_4$	.51500000E-07
0	V_2O_5	.39250000E-07
4	$Ni(OH)_2$	.26250000E-07
4	V_2O_4	.19375000E-07
4	VO	.19000000E-07
4	V	.18750000E-07
4	$NaNO_3$	.17625000E-07
4	NiO	.12750000E-07
4	Ni	.12500000E-07
4	Na_2O	.11734375E-07
4	Na	.11718750E-07
4	$Ni(NO_3)_2$	.10000000E-08
TOTAL CONDENSED		.28898727E-05
0	N_2	.46007978E+02
0	CO_2	.72499730E+01
0	H_2O	.63999475E+01
0	O_2	.10429742E+01
0	Ne	.10000000E+01
0	He	.10000000E+01
0	Ar	.10000000E+01
0	SO_3	.55877658E-02
2	SO_2	.57078213E-03
0	NO	.39612055E-04
1	CH_4	.26115257E-04
0	NO_2	.33971930E-05
1	S_2	.47750700E-07
0	N_2O	.32860917E-08
0	HNO_3	.23849630E-09
0	H_2	.25719345E-11
1	H_2SO_4	.91518757E-12
0	CO	.68654906E-12
0	H_2SO_3	.16119011E-13
1	N_2O_4	.94485726E-18
1	N_2O_5	.82734369E-22
1	COS	.46293853E-33
TOTAL GASEOUS		.63707201E+02

#2 Fuel Oil, 10% Excess Air, 1 Atm, 650 K

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	$NaHSO_4$	.96475000E-06
4	C	.86408078E-06
4	S_2	.76401068E-06
4	$NaNO_2$	.37600000E-06
4	Na_2CO_3	.32887500E-06
4	Na_2SO_4	.24118750E-06
4	Na_2SO_3	.21225000E-06
4	NaOH	.53812500E-07
0	$NiSO_4$	.51500000E-07
0	V_2O_5	.39250000E-07
4	$Ni(OH)_2$	.26250000E-07
4	V_2O_4	.19375000E-07
4	VO	.19000000E-07
4	V	.18750000E-07
4	$NaNO_3$	.17625000E-07
4	NiO	.12750000E-07
4	Ni	.12500000E-07
4	Na_2O	.11734375E-07
4	Na	.11718750E-07
4	$Ni(NO_3)_2$	.10000000E-08
TOTAL CONDENSED		.40464196E-05
0	N_2	.46007998E+02
0	CO_2	.72499711E+01
0	H_2O	.63993381E+01
0	O_2	.10426861E+01
0	Ne	.10000000E+01
0	He	.10000000E+01
0	Ar	.10000000E+01
0	SO_3	.56097212E-02
0	H_2SO_4	.50602018E-03
0	SO_2	.41174398E-04
1	CH_4	.27656554E-04
0	NO	.17216037E-05
0	NO_2	.11227998E-05
1	COS	.95501823E-07
0	HNO_3	.33457872E-09
0	N_2O	.18994185E-09
0	H_2SO_3	.22321371E-13
0	H_2	.38084575E-15
0	CO	.36795518E-16
1	N_2O_4	.64805631E-18
1	N_2O_5	.47147359E-22
TOTAL GASEOUS		.63706281E+02

#2 Fuel Oil, 10% Excess Air, 1 Atm, 500K

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	$NaHSO_4$	.96475000E-06
4	S_2	.82367159E-06
4	C	.51240753E-06
4	$NaNO_2$	.37600000E-06
4	Na_2CO_3	.32887500E-06
4	Na_2SO_4	.24118750E-06
4	Na_2SO_3	.21225000E-06
4	NaOH	.53812500E-07
0	$NiSO_4$	.38999994E-07
0	V_2O_5	.38968750E-07
4	$Ni(NO_3)_2$	.26000000E-07
4	V_2O_4	.21875000E-07
4	$Ni(OH)_2$	.20000000E-07
4	V	.18750000E-07
4	$NaNO_3$	.17625000E-07
4	VO	.14562500E-07
4	NiO	.12750000E-07
4	Na_2O	.11734375E-07
4	Na	.11718750E-07
4	Ni	.62500000E-08
TOTAL CONDENSED		.37521885E-05
0	N_2	.46008000E+02
0	CO_2	.72499980E+01
0	H_2O	.63938912E+01
0	O_2	.10426138E+01
0	Ne	.10000000E+01
0	He	.10000000E+01
0	Ar	.10000000E+01
0	H_2SO_4	.61064013E-02
0	SO_3	.15030619E-03
1	CH_4	.92583138E-06
1	COS	.19249217E-06
0	NO_2	.18990997E-06
0	NO	.11412770E-07
0	SO_2	.45275787E-08
0	HNO_3	.87198664E-09
0	N_2O	.20275414E-11
0	H_2SO_3	.25957001E-15
0	N_2O_4	.38572140E-18
0	H_2	.64996617E-21
0	N_2O_5	.22143348E-22
0	CO	.53502725E-23
TOTAL GASEOUS		.63700761E+02

#2 Fuel Oil, -2% Excess Air, 1 Atm., 1800K

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
4	C	.86411559E-06
0	Na_2SO_3	.65675098E-06
4	Na	.45094531E-06
4	Na_2CO_3	.22928369E-06
4	Na_2O	.18910352E-06
4	Na_2SO_4	.15547583E-06
4	NaOH	.85100830E-07
0	Ni	.50625000E-07
0	V_2O_4	.43750000E-07
4	$NiSO_4$	.26000000E-07
4	NiO	.25375000E-07
4	V	.18750000E-07
4	V_2O_5	.17093750E-07
4	VO	.14562500E-07
4	$NaHSO_4$	.69785156E-08
4	$NaNO_3$	.67473145E-08
4	$Ni(OH)_2$	.10000000E-08
4	$Ni(NO_3)_2$	.10000000E-08
4	$NaNO_2$	.10000000E-08
TOTAL CONDENSED		.28436578E-05
0	N_2	.40987905E+02
0	CO_2	.69096457E+01
0	H_2O	.63176848E+01
0	Ne	.10000000E+01
0	Ar	.10000000E+01
0	He	.10000000E+01
0	CO	.34035316E+00
0	H_2	.82315142E-01
0	SO_2	.62588732E-02
0	NO	.21892838E-02
0	O_2	.97927352E-03
0	SO_3	.27325846E-06
0	N_2O	.10695843E-06
0	NO_2	.46605743E-07
0	COS	.17181192E-07
0	S_2	.94090355E-10
0	H_2SO_4	.56149569E-12
0	H_2SO_3	.39402500E-13
0	HNO_3	.18473443E-13
0	CH_4	.18884734E-14
0	N_2O_4	.41442216E-23
0	N_2O_5	.21970399E-28
TOTAL GASEOUS		.57647332E+02

FUEL OIL #6
10% excess air
1800 K

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	N_2	.43884381E+02
0	CO_2	.70788956E+01
0	H_2O	.55976751E+01
0	O_2	.96703922E+00
0	SO_2	.87472062E-01
0	NO	.71181380E-01
0	CO	.11101093E-01
0	H_2	.23219542E-02
0	SO_3	.11995680E-03
0	NO_2	.47601114E-04
0	N_2O	.35970374E-05
0	H_2SO_4	.21819756E-09
0	HNO_3	.99492200E-10
0	COS	.79306120E-11
0	H_2SO_3	.48746835E-12
0	S_2	.18863487E-13
0	N_2O_4	.43191666E-17
0	CH_4	.15574554E-20
0	N_2O_5	.71923466E-21
TOTAL GASEOUS		.57700239E+02

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	SiO_2	.58130738E-03
0	Al_2O_3	.46363969E-03
0	Fe_2O_3	.23358548E-03
0	V_2O_5	.21953896E-03
0	MgO	.82061434E-04
0	NiO	.65463405E-04
0	Na_2SiO_3	.35092378E-04
0	CaO	.30043799E-04
0	Cr_2O_3	.14871313E-04
0	CoO	.14320763E-04
0	TiO_2	.78151250E-05
4	$NaNO_3$	.99767920E-06
4	Co_3O_4	.98998014E-06
4	Co	.97971692E-06
4	VO	.97119531E-06
4	Cr	.95937500E-06
4	$Ni(OH)_2$	.94783496E-06
4	$NiSO_4$	.94770996E-06
4	$CaCO_3$	.93638867E-06
4	$FeSO_4$	.91602344E-06
4	Fe	.91601563E-06
4	NaOH	.91117975E-06
4	$Al_2(SO_4)_3$	.90821094E-06
4	Al	.90820313E-06
4	V	.86328125E-06
4	C	.84384175E-06
4	Na_2SO_3	.83366042E-06
4	Na_2CO_3	.79784643E-06
4	Ti_2O_3	.78181250E-06
4	TiO	.78137500E-06
4	Ti	.78125000E-06
4	Ni	.74405005E-06
4	$CoCO_3$	.73742554E-06
4	$CoSO_4$	.66427930E-06
4	Mg	.65078125E-06
4	$Co(OH)_3$	.63487500E-06
4	Na_2O	.61377197E-06
4	Na_2SO_4	.60318153E-06
4	Si	.60224075E-06
4	$MgSO_4$	.58978515E-06
4	V_2O_4	.54630029E-06
4	Ti_3O_5	.52187500E-06
4	$CaSO_4$	.50806250E-06
4	$Ca(OH)_2$	.50793750E-06
4	Ca	.50781250E-06
4	Na	.21242554E-06
4	$Ni(NO_3)_2$	.10000000E-08
4	$NaNO_2$	.10000000E-08
4	$Co(OH)_2$	.10000000E-08
4	$Co(NO_3)_2$	.10000000E-08
4	$Mg(NO_3)_2$	.10000000E-08
4	$Fe(NO_3)_2$	.10000000E-08
4	$Al(NO_3)_3$	.10000000E-08
4	$Ca(NO_3)_2$	.10000000E-08
4	$Co(NO_2)_2$	.10000000E-08
TOTAL CONDENSED		.17745761E-02

FUEL OIL #6

10% excess air

800 K

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	N_2	.43919976E+02
0	CO_2	.70899753E+01
0	H_2O	.55999527E+01
0	O_2	.95689992E+00
0	SO_3	.78060269E-01
0	SO_2	.93067716E-02
0	NO	.37069402E-04
1	CH_4	.22022118E-04
1	NO_2	.32009914E-05
0	N_2O	.31583556E-08
1	S_2	.12777309E-08
0	HNO_3	.22173570E-09
1	H_2SO_4	.34046815E-11
0	H_2	.22350941E-11
0	CO	.66681925E-12
0	H_2SO_3	.21623693E-12
0	N_2O_4	.92711907E-18
1	N_2O_5	.81731712E-22
0	COS	.67989404E-32
TOTAL GASEOUS		.57654234E+02

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	SiO_2	.61624488E-03
0	Al_2O_3	.46322866E-03
0	Fe_2O_3	.23362126E-03
0	V_2O_5	.21953896E-03
0	$MgSO_4$	.81106559E-04
0	$NiSO_4$	.66407096E-04
0	Na_2SO_4	.35952507E-04
0	$CaSO_4$	.29459095E-04
0	$CoSO_4$	.15349777E-04
0	Cr_2O_3	.14871313E-04
0	TiO_2	.78151250E-05
4	VO	.97119531E-06
4	Cr	.95937500E-06
4	Fe	.91601563E-06
4	$Al(NO_3)_3$	.90820703E-06
4	Al	.90820313E-06
4	MgO	.89484766E-06
4	Na_2CO_3	.88311133E-06
4	$Al_2(SO_4)_3$	.86563583E-06
4	V	.86328125E-06
4	$FeSO_4$	.84445728E-06
4	Ti_2O_3	.78181250E-06
4	TiO	.78137500E-06
4	Ti	.78125000E-06
4	Co_3O_4	.76683464E-06
4	C	.75661365E-06
4	$NaHSO_4$	.72142017E-06
4	$Mg(NO_3)_2$	.65081250E-06
4	Mg	.65078125E-06
4	$Co(OH)_3$	.63490625E-06
4	$Co(OH)_2$	.63465625E-06
4	$NaNO_2$	.61100000E-06
4	Si	.60238991E-06
4	NiO	.59855078E-06
4	$Ni(OH)_2$	.56532227E-06
4	CoO	.55531055E-06
4	V_2O_4	.54630029E-06
4	$NaOH$	.53509375E-06
4	Na_2SO_3	.53471875E-06
4	$NaNO_3$	.53462500E-06
4	Ni	.53203125E-06
4	Ti_3O_5	.52187500E-06
4	$CoCO_3$	.51565820E-06
4	$Ca(NO_3)_2$	.50831250E-06
4	$Ca(NO_2)_2$	.50806250E-06
4	$Ca(OH)_2$	.50793750E-06
4	CaO	.50787500E-06
4	Ca	.50781250E-06
4	$CaCO_3$	.50690466E-06
4	Co	.31718750E-06
4	Na_2O	.30449219E-06
4	Na_2SiO_3	.15473438E-06
4	Na	.15273438E-06
4	$Co(NO_3)_2$	.10000000E-08
4	$Fe(NO_3)_2$	.10000000E-08
4	$Ni(NO_3)_2$	.10000000E-08
TOTAL CONDENSED		.18104020E-02

FUEL OIL #6

10% excess air

650 K

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	N_2	.43919994E+02
0	CO_2	.70899689E+01
0	H_2O	.55918849E+01
0	O_2	.95267617E+00
0	SO_3	.76892168E-01
2	H_2SO_4	.80224802E-02
1	SO_2	.56166598E-03
1	CH_4	.27046176E-04
0	NO	.16078625E-05
1	COS	.13085647E-05
0	NO_2	.10537585E-05
1	S_2	.65428211E-06
0	HNO_3	.30934335E-09
0	N_2O	.18221320E-09
1	H_2SO_3	.29407640E-12
0	H_2	.33116284E-15
0	CO	.35807449E-16
1	N_2O_4	.63087181E-18
1	N_2O_5	.46122263E-22
TOTAL GASEOUS		.57640032E+02

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	SiO_2	.61624488E-03
0	$FeSO_4$	.46591243E-03
0	$Al_2(SO_4)_3$	.46346990E-03
0	V_2O_5	.21953896E-03
0	$MgSO_4$	.81106559E-04
0	$NaHSO_4$	.71183593E-04
0	$NiSO_4$	.66407096E-04
0	$CaSO_4$	.29459095E-04
0	$CoSO_4$	.15349777E-04
0	Cr_2O_3	.14871313E-04
0	TiO_2	.78151250E-05
4	VO	.97119531E-06
4	Cr	.95937500E-06
4	$Fe(NO_3)_2$	.91602344E-06
4	Fe	.91601563E-06
4	$Al(NO_3)_3$	.90820703E-06
4	Al	.90820313E-06
4	MgO	.89484766E-06
4	Na_2CO_3	.88311133E-06
4	V	.86328125E-06
4	C	.84263722E-06
4	Ti_2O_3	.78181250E-06
4	TiO	.78137500E-06
4	Ti	.78125000E-06
4	Co_3O_4	.76683464E-06
4	Na_2SO_4	.72142017E-06
4	$Mg(NO_3)_2$	.65081250E-06
4	Mg	.65078125E-06
4	$Co(OH)_3$	.63490625E-06
4	$Co(OH)_2$	.63465625E-06
4	Fe_2O_3	.62976563E-06
4	Al_2O_3	.62439209E-06
4	$NaNO_2$	.61100000E-06
4	Si	.60238991E-06
4	NiO	.59855078E-06
4	$Ni(OH)_2$	.56532227E-06
4	CoO	.55531055E-06
4	V_2O_4	.54630029E-06
4	NaOH	.53509375E-06
4	Na_2SO_3	.53471875E-06
4	$NaNO_3$	.53462500E-06
4	Ni	.53203125E-06
4	Ti_3O_5	.52187500E-06
4	$CoCO_3$	.51565820E-06
4	$Ca(NO_3)_2$	.50831250E-06
4	$Ca(NO_2)_2$	.50806250E-06
4	$Ca(OH)_2$	.50793750E-06
4	CaO	.50787500E-06
4	Ca	.50781250E-06
4	$CaCO_3$	.50690466E-06
4	CO	.31718750E-06
4	Na_2O	.30449219E-06
4	Na_2SiO_3	.15473438E-06
4	Na	.15273438E-06
4	$Ni(NO_3)_2$	.10000000E-08
4	$Co(NO_3)_2$	.10000000E-08
TOTAL CONDENSED		.20787106E-02

FUEL OIL #6

10% excess air

500 K

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	N_2	.43919994E+02
0	CO_2	.70899245E+01
0	H_2O	.55164930E+01
0	O_2	.95248244E+00
0	H_2SO_4	.83328060E-01
0	SO_3	.21483515E-02
1	CH_4	.69896899E-04
1	COS	.26332044E-05
1	NO_2	.17830542E-06
1	SO_2	.64361689E-07
0	NO	.10658516E-07
1	HNO_3	.80219593E-09
0	N_2O	.19461904E-11
1	H_2SO_3	.35228454E-14
1	N_2O_4	.37630480E-18
1	H_2	.55768824E-21
1	N_2O_5	.21720431E-22
1	CO	.52037133E-23
TOTAL GASEOUS		.57564443E+02

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	SiO_2	.61624488E-03
0	$FeSO_4$	.46591243E-03
0	$Al_2(SO_4)_3$	.46346990E-03
0	V_2O_5	.21965019E-03
0	$MgSO_4$	.81106559E-04
0	$NaHSO_4$	.72102641E-04
0	$NiSO_4$	.65377199E-04
0	$CaSO_4$	.29459095E-04
0	Cr_2O_3	.14871313E-04
0	$CoSO_4$	.14403573E-04
0	TiO_2	.78151250E-05
4	C	.98304550E-06
4	$Ni(OH)_2$	.96439258E-06
4	Cr	.95937500E-06
4	Na_2CO_3	.94995117E-06
4	$Fe(NO_3)_2$	.91602344E-06
4	Fe	.91601563E-06
4	$Al(NO_3)_3$	.90820703E-06
4	Al	.90820313E-06
4	MgO	.89484766E-06
4	V	.86328125E-06
4	Co_3O_4	.84612500E-06
4	VO	.81017841E-06
4	Ti_2O_3	.78181250E-06
4	TiO	.78137500E-06
4	Ti	.78125000E-06
4	Na_2SO_4	.72977515E-06
4	S_2	.70320359E-06
4	NiO	.69831445E-06
4	$Mg(NO_3)_2$	.65081250E-06
4	Mg	.65078125E-06
4	$Co(NO_3)_2$	.63462500E-06
4	Fe_2O_3	.62976563E-06
4	Al_2O_3	.62439209E-06
4	$NaNO_2$	.61100000E-06
4	Si	.60238991E-06
4	CoO	.59994824E-06
4	$Co(OH)_3$	.55564063E-06
4	$Co(OH)_2$	.55539063E-06
4	$NaOH$	.53509375E-06
4	$NaNO_3$	.53462500E-06
4	$Ni(NO_3)_2$	.53206250E-06
4	Ni	.53203125E-06
4	Ti_3O_5	.52187500E-06
4	Co	.52063574E-06
4	V_2O_4	.51558238E-06
4	$Ca(NO_3)_2$	.50831250E-06
4	$Ca(NO_2)_2$	.50806250E-06
4	$Ca(OH)_2$	.50793750E-06
4	CaO	.50787500E-06
4	Ca	.50781250E-06
4	$CaCO_3$	.50690466E-06
4	$CoCO_3$	.50081152E-06
4	Na_2O	.30449219E-06
4	Na_2SiO_3	.15473438E-06
4	Na	.15273438E-06
4	Na_2SO_3	0.
TOTAL CONDENSED		.20797746E-02

FUEL OIL #6
2% excess air
1800 K

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	N_2	.40710527E+02
0	CO_2	.70662990E+01
0	H_2O	.55950338E+01
0	O_2	.19685381E+00
0	SO_2	.87536524E-01
0	NO	.30932445E-01
0	CO	.23697685E-01
0	H_2	.49632453E-02
0	SO_3	.56133684E-04
0	NO_2	.96725918E-05
0	N_2O	.15604505E-05
0	H_2SO_4	.10962699E-09
0	COS	.83230519E-10
0	HNO_3	.14324873E-10
0	H_2SO_3	.52377324E-12
0	S_2	.42440490E-12
0	N_2O_4	.19156937E-18
0	CH_4	.37484700E-19
0	N_2O_5	.14916917E-22
TOTAL GASEOUS		.53715911E+02

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	SiO_2	.58130738E-03
0	Al_2O_3	.46385290E-03
0	Fe_2O_3	.23358548E-03
0	V_2O_5	.21953896E-03
0	MgO	.82061434E-04
0	NiO	.65463405E-04
0	Na_2SiO_3	.35092378E-04
0	CaO	.30043799E-04
0	Cr_2O_3	.14871313E-04
0	CoO	.14320763E-04
0	TiO_2	.78151250E-05
4	$NaNO_3$	.99767920E-06
4	Co_3O_4	.98998014E-06
4	Co	.97971692E-06
4	VO	.97119531E-06
4	Cr	.95937500E-06
4	$Ni(OH)_2$	.94783496E-06
4	$NiSO_4$	.94770996E-06
4	$CaCO_3$	.93638867E-06
4	$FeSO_4$	.91602344E-06
4	Fe	.91601563E-06
4	NaOH	.91117975E-06
4	Al	.90820313E-06
4	V	.86328125E-06
4	C	.84385353E-06
4	Na_2SO_3	.83366042E-06
4	Na_2CO_3	.79784643E-06
4	Ti_2O_3	.78181250E-06
4	TiO	.78137500E-06
4	Ti	.78125000E-06
4	Ni	.74405005E-06
4	$CoCO_3$	.73742554E-06
4	$Al_2(SO_4)_3$	.69500338E-06
4	$CoSO_4$	.66427930E-06
4	Mg	.65078125E-06
4	$Co(OH)_3$	.63487500E-06
4	Na_2O	.61377197E-06
4	Na_2SO_4	.60318153E-06
4	Si	.60224075E-06
4	$MgSO_4$	.58978516E-06
4	V_2O_4	.54630029E-06
4	Ti_3O_5	.52187500E-06
4	$CaSO_4$	.50806250E-06
4	$Ca(OH)_2$	.50793750E-06
4	Ca	.50781250E-06
4	Na	.21242554E-06
4	$NaHSO_4$	.21003906E-06
4	$Ni(NO_3)_2$	.10000000E-08
4	$NaNO_2$	.10000000E-08
4	$Co(OH)_2$	.10000000E-08
4	$Co(NO_3)_2$	.10000000E-08
4	$Mg(NO_3)_2$	.10000000E-08
4	$Fe(NO_3)_2$	.10000000E-08
4	$Al(NO_3)_3$	.10000000E-08
4	$Ca(NO_3)_2$	.10000000E-08
4	$Ca(NO_3)_2$	.10000000E-08
TOTAL CONDENSED		.17745762E-02

FUEL OIL #6
-2%
1800 K

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	N_2	.39127991E+02
0	CO_2	.67550697E+01
0	H_2O	.55275040E+01
0	CO	.33492673E+00
0	SO_2	.87587928E-01
0	H_2	.72493096E-01
0	NO	.20165473E-02
0	O_2	.87030478E-03
0	SO_3	.37990584E-05
0	COS	.26622811E-06
0	N_2O	.10143804E-06
0	NO_2	.42647429E-07
0	S_2	.21007064E-07
0	H_2SO_4	.75850959E-11
0	H_2SO_3	.53574300E-12
0	HNO_3	.16608650E-13
0	CH_4	.17893382E-14
0	N_2O_4	.38538148E-23
0	N_2O_5	.20297373E-28
TOTAL GASEOUS		.51908464E+02

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	SiO_2	.58103865E-03
0	Al_2O_3	.46372484E-03
0	Fe_2O_3	.23358548E-03
0	V_2O_4	.21953464E-03
0	MgO	.82061434E-04
0	Ni	.65515371E-04
0	Na_2SiO_3	.35361107E-04
0	CaO	.30043799E-04
0	Cr_2O_3	.14871313E-04
0	CoO	.14330981E-04
0	TiO_2	.78151250E-05
4	Co_3O_4	.98998014E-06
4	Co	.96949884E-06
4	Cr	.95937500E-06
4	$Ni(OH)_2$	.94783496E-06
4	$NiSO_4$	.94770996E-06
4	$CaCO_3$	.93638867E-06
4	Na	.91855685E-06
4	$FeSO_4$	.91602344E-06
4	Fe	.91601563E-06
4	Na_2SO_4	.91297302E-06
4	Al	.90820313E-06
4	V	.86328125E-06
4	C	.84385472E-06
4	VO	.83504861E-06
4	Na_2CO_3	.82898929E-06
4	$Al_2(SO_4)_3$	.82306274E-06
4	Ti_2O_3	.78181250E-06
4	TiO	.78137500E-06
4	Ti	.78125000E-06
4	NaOH	.77932458E-06
4	Na_2SO_3	.76305620E-06
4	$CoCO_3$	.73742554E-06
4	NiO	.69208435E-06
4	$CoSO_4$	.66427930E-06
4	Mg	.65078125E-06
4	$Co(OH)_3$	.63487500E-06
4	V_2O_5	.61869900E-06
4	Si	.60224075E-06
4	$MgSO_4$	.58978516E-06
4	$NaNO_3$	.57282812E-06
4	Ti_3O_5	.52187500E-06
4	$CaSO_4$	.50806250E-06
4	$Ca(OH)_2$	.50793750E-06
4	Ca	.50781250E-06
4	$NaHSO_4$	.21003906E-06
4	$Co(OH)_2$	.10000000E-08
4	$Ni(NO_3)_2$	.10000000E-08
4	$Co(NO_3)_2$	.10000000E-08
4	$Fe(NO_3)_2$	.10000000E-08
4	$NaNO_2$	.10000000E-08
4	$Al(NO_3)_3$	.10000000E-08
4	$Ca(NO_2)_2$	.10000000E-08
4	$Ca(NO_3)_2$	.10000000E-08
4	$Mg(NO_3)_2$	.10000000E-08
4	Na_2O	0.
TOTAL CONDENSED		.17743141E-02

FUEL OIL #6
2% excess air
800 K

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	N_2	.40725989E+02
0	CO_2	.70899915E+01
0	H_2O	.55999849E+01
0	O_2	.16373254E+00
0	SO_3	.58358114E-01
0	SO_2	.19008927E-01
1	NO	.14765380E-04
1	CH_4	.58942316E-05
0	NO_2	.54670022E-06
1	S_2	.12777309E-08
1	N_2O	.12556149E-08
0	HNO_3	.25700702E-10
0	H_2	.52130718E-11
1	H_2SO_4	.34672177E-11
0	CO	.15552492E-11
0	H_2SO_3	.47447737E-12
1	N_2O_4	.29046152E-19
1	N_2O_5	.10979418E-23
1	COS	.18931330E-30
TOTAL GASEOUS		.53667086E+02

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	SiO_2	.51624488E-03
0	Al_2O_3	.46322866E-03
0	Fe_2O_3	.23362126E-03
0	V_2O_5	.21953896E-03
0	$MgSO_4$	.81106559E-04
0	$NiSO_4$	.66407096E-04
0	Na_2SO_4	.35952507E-04
0	$CaSO_4$	.29459095E-04
0	$CoSO_4$	.15349777E-04
0	Cr_2O_3	.14871313E-04
0	TiO_2	.78151250E-05
4	VO	.97119531E-06
4	Cr	.95937500E-06
4	Fe	.91601563E-06
4	$Al(NO_3)_3$	.90820703E-06
4	Al	.90820313E-06
4	MgO	.89484766E-06
4	Na_2CO_3	.88311133E-06
4	$Al(SO_4)_3$	.86563583E-06
4	V	.86328125E-06
4	$FeSO_4$	.84445723E-06
4	Ti_2O_3	.78181250E-06
4	TiO	.78137500E-06
4	Ti	.78125000E-06
4	Co_3O_4	.75683464E-06
4	C	.75054018E-06
4	$NaHSO_4$	.72142017E-06
4	$Mg(NO_3)_2$	.65081250E-06
4	Mg	.65078125E-06
4	$Co(OH)_3$	.63490625E-06
4	$Co(OH)_2$	.63465625E-06
4	$NaNO_2$	.61100000E-06
4	Si	.60238991E-06
4	NiO	.59855078E-06
4	$Ni(OH)_2$	.56532227E-06
4	CoO	.55531055E-06
4	V_2O_4	.54630029E-06
4	$NaOH$	.53509375E-06
4	Na_2SO_3	.53471875E-06
4	$NaNO_3$	.53462500E-06
4	Ni	.53203125E-06
4	Ti_3O_5	.52187500E-06
4	$CoCO_3$	.51565820E-06
4	$Ca(NO_3)_2$	.50831250E-06
4	$Ca(NO_2)_2$	.50806250E-06
4	$Ca(OH)_2$	.50793750E-06
4	CaO	.50787500E-06
4	Ca	.50781250E-06
4	$CaCO_3$	.50690466E-06
4	Co	.31718750E-06
4	Na_2O	.30449219E-06
4	Na_2SiO_3	.15473438E-06
4	Na	.15273438E-06
4	$Co(NO_3)_2$	.10000000E-08
4	$Fe(NO_3)_2$	.10000000E-08
4	$Ni(NO_3)_2$	.10000000E-08
TOTAL CONDENSED		.18103959E-02

FUEL OIL #6

2% excess air

650 K

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	N_2	.40725995E+02
0	CO_2	.70899892E+01
0	H_2O	.55914658E+01
0	O_2	.15501712E+00
0	SO_3	.75672226E-01
2	H_2SO_4	.84821237E-02
2	SO_2	.13219644E-02
1	CH_4	.67615441E-05
1	COS	.13085647E-05
1	S_2	.65428211E-06
0	NO	.62453378E-06
1	NO_2	.17113506E-06
0	N_2O	.70644301E-10
1	HNO_3	.33670900E-10
1	H_2SO_3	.74360756E-12
1	H_2	.79201688E-15
1	CO	.85643265E-16
1	N_2O_4	.17879748E-19
1	N_2O_5	.54655465E-24
TOTAL GASEOUS		.53647953E+02

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	SiO_2	.61624488E-03
0	$FeSO_4$	.46591243E-03
0	$Al_2(SO_4)_3$	.46346990E-03
0	V_2O_5	.21953896E-03
0	$MgSO_4$	.81106559E-04
0	$NaHSO_4$	.71183593E-04
0	$NiSO_4$	.66407096E-04
0	$CaSO_4$	.29459095E-04
0	$CoSO_4$	.15349777E-04
0	Cr_2O_3	.14871313E-04
0	TiO_2	.78151250E-05
4	VO	.97119531E-06
4	Cr	.95937500E-06
4	$Fe(NO_3)_2$	.91602344E-06
4	Fe	.91601563E-06
4	$Al(NO_3)_3$	.90820703E-06
4	Al	.90820313E-06
4	MgO	.89484766E-06
4	Na_2CO_3	.88311133E-06
4	V	.86328125E-06
4	C	.84263722E-06
4	Ti_2O_3	.78181250E-06
4	TiO	.78137500E-06
4	Ti	.78125000E-06
4	Co_3O_4	.76683464E-06
4	Na_2SO_4	.72142017E-06
4	$Mg(NO_3)_2$	.65081250E-06
4	Mg	.65078125E-06
4	$Co(OH)_3$	.63490625E-06
4	$Co(OH)_2$	.63465625E-06
4	Fe_2O_3	.62976563E-06
4	Al_2O_3	.62439209E-06
4	$NaNO_2$	.61100000E-06
4	Si	.60238991E-06
4	NiO	.59855078E-06
4	$Ni(OH)_2$	.56532227E-06
4	CoO	.55531055E-06
4	V_2O_4	.54630029E-06
4	$NaOH$	.53509375E-06
4	Na_2SO_3	.53471875E-06
4	$Na(NO_3)$	.53462500E-06
4	Ni	.53203125E-06
4	Ti_3O_5	.52187500E-06
4	$CoCO_3$	.51565820E-06
4	$Ca(NO_3)_2$	.50831250E-06
4	$Ca(NO_2)_2$	.50806250E-06
4	$Ca(OH)_2$	.50793750E-06
4	CaO	.50787500E-06
4	Ca	.50781250E-06
4	$CaCO_3$	.50690466E-06
4	Co	.31718750E-06
4	Na_2O	.30449219E-06
4	Na_2SiO_3	.15473438E-06
4	Na	.15273438E-06
4	$Co(NO_3)_2$	.10000000E-08
4	$Ni(NO_3)_2$	.10000000E-08
TOTAL CONDENSED		.20787106E-02

FUEL OIL #6
2% excess air
500 K

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	N_2	.40725994E+02
0	CO_2	.70899865E+01
0	H_2O	.55164714E+01
0	O_2	.15435873E+00
0	H_2SO_4	.83473517E-01
0	SO_3	.20028144E-02
1	CH_4	.79421950E-05
1	COS	.26332044E-05
1	SO_2	.14378779E-06
1	NO_2	.28843668E-07
0	NO	.41317616E-08
1	HNO_3	.86894965E-10
0	N_2O	.75307036E-12
1	H_2SO_3	.84568816E-14
1	N_2O_4	.10580974E-19
1	H_2	.13364686E-20
1	CO	.12470393E-22
1	N_2O_5	.25485811E-24
TOTAL GASEOUS		.53572298E+02

C VECTOR		EQUILIBRIUM CONCENTRATION (MOLES)
0	SiO_2	.61624488E-03
0	$FeSO_4$	.46591243E-03
0	$Al_2(SO_4)_3$	.46346990E-03
0	V_2O_5	.21965019E-03
0	$MgSO_4$	.81106559E-04
0	$NaHSO_4$	.72102641E-04
0	$NiSO_4$	.65377199E-04
0	$CaSO_4$	.29459095E-04
0	Cr_2O_3	.14871313E-04
0	$CaSO_4$	.14403573E-04
0	TiO_2	.78151250E-05
4	C	.98304550E-06
4	$Ni(OH)_2$	.96439258E-06
4	Cr	.95937500E-06
4	Na_2CO_3	.94995117E-06
4	$Fe(NO_3)_2$	.91602344E-06
4	Fe	.91601563E-06
4	$Al(NO_3)_3$	.90820703E-06
4	Al	.90820313E-06
4	MgO	.89484766E-06
4	V	.86328125E-06
4	Co_3O_4	.84612500E-06
4	VO	.81017841E-06
4	Ti_2O_3	.78181250E-06
4	TiO	.78137500E-06
4	Ti	.78125000E-06
4	Na_2SO_4	.72977515E-06
4	S_2	.70320359E-06
4	NiO	.69831445E-06
4	$Mg(NO_3)_2$	.65081250E-06
4	Mg	.65078125E-06
4	$Co(NO_3)_2$	.63462500E-06
4	Fe_2O_3	.62976563E-06
4	Al_2O_3	.62439209E-06
4	$NaNO_3$	.61100000E-06
4	Si	.60238991E-06
4	CoO	.59994824E-06
4	$Co(OH)_3$	.55564063E-06
4	$Co(OH)_2$	.55539063E-06
4	$NaOH$	.53509375E-06
4	$NaNO_3$	.53462500E-06
4	$Ni(NO_3)_2$	.53206250E-06
4	Ni	.53203125E-06
4	Ti_3O_5	.52187500E-06
4	Co	.52063574E-06
4	V_2O_4	.51558238E-06
4	$Ca(NO_3)_2$	.50831250E-06
4	$Ca(NO_3)_2$	.50806250E-06
4	$Ca(OH)_2$	.50793750E-06
4	CaO	.50787500E-06
4	Ca	.50781250E-06
4	$CaCO_3$	.50690466E-06
4	$CoCO_3$	.50081152E-06
4	Na_2O	.30449219E-06
4	Na_2SiO_5	.15473438E-06
4	Na	.15273438E-06
4	Na_2SO_3	0.
TOTAL CONDENSED		.20797746E-02

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-77-041	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE A Survey of Sulfate, Nitrate, and Acid Aerosol Emissions and Their Control		5. REPORT DATE April 1977
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) J. F. Kircher, A. A. Putnam, D. A. Ball, H. H. Krause, J. M. Genco, R. W. Coutant, J. O. L. Wendt, and A. Levy		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Battelle-Columbus Laboratories 505 King Avenue Columbus, Ohio 43201		10. PROGRAM ELEMENT NO. EHE624a
		11. CONTRACT/GRANT NO. 68-02-1323, Task 49
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Task Final; 3-12/76
		14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP Task Officer for this report is W. S. Lanier, Mail Drop 65, 919/549-8411 Ext 2432.

16. ABSTRACT The report gives results of an evaluation of the effects of fuel and combustion modifications on the formation of primary acid aerosols (used broadly to include all sulfates, nitrates, chlorides, and fluorides in all their forms) and their significance as combustion-generated pollutants from large stationary sources. Primary acid aerosols are emitted directly from a source or formed (primarily by condensation reactants) in the immediate vicinity (0.5 mile); secondary aerosols, formed downstream in the plume, are not considered. Available, rather meager field data were collected and interpreted in view of current knowledge of mechanisms of formation of potential acid aerosols and their precursors. Although sulfates, nitrates, chlorides, and fluorides were considered, based on available data, only sulfates appear to be significant as primary acid aerosols. All of the various combustion modifications for NOx control are expected to have little effect on primary acid aerosol emissions, except perhaps firing with low excess air which has a potential to abate both NOx and acid aerosol emissions. Combustion modifications and fuel changes may lead to an increased formation of small particles which could increase the formation of acid aerosols through heterogeneous reactions. Most effects, however, are speculative due to the meager data available. Information gaps have been identified; further research is indicated.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Air Pollution	Coal	Air Pollution Control	13B	
Aerosols	Fuel Oil	Stationary Sources	07D	
Fuels	Sulfates	Acid Aerosols	21D	07B
Combustion	Chlorides	Combustion Modification	21B	
Boilers	Fluorides	No. 6 Oil	13A	
Furnaces	Nitrogen Oxides	Nitrates		

18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 177
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)