March 31, 1972

A STUDY OF THE FATE OF SO_2 IN FLUE GAS

Contract No. CPA 70-121

Battelle
Columbus Laboratories

A report of research conducted for the

ENVIRONMENTAL PROTECTION AGENCY

AMERICAN PETROLEUM INSTITUTE

BITUMINOUS COAL RESEARCH, INC.

EDISON ELECTRIC INSTITUTE

FINAL REPORT

on

A STUDY OF THE FATE OF SO_2 IN FLUE GAS

Contract No. CPA 70-121

to

ENVIRONMENTAL PROTECTION AGENCY
AMERICAN PETROLEUM INSTITUTE
BITUMINOUS COAL RESEARCH, INC.
EDISON ELECTRIC INSTITUTE

March 31, 1972

by

R. W. Coutant, E. L. Merryman, R. E. Barrett,
R. D. Giammar, and A. Levy

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

TABLE OF CONTENTS

	Page
MANAGEMENT SUMMARY	i
INTRODUCTION	1
SUMMARY	2
EXPERIMENTAL PROCEDURE	3
EXPERIMENTAL RESULTS	4
General Trends	4
Specific Fuel Effects	7
SO_3	7
Sulfur in Ash	8
NO_x Emissions	8
General Observations	8
OTHER INVESTIGATIONS OF SO_2 DECAY IN PLUMES	9
CONCLUSIONS	10
ACKNOWLEDGMENTS	11
REFERENCES	11

APPENDICES

APPENDIX A – EXPERIMENTAL EQUIPMENT AND METHODS	A-1
APPENDIX B – FURNACE-STACK DATA	B-1
APPENDIX C – PLUME-CHAMBER DATA	C-1
APPENDIX D – PARTICULATE ANALYSES	D-1

A STUDY OF THE FATE OF SO_2 IN FLUE GAS

MANAGEMENT SUMMARY

Previous studies attempting to determine the fate of SO_2 in power-plant flue gases have indicated a possible rapid loss of SO_2 either within the stack or in the early plume. Sampling plumes with fixed wing aircraft to examine the fate of SO_2 at distances of a mile or less from the stack is difficult. It was the purpose of this program to provide additional data to support and/or to clarify these observations through the use of a laboratory-scale system designed to simulate the time-temperature profile of a central-station power plant and the early plume. This was accomplished using the Battelle Multifuel Furnace Facility. This facility included a multipurpose furnace fired either with pulverized coal at approximately 30 lb/hr or with residual oil at 3 gal/hr; a simulated boiler/economizer section; an electrostatic precipitator for use with coal firing; a stack section, in which temperature distribution was controlled independently by electrical heating; and a dilution and expansion chamber to simulate the early stages of plume development.

The five specific objectives of the program were:

1. Identification of sections of the system wherein major depletion in SO_2 could be observed

2. Determination of the effect of fuel type on SO_2 depletion

3. Determination of the significance of the contribution of fly ash to the overall SO_2 depletion

4. Investigation of the rate of oxidation of SO_2 in the early stages of plume development, e.g., equivalent to effective ranges of less than one-half mile from the stack exit

5. Assessment of the effects of relative humidity, temperature, and process variables on the rate of SO_2 loss in the early plume.

To meet these objectives an experimental work plan was developed, in conjunction with the EPA/API/BCR/EEI Steering Committee, which included measurement of the sulfur content of both the flue gas and the particulate matter at selected points within the system. Results of this work indicate little difference in the overall behavior of SO_2 produced by coal or oil firing. In general, there was about a 10 percent loss in SO_2 concentration in the flue gas within the boiler/economizer section of the unit. With coals, this sulfur was found to be associated primarily with the fly ash collected in the electrostatic precipitator, and the fraction of the fuel sulfur in the fly ash was roughly proportional to the ash content of the coal. Data with oils were insufficient to identify the source of the loss of SO_2 with these fuels.

No loss in SO_2 in the flue gas was observed in the stack section of the unit. Data for the early plume showed considerable scatter, but, when a loss of SO_2 was noted, the observations could be described in terms of a first-order rate process with a rate constant in the range of 2×10^{-3} to 13×10^{-3} min^{-1}. This is equivalent to the SO_2 half-life of about 1-6 hr, which is in

agreement with the findings of earlier full-scale plume-sampling studies. It appears that humidity effects, of themselves, are insufficient to explain the observed variations in rate of loss of SO_2 in plumes. It thus may be necessary to examine the role of droplets in more detail than has been done in this or other investigations in order to establish actual rates of loss of SO_2 in plumes.

Implications of the results of this program are that: (1) On the average, about 90 percent of the sulfur in pulverized coal or fuel oil can be expected to leave the stack as SO_2; (2) The percentage of fuel sulfur leaving the stack as SO_2 is affected only slightly by the nature of the fuel; and (3) The effect of relative humidity on the half-life of SO_2 in the plume needs to be further clarified.

FINAL REPORT

on

A STUDY OF THE FATE OF SO_2 IN FLUE GAS

Contract No. CPA 70-121

to

ENVIRONMENTAL PROTECTION AGENCY
AMERICAN PETROLEUM INSTITUTE
BITUMINOUS COAL RESEARCH, INC.
EDISON ELECTRIC INSTITUTE

from

BATTELLE
Columbus Laboratories

March 31, 1972

INTRODUCTION

Sulfur dioxide emissions are a major contribution to air pollution in the United States. Effective and economic control of such emissions must be based on sufficient knowledge of the behavior and manner of dispersal of SO_2 within the boiler, the stack, and the plume.

Ideally, of course, the most positive SO_2 control is accomplished by burning low-sulfur fuels. Current availability and technology makes this generally uneconomical. To provide adequate and economical regulation and control therefore, it would be desirable to know the maximum level of sulfur that can realistically remain in a fuel for which sufficiently low-cost removal of SO_2 by other control techniques can be achieved. To provide the basis for such decisions, information is needed on the fate of SO_2 from the time the fuel is burned to its exit and dispersal in the atmosphere.

It is generally accepted that, in combustion of pulverized coal and fuel oil, most of the sulfur in the fuel leaves the stack as SO_2. About 1 to 2 percent of the sulfur is converted to SO_3(1)*, and another 5 percent or less is claimed to be absorbed by the fly ash during transit through the boiler up to the base of the stack(2).

In an earlier program conducted by GCA, the evidence indicated rapid decay of SO_2 either within the stack or in the early plume.(3) Recent work at a Florida power station indicated less rapid consumption of the SO_2 except when the relative humidity of the surrounding atmosphere was greater than 78-80 percent.(4) In both of these studies, sampling of plumes was conducted using fixed-wing aircraft. This is an extremely difficult experiment to conduct with meaningful accuracy, especially at distances of one mile or less from the stack.

*References are listed at the end of the report.

The purpose of the current program was to provide additional data to support and/or clarify these observations through the use of a laboratory-scale system designed to simulate the time-temperature profile of a power-generation station. Specific objectives of the program included:

1. Identification of sections of the system wherein major depletion in SO_2 could be observed

2. Determination of the effect of fuel type on SO_2 depletion

3. Determination of the significance of the contribution of fly ash to the overall SO_2 depletion

4. Investigation of the rate of oxidation of SO_2 in the early stages of plume development, e.g., equivalent to effective ranges of less than one-half mile from the stack exit

5. Assessment of the effects of relative humidity, temperature, and process variables on the rate of SO_2 loss in the early plume.

SUMMARY

A study of the fate of SO_2 in flue gas has been conducted for both residual oil and pulverized coal firing with a laboratory-scale system designed to simulate the combustion, boiler/economizer, stack, and early plume portions of a power-generation station. Three residual oils and two coals typical of those in current use were fired. These fuels included a high vanadium (0.026 percent) residual oil from a Venezuelan crude, a desulfurized residual oil from the same Venezuelan crude, a midcontinent residual oil, a raw Pittsburgh-seam coal, and a washed coal from the same mine. The oils were fired at 3 gal/hr and the coals at 30 lb/hr.

In general, the behavior of SO_2 in the laboratory-scale system was relatively independent of the type of fuel being fired. A loss of SO_2 from the flue gas amounting to about 10 percent was noted across the boiler-economizer section of the system. SO_2 losses in the stack section were very slight at the most, being less than 3 percent for either coal or oil firing. In the early plume, the data may be represented in terms of a first-order rate process with an average rate constant of 8×10^{-3} min^{-1} and a probable range of 2×10^{-3} to 13×10^{-3} min^{-1} (half-life of 1-6 hr) for both coal and oil firing. A weak correlation was found between the rate constants and the relative humidity of the dilution air but only about 40 percent of the variance in the data is attributed to variations in relative humidity.

Particulate analyses indicated that about 3 percent of the fuel sulfur was associated with the fly ash in the stack section for both coal and oil firing. With coals, the amount of sulfur associated with the precipitator catch was approximately proportional to the ash content of the coal – as high as 15 percent with 18 percent ash coal.

With the coal runs, the SO_3 content of the flue gas in the stack section was less than 1 ppm, on the average, compared with about 10 ppm observed with oil firing. The low SO_3 in the

coal-fired flue gas was attributed to the stack section being operated at temperatures (250-275 F) below the dew point of sulfuric acid. For oil firing, the stack was operated at slightly higher temperatures (300-325 F) that allowed the sulfuric acid to remain a vapor in the flue gas.

Incidental measurements were also made of the NO_x content of the flue gas. The NO_x levels for oil firing correlated roughly with the nitrogen content of the fuels. With coal firing, the fuel nitrogen did not vary significantly among the coals employed, hence no comparison can be made.

EXPERIMENTAL PROCEDURE

Apparatus used in the experimental work consisted of the Battelle Multifuel Furnace, along with an associated simulated stack and plume simulation chamber that were designed and constructed for this program. The flexibility of this system allowed firing with either residual oil or pulverized coal and permitted production and conditioning of flue gas and fly ash under conditions closely simulating those of a typical central-station power plant. The facility and associated equipment are described in Appendix A.

Normal operating procedure for the furnace was to fire natural gas during "off periods", when data were not being taken. This permitted ready establishment of steady state temperature upon firing of either the residual oils or coals. When a run was to be made, the furnace was switched from gas firing to coal or oil firing and the entire system was allowed to equilibrate over a period of several hours. During this time, appropriate adjustments were made to obtain the desired operational conditions, and SO_2 and O_2 concentrations in the flue gas were taken to certify the attainment of a steady state. Oxygen readings were made at the furnace exit, and SO_2 readings were taken via a gas-manifold sampling system at the three gas-sampling points indicated in Figure A-1.

The oxygen content of the flue gas was measured continuously throughout each run, both as a check on the stability of the combustion system and to aid in interpretation of the SO_2 readings. Temperatures throughout the system were also monitored continuously. Through the use of a manifold sampling system, readings for SO_2 could be obtained quickly at each of the three gas sampling points. Goksøyr-Ross condensers were incorporated into the SO_2 sampling lines so that SO_3 samples could be taken simultaneously with the SO_2 samples.

In operation of the plume chamber, the appropriate mixture of flue gas and humidified air was established, and the SO_2 concentration and temperature of the chamber were monitored until a steady state was achieved. Samples for SO_2 were then taken along the centerline of the chamber. Whenever the dilution ratio was changed in the chamber, the system was restabilized before data were taken.

Particulate samples were taken at appropriate points in the system simultaneously with the SO_2 sampling. For this, the standard EPA probe-filter-impinger assembly was used. After completion of a particulate run, the rig was immediately disassembled, and the probe and impinger catches were washed into glass bottles for storage prior to analysis. These then were analyzed colorimetrically for sulfate content using barium chloranilate as the reagent. The filter

plus the filter catch were analyzed for sulfur using X-ray fluorescence. In this procedure, a weighed fraction of the filter plus particulate was homogenized by grinding to form the analysis sample. A blank was prepared from a sample of the filter material obtained from the same stock. A standard reference sample for the analysis was prepared similarly, using the same stock filter material and prestandardized sodium sulfate.

Details of the sampling and analytical procedures are given in Appendix A.

EXPERIMENTAL RESULTS

Details of the firing conditions, system temperatures, and analytical data are given in Appendixes B, C, and D.

GENERAL TRENDS

In this study of the fate of SO_2 with several types of both residual oils and coals, a number of qualitatively similar trends have been observed. These similarities are readily apparent from the data cited in Table 1. The observed decreases in SO_2 throughout the experimental system are further illustrated for the oils and coals in Figures 1 and 2, respectively.

TABLE 1. PERCENTAGE SO_2 DECAY[a] WITHIN COMBUSTION SYSTEM

Fuel	Superheater/Economizer	Stack
V-954[b]	9 ± 3[c]	-1 ± 2
V-950[d]	12 ± 4	0
SX-7812[e]	12 ± 5	-3 ± 3
Raw Coal[f]	9 ± 4	-0.4 ± 3
Washed Coal[g]	9 ± 3	0.7 ± 2
Averages		
Oils	11 ± 4	-0.4 ± 4
Coals	9 ± 4	-0.1 ± 3
All fuels	10 ± 4	-0.2 ± 3

(a) Relative to measured values at furnace exit.
(b) Venezuelan residual oil.
(c) Standard deviation.
(d) Desulfurized V-954.
(e) Mid-continent residual oil.
(f) Raw Pittsburgh-seam coal.
(g) Washed Pittsburgh-seam coal.

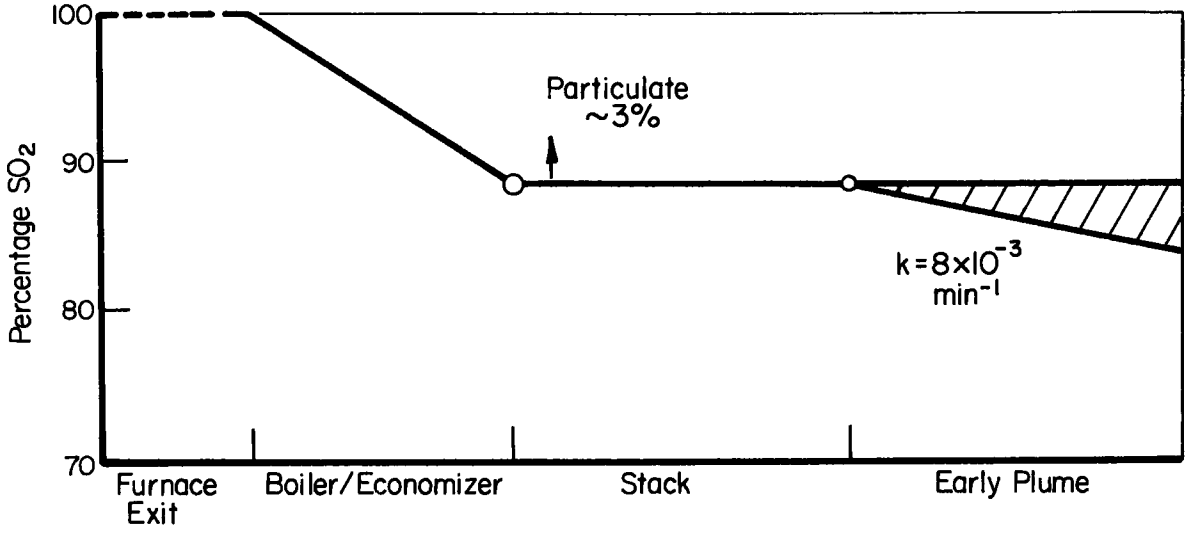

Figure 1. General SO_2 Loss Profile for Oil

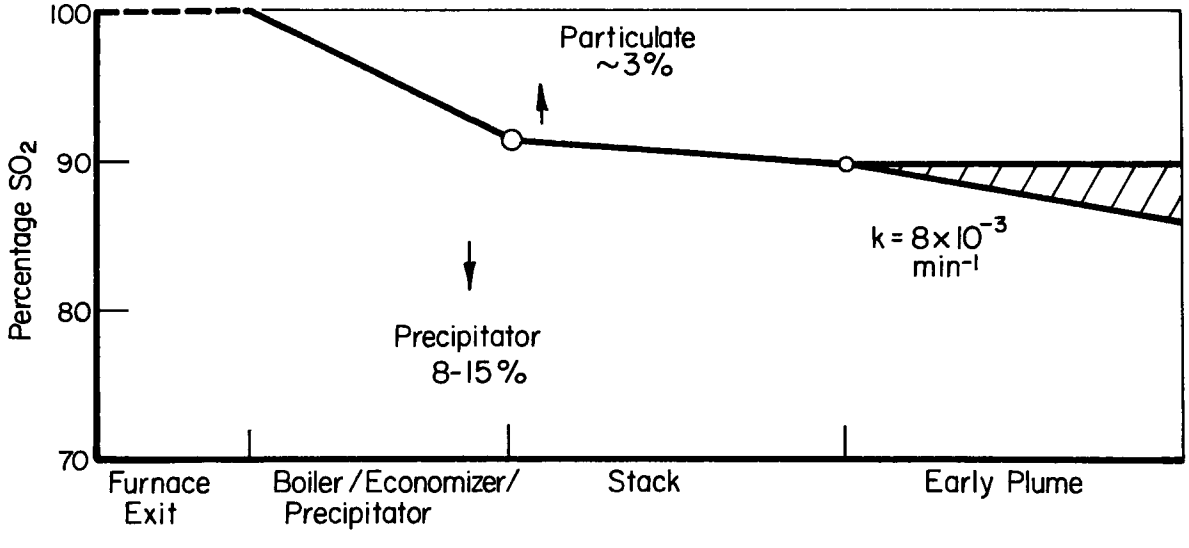

Figure 2. General SO_2 Loss Profile for Coal

For both fuels, a loss of approximately 10 percent of the SO_2 from the flue gas was noted across the boiler/economizer section of the system. Recent data obtained by TVA at the Shawnee plant in Paducah[5] indicate similar losses of SO_2 in a boiler under some operating conditions. The TVA data show losses of SO_2 across the superheater/economizer amounting to 5-10 percent for some of the test conditions.

In the stack section of the laboratory system, losses were very slight, being no more than 0 to 3 percent for either the oils or the coals. Sulfur associated with the particulate material at the entrance to the stack also amounted to about 3 percent of the total sulfur on the average for both the oils and the coals.

In the plume section, loss of SO_2 was not always observed for firing with either fuel. However, loss of SO_2 was noted in the plume for 15 experiments with residual oils and 27 runs with coal. Approximately 65 percent of these runs showed first-order rate constants in the range of 1×10^{-3} to 2×10^{-2} min^{-1} (see Table C-3). Figure 3 shows the distribution of rate constants in this group. A least-squares analysis of these data indicates a best value of 8×10^{-3} min^{-1} with a probable range of 2×10^{-3} to 13×10^{-3} min^{-1}.

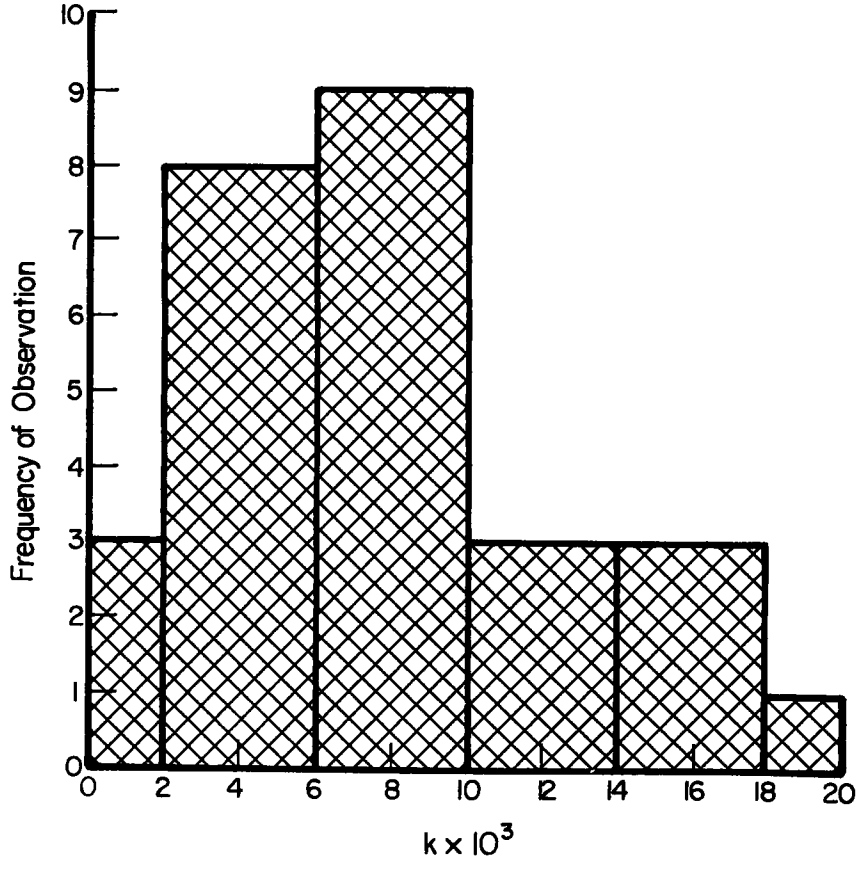

Figure 3. Distribution of Rate Constants

An attempt was made to correlate the observed rate constants with the major variables of the system; the relative humidity of the dilution air, the plume temperature, and degree of dilution (concentration). Results of these correlations are shown in Table 2.

TABLE 2. CORRELATION OF RATE CONSTANTS WITH SYSTEM VARIABLES

Variable	Correlation Coefficient	Degree of Determination[a]
Relative humidity	0.63	0.39
Temperature	-0.21	0.04
Dilution	0.13	0.02

(a) Fraction of data variance accounted for by this correlation.

It is readily apparent that the relative humidity of the dilution air was the most important factor in determining the rate of reaction of SO_2 for these plume experiments. However, it should be noted from the data in Table C-3 that this conclusion is heavily weighted by results taken without any dilution air. The fact that a first-order rate expression seemed to fit the data best is in agreement with the low correlation coefficient obtained for dilution, i.e., the half-life is not affected by dilution. The negative correlation coefficient obtained for temperature is reasonable in as much as it is expected that the solubility of SO_2 in the plume mist, and hence its availability for reaction within the droplets, decreases with increasing temperature.

These results imply that the general behavior of SO_2 in a power-plant combustion-plume system is relatively independent of whether pulverized coal or oil is being burned. However, some differences need to be cited to qualify this conclusion.

SPECIFIC FUEL EFFECTS

Although the general trends apply to both coal and oil, some specific differences in distribution of sulfur within the combustion system occur due to the different firing practices for the two fuels. With oil firing, the ash content is low and an electrostatic precipitator is generally not used to scavenge fly ash from the flue gas. Also, stack temperatures with oil firing are generally slightly higher than those with coal firing.

SO_3

In the coal experiments, the stack simulator was generally run at temperatures of 250 to 275 F, i.e., at temperatures below the dew point of sulfuric acid with normal flue-gas compositions. As a result, little or no SO_3 was observed in the stack. On the other hand, runs with oil firing were made with stack temperatures of 300-350 F, and SO_3 amounting to about 1 to 2 percent of the total sulfur was observed in the stack.

Sulfur in Ash

In the coal-fired runs, appreciable amounts of sulfur were found in the precipitator catch; the collected ash contained approximately 12 to 17 percent sulfur expressed as SO_4. Furthermore, as indicated in Table D-3, the amount of sulfur found in the precipitator catch varied with the two coals fired. With the raw Pittsburgh-seam coal, the percentage of fuel sulfur associated with the ash in the precipitator was about twice as much as with the washed Pittsburgh-seam coal. Since the raw coal contained approximately twice as much ash, it appears that the percentage of fuel sulfur associated with the precipitator catch was proportional to the ash content of the coal.

NO_x Emissions

The study of NO_x emissions was not a prime objective of this work. An interesting observation, however, merits attention. Listed in Table 3 are the nitrogen contents of the three residual oils used. Also listed in this table are typical ranges of values of NO_x measured at similar excess air levels (O_2 = 2.4-2.7 percent). It is interesting to note that the trends indicated by the fuel nitrogen values correlate with observed NO_x levels. It therefore appears that the nitrogen content of the fuels plays a significant role in determining the level of NO_x in the flue gas under the firing conditions employed. With the coals, the range of nitrogen content was too limited to estimate the influence of fuel nitrogen on NO_x formation.

TABLE 3. EFFECT OF NITROGEN IN FUEL OIL

Fuel	Nitrogen Content, weight percent	Measured NO_x, ppm
V-954	0.44	550-750
SX-7812	0.38	570-750
V-950	0.23	300-450

General Observations

Several aspects of the data for both the oil and coal runs merit attention.

The particulate data for the coal runs present a reasonable picture of the sulfur distribution in the particulate, and the amount of sulfur removed from the flue gas in the electrostatic precipitator for this laboratory system. However, the paucity of particulate data for the oil runs mitigates against any firm conclusions concerning the amount of sulfur associated with the particulate in those runs. The data obtained are reasonable, but any conclusions based on these data must be considered only in a qualitative sense.

The fact that a loss of SO_2 was not observed consistently in the plume chamber is perplexing. Although a reasonably large number (42) of incidences of SO_2 loss in the plume chamber were observed, many of these occurred with relatively long residence times. Design

parameters of the plume chamber and initial verification of the plug-flow operation of the chamber do not, in general, cover these longer residence times, so the actual dynamics of flow, upon which treatment of the data is based, cannot be stated with certainty. Plug flow was assumed for all calculations of rate constants in the plume chamber.

OTHER INVESTIGATIONS OF SO_2 DECAY IN PLUMES

The decay of SO_2 in real and simulated plume systems has been studied by a number of other investigators. Johnstone and Coughanowr(6), Johnstone and Moll(7), and Matteson et al(8) showed that the oxidation of SO_2 in aerosols is much faster than the photochemical oxidation of SO_2 in dry air and that this oxidation could be greatly accelerated in the presence of iron and manganese salts normally found as fly ash constituents. The work of Matteson indicates that the observed rates of oxidation of SO_2 in aerosols are consistent with rates of oxidation of SO_2 in solution, implying that the oxidation occurs within aqueous droplets formed in a plume. Foster(9) has extended this notion with the development of a model based on oxidation of the SO_2 within droplets which form and grow as a result of the rapid cooling of flue gas during the early stages of plume development.

Gartrell(10), Dennis(3), and, most recently, Stephens and McCaldin(4) have employed aerial sampling of power station plumes as a means for direct measurement of the rates of oxidation of SO_2 under totally realistic conditions. Although each of these studies was confounded to some extent by the meteorological variability inherent in any real plume system and the difficulties of aerial sampling, the results agree, at least qualitatively, with those of the earlier laboratory studies. The conclusions of these full-scale studies can be summarized as follows:

1. The overall rate of oxidation of SO_2 can be described in terms of a first-order process with an apparent rate constant of the order of 10^{-3} to 10^{-2} min^{-1}.

2. The relative humidity and/or the existence of a mist or fog in the atmosphere are important in determining the apparent oxidation rate. According to Stephens, the rate of oxidation of SO_2 is appreciable only when the relative humidity of the ambient air is greater than about 40 percent.

Because of the appreciable scatter in the data for these full-scale studies, they cannot readily be subjected to analysis with respect to any of the models developed from laboratory studies. The assumption of a simple first-order rate process cannot be fully justified on the basis of existing data. The importance of relative humidity of the ambient air is still not adequately resolved; in fact, the use of this variable is probably somewhat misleading. The relative humidity within a plume is probably close to 100 percent in the early stages of plume development. According to Foster's model, the droplet concentration and size distribution are more important parameters to be considered. Although these parameters are influenced by the relative humidity of the surrounding atmosphere, they cannot be determined directly from a knowledge of the relative humidity.

As indicated in the previous section, a decline in SO_2 concentration was not noted consistently in the current plume-chamber experiments. However, for those experiments where a decline was observed, a best value of about 8×10^{-3} min^{-1} was obtained from a least-squares treatment of the data. This value is intermediate between the values of 4.7×10^{-3} and 9.9×10^{-3} min^{-1} reported by Stephens for relative humidity ranges of 40-55 and 78-80 percent, respectively. It is toward the upper end of the range of rate constants which is calculated from Gartrell's results and is about the same as the value of 7.6×10^{-3} min^{-1} cited by Stephens for the work of Dennis, but each of these values is certainly within the limits of experimental error of the others. Indeed, the scatter in data for all of these investigators, our own included, is such that statement of a specific value of k is of questionable validity. This only emphasizes the need for a more detailed and precise investigation of the kinetics and modeling of real systems.

Unfortunately, the current work has not provided any firm conclusions concerning the effect of relative humidity on the rate of oxidation of SO_2. Although a weak correlation between rate constants and relative humidity was found, the data do not establish this variable as the main influence on the rate of loss of SO_2 in the plume.

CONCLUSIONS

Indications of this work as they relate to the five objectives are:

1. The major source of decay of SO_2 within the combustion-boiler-stack system was in the boiler-economizer section, wherein sorption of about 10 percent of the SO_2 by fly ash occurs. Essentially no loss of SO_2 was observed in the stack.

2. Within the range of fuels studied, the type of fuel used had little effect on the behavior of SO_2, either within the combustion-boiler-stack system or in the plume chamber.

3. With coals, the fraction of the fuel sulfur retained by the fly ash collected in the electrostatic precipitator was approximately proportional to the ash content of the coal.

4. First-order rate constants for the decay of SO_2 in the plume agreed with those found by other investigators. These rate constants indicate a half-life for SO_2 on the order of 1-6 hours.

5. The effect of relative humidity on the rate of decay of SO_2 in the plume was not adequately resolved in this program. Special effort in further defining this effect is clearly required. Such an effort should also include the role of droplet concentration and size distribution in the plume.

ACKNOWLEDGMENTS

The authors express their appreciation to the members of the Steering Committee; L. E. Niemeyer, Environmental Protection Agency; A. R. Rescorla, American Petroleum Institute; F. W. Church, Esso Research & Engineering Co.; J. W. Tieman, Bituminous Coal Research, Inc.; J. Endres, EEI; W. L. Wingert, The Detroit Edison Co.; J. R. Garvey, Bituminous Coal Research, Inc.; and J. Wagman, Environmental Protection Agency, who assisted both in the design of the experimental program and in preparation of this report. Special thanks are due to Mr. L. Montgomery and Dr. F. Gartrell of the Tennessee Valley Authority for their helpful participation in Steering Committee meetings.

REFERENCES

(1) Wickert, K., "Chemical Reactions in the Combustion Chamber of a Slag-Tap Boiler", Brennstaff-Warme-Kraft, **9**, 104 (1957).

(2) Smith, W. S., and Gruber, C. W., "Atmospheric Emissions from Coal Combustion – An Inventory Guide", PHS Pub. No. 999-AP-24, April, 1966.

(3) Dennis, R., et al, "Measurement of Sulfur Dioxide Losses from Stack Plumes", APCA Paper No. 69-156 presented at the 62nd Annual Meeting of the Air Pollution Control Association, June 26, 1969, New York; "Study of Reactions of Sulfur in Stack Plumes", Second Annual Report by GCA Corporation for National Air Pollution Control Association, December, 1969.

(4) Stephens, N. T., and McCaldin, R. O., "Attenuation of Power Station Plumes as Determined by Instrumented Aircraft", Environ. Sci. Technol., **5**, 615 (1971).

(5) Private communication from Mr. L. Montgomery of Tennessee Valley Authority.

(6) Johnstone, H. F., and Coughanowr, D. R., "Absorption of Sulfur Dioxide from Air", I & EC, **50**, 1169 (1958).

(7) Johnstone, H. F., and Moll, A. J., "Formation of Sulfuric Acid in Fogs", I & EC, **52**, 861 (1960).

(8) Matteson, M. J., et al, "Kinetics of Oxidation of Sulfur Dioxide by Aerosols of Manganese Sulfate", I & EC Fundamentals, **8**, 677 (1969).

(9) Foster, P. M., "The Oxidation of Sulfur Dioxide in Power Station Plumes", Atmos. Environ., **3**, 157 (1969).

(10) Gartrell, F. E., et al, "Full-Scale Study of Dispersion of Stack Gases", TVA Summary Report (August, 1964).

(11) Goksøyr, H., and Ross, K., "The Determination of Sulfur Trioxide in Flue Gases", J. Inst. Fuel, **35**, 177-179 (1962).

(12) Bertolacini, R. J., and Barney, J. E., II, "Colorimetric Determination of Sulfate with Barium Chloranilate", Anal. Chem., **29**, 281-83 (1957).

(13) Eschka, A., Ost.Z. Berg. u. Huttenw., **22**, 11-13 (1874); Dinglers Polytech., J., **212**, 403-4 (1874).

(14) "Standards of Performance for New Stationary Sources", Federal Register, **36**, No. 159, 15713-14, Aug. 17, 1971.

APPENDIX A

EXPERIMENTAL EQUIPMENT AND METHODS

APPENDIX A

EXPERIMENTAL EQUIPMENT AND METHODS

MULTIFUEL FURNACE FACILITY

Design Features

The multifuel furnace used for this program was designed to generate flue gas and fly ash under conditions closely simulating those of a power-generation station. This implies combustion at a high enough temperature with a proper cooling schedule to produce flue gas and fly ash having physicochemical properties similar to those of a typical central-station boiler and its associated stack and plume. In addition, the laboratory-scale system used in this program had to be flexible enough to permit firing with either pulverized coal or residual oil.

The Multifuel Furnace Facility was operated with an electrostatic precipitator for coal firing but without the electrostatic precipitator in firing oils. The time-temperature profiles in the other sections of the facility were appropriately adjusted for the inclusion or exclusion of the precipitator.

Figure A-1 is a schematic of the gas-combustion and flue-gas-conditioning system with major sections and sampling points indicated. Design and operation of the plume chamber are discussed later. The other major sections of the system are discussed below.

The Multifuel Furnace. Figure A-2 is a photograph of the Battelle multifuel furnace used on this program. This small-scale furnace consists of a cylindrical combustion chamber approximately 17 inches in diameter by 90 inches in length. The furnace is lined with three layers of firebrick and insulation to accommodate surface temperatures up to 2900 F. At the outlet, the diameter of the furnace is reduced to 5 inches to enclose the flame, provide for normal recirculation, limit radiation losses, and provide sufficient gas velocity to keep fly ash suspended in the gas stream. Viewports along the axial dimension of the furnace provide for visual access during periods of adjustment of firing conditions.

In normal operation of the furnace, natural gas was fired to maintain system temperatures at approximately the desired levels on a more or less continuous basis while runs were not being made. Upon switching to either coal or oil firing, the entire system was allowed to equilibrate for several hours before any data were taken.

An adjustable-flow, positive-displacement pump that was precalibrated was used to regulate the supply of residual oil to the furnace at about 3 gal/hr, and the oil was preheated to insure the desired viscosity at the burner nozzle. With coal firing, a dispersion of the fuel in air was fed to the burner (at a rate of about 30 lb/hr) via a screw feeder mounted within a pressurized coal hopper.

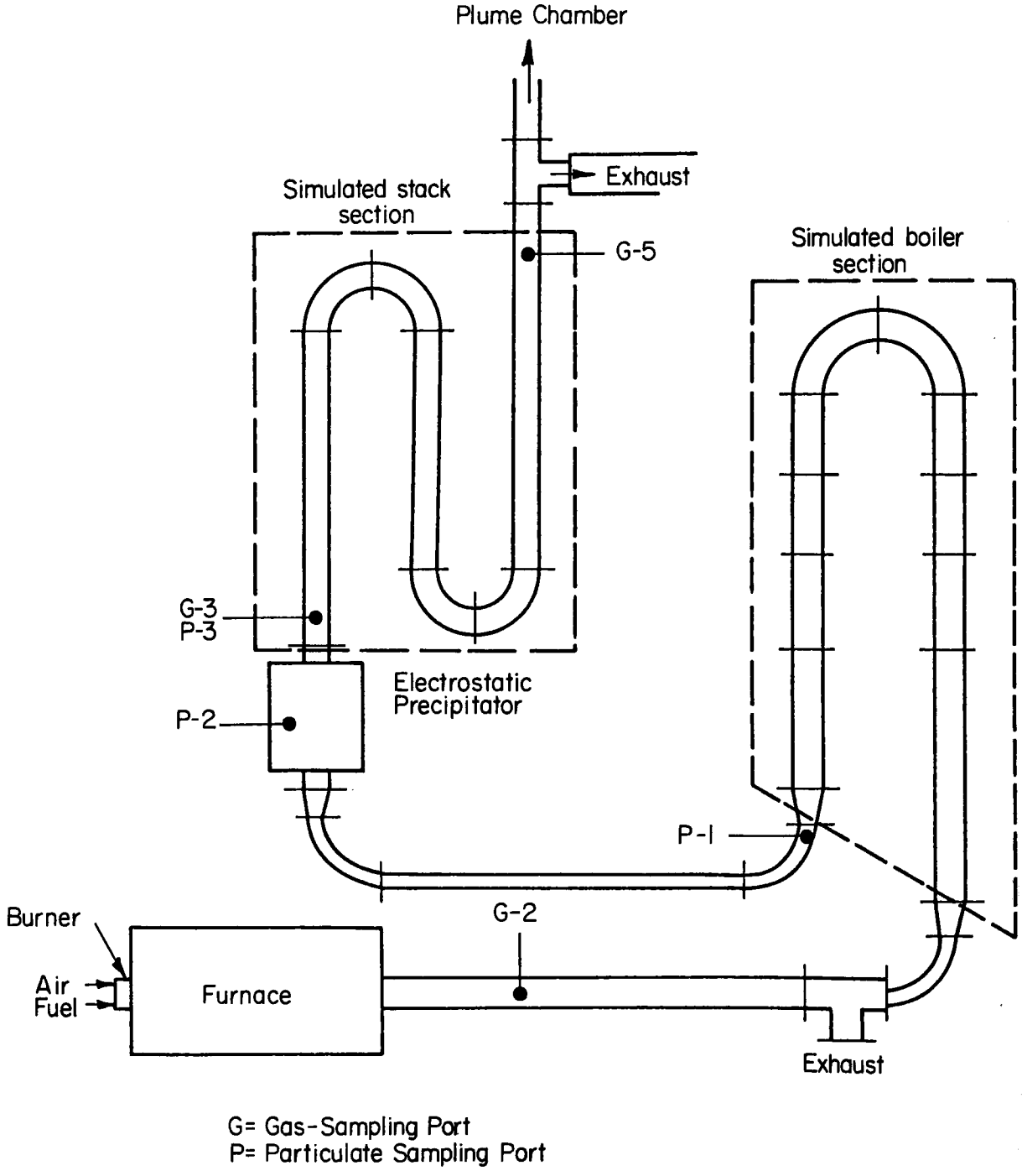

Figure A-1. Schematic of Laboratory System

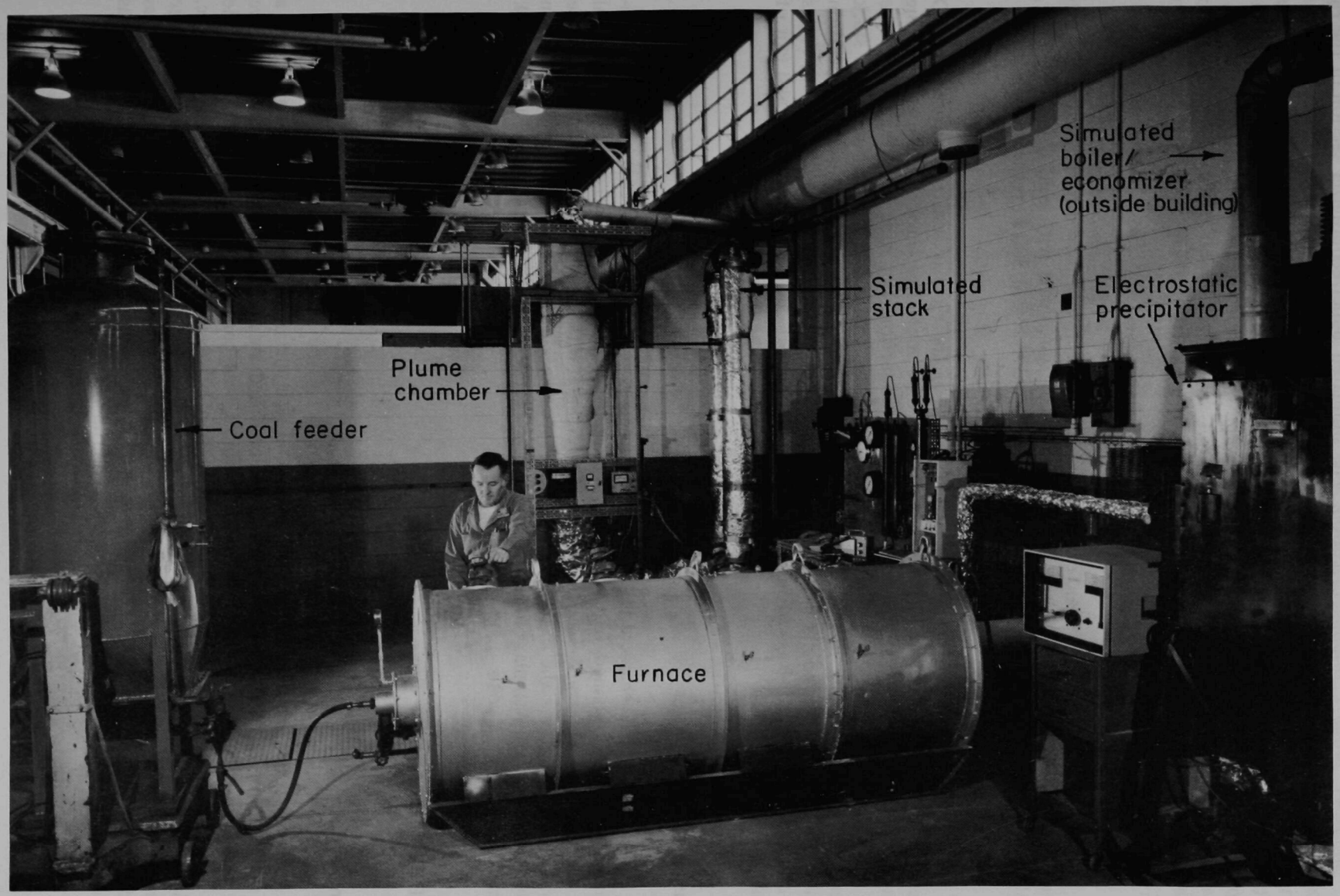

Figure A-2. Battelle Multifuel Furnace

Simulated Boiler/Economizer Section. The simulated boiler/economizer section of the rig was constructed of stainless steel pipe lined with a castable refractory material. Gas velocities within this section were modulated using a variable exhaust duct at the head of the section. This operation also helped in maintaining desired temperatures, and additional control over temperature profiles was gained through the use of removable insulation on the outside of the section. Gas velocities in horizontal portions of this section were typically 60 ft/sec, and velocities in vertical portions were about 5 ft/sec. Temperatures dropped from about 2600 F at the inlet to about 400 F or less at the outlet.

Electrostatic Precipitator. An electrostatic precipitator was used for removal of fly ash between the boiler and stack sections of the system for runs made with coal firing. Typically, the inlet and outlet temperatures of the precipitator were 375 F and 300 F, respectively.

Stack. The 37-foot-long simulated stack section of the rig was constructed of 5-inch-OD stainless steel pipe. Temperatures in the stack section were controlled through the use of heating tape and insulation applied throughout the length of the section. For runs with residual oils, the stack temperature was maintained at about 300 F. With coal firing of the unit, the stack temperature was maintained at 250-275 F. These values are typical of central-station operation with these fuels. Sampling points were provided at 3-foot intervals along the stack section, but as little or no SO_2 loss was observed in the stack, only the ports nearest the entrance and exit of the stack were used.

Operational Characteristics

The operational characteristics of prime interest to this program concerned the time-temperature profiles obtained in the system. Typical time-temperature profiles for oil and coal firing are shown in Figures A-3 and A-4. Residence times with coal firing were similar to those with oil firing except for the extra 5-second residence time in the precipitator. Temperatures in the system were also similar for both types of fuel except for the slightly lower stack temperatures used with coals.

PLUME CHAMBER

Design Features

Figure A-5 is a schematic of the plume-dilution chamber. This apparatus consists of a small chamber for mixing of the flue gas with humidified air and a semiconical section to serve as an expansion and reaction chamber. The chamber was constructed of aluminum, with the walls Teflon coated to minimize chemical interaction between them and the simulated plume. The 6-degree angle of the conical portion of the chamber was specifically designed to minimize dynamic interaction effects between the walls and the flowing gas stream. The chamber was heated electrically to maintain constant temperature, and sampling of the flue gas was accomplished with a movable probe along the centerline of the chamber.

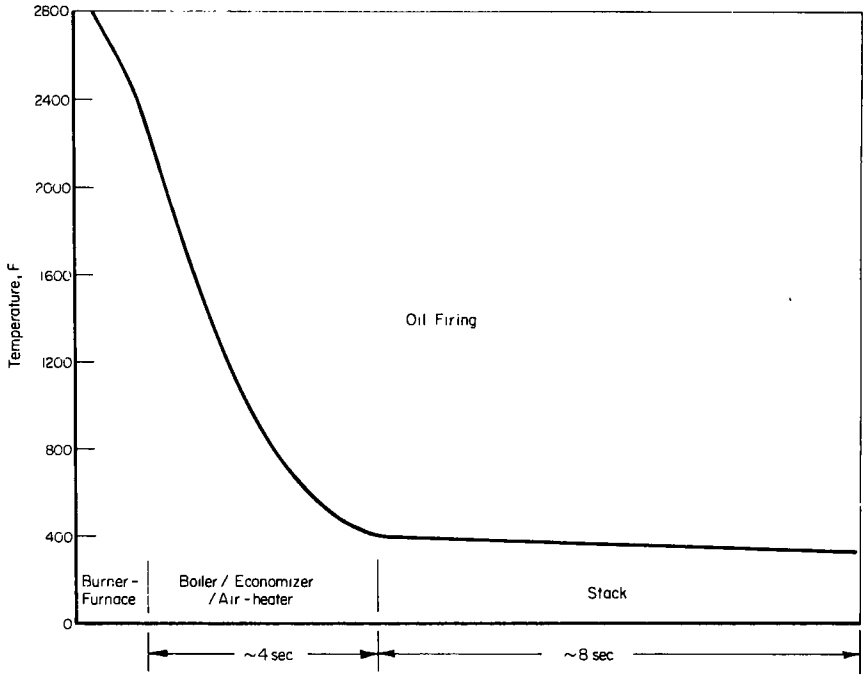

Figure A-3. Time-Temperature Profile Typical of Oil Firing

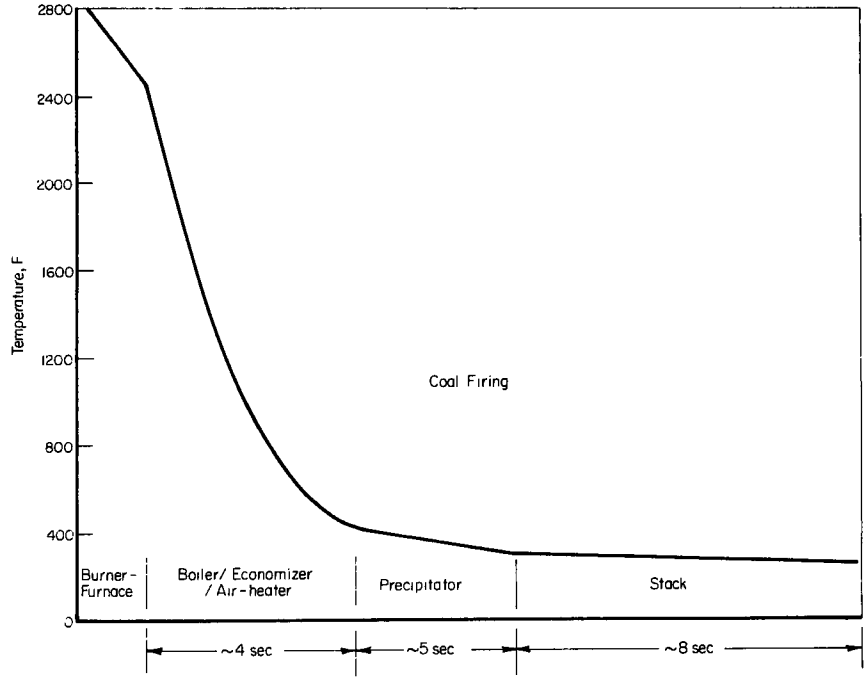

Figure A-4. Time-Temperature Profile Typical of Coal Firing

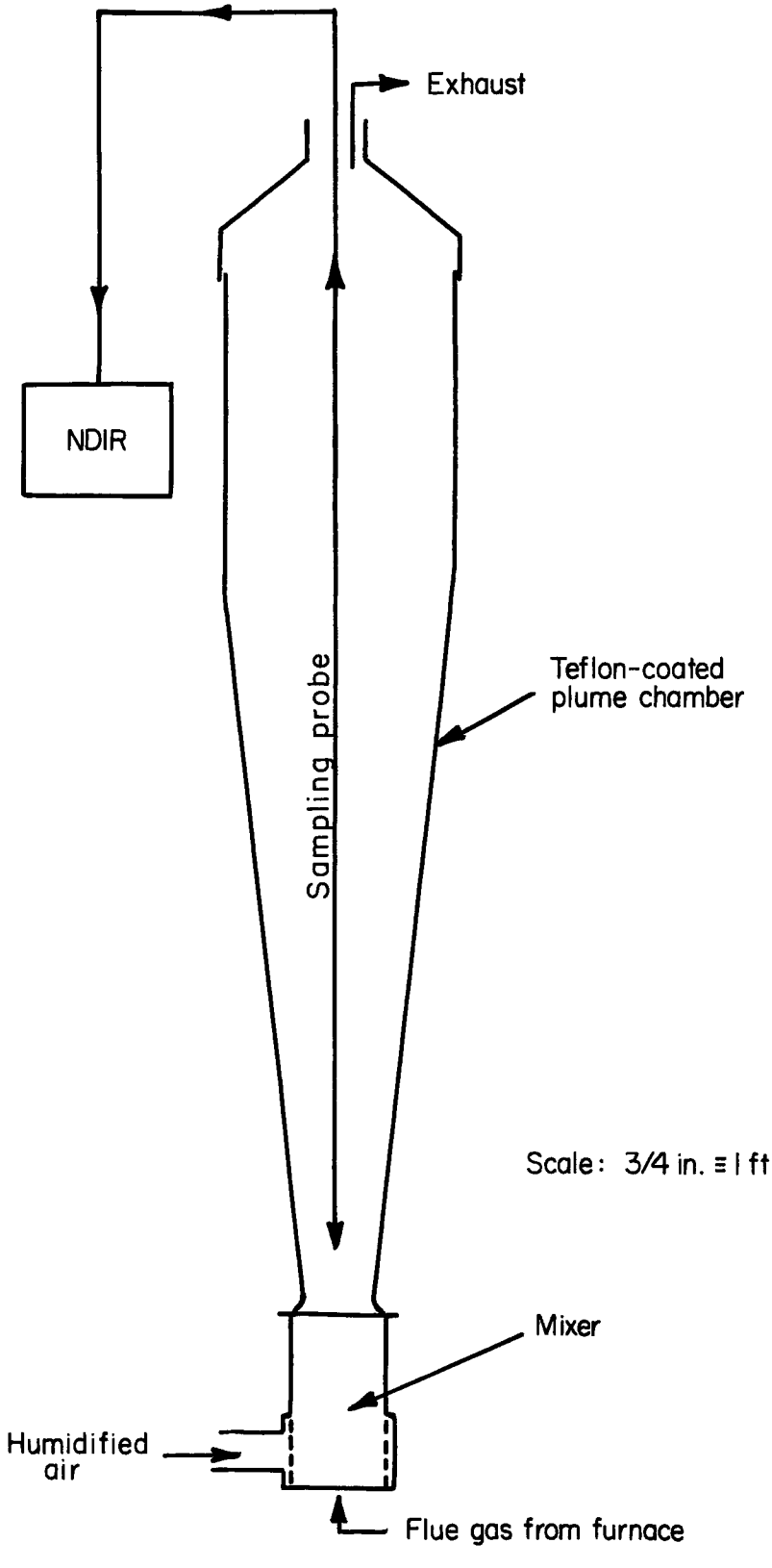

Figure A-5. Schematic of Plume Chamber Layout

Operational Characteristics

Probe Assembly. The sampling probe used in the plume chamber consisted of a 10-ft length of 1/4-inch-OD Teflon tubing, the tip of which was tapered to approximately 1/16-inch OD. The probe was mounted on a movable pulley system, fully contained within the chamber and exhaust duct. Thus, the entire probe was kept at temperature, and a constant probe length was maintained. Gas was pumped through the probe into a condenser-trap-arrangement where samples were collected for sulfuric acid analyses. The remaining gas was then directed into an NDIR instrument or an electrochemical transducer (Faristor) for continuous monitoring of SO_2 or NO_x concentrations, respectively.

The ID of the Teflon tube used as a probe was approximately 3/16 inch, and gas was drawn through the probe at a rate of approximately 1500 cm^3/min. This is equivalent to a linear flow of 4.6 ft/sec, thus giving about 2 seconds residence of the gas in the probe.

Mixer. Compressed air was used as a source for dilution. The supply stream was divided into two branches, with appropriate orifice metering on each segment. Provision was made for injection of steam into one branch of the air supply to saturate that part of the air with water vapor. This saturated portion of the air was then led through a cooled cyclone-type separator to remove excess water and return the air temperature to near ambient. This humidified air was mixed with relatively dry air from the second branch of the air supply system and passed through a baffle chamber to remove any entrained water droplets prior to entrance into the mixing chamber at the bottom of the plume chamber. Through adjustment of the air flows through the two branches of the system, any desired relative humidity up to approximately 100 percent could be achieved. The humidity was monitored continuously at a point just prior to entry into the dilution chamber.

Flow Profiles. The plume-dilution chamber was designed to provide for plug flow of gases. This aspect of the performance was checked out using both hot-wire anemometers and boron trifluoride for visual display. The hot-wire anemometer proved to be unsatisfactory for use in the plume chamber experiments because of the low linear flow rates to be used. However, injection of boron trifluoride provided a smoke which enabled visualization of the flow patterns. Results of this work indicated no appreciable eddy or jet formation. It therefore appears that flow through the chamber under conditions employed in full-scale runs can best be described as plug flow.

Temperature Profiles. The plume chamber was designed to operate as an isothermal chamber, with automatic control of the chamber temperature to match that of the flue gas-air mixture in the mixing chamber. The control system was sufficiently flexible, however, to permit operation of the chamber at higher temperatures for some of the runs.

Temperature profiles of the chamber were obtained both with and without gas flowing through the chamber. Results of these measurements indicate that temperatures within the chamber were constant to within ±10 F.

ANALYSIS METHODS

Flue Gas

SO_2. Sulfur dioxide concentrations in the flue gas were monitored continuously using a Beckman Model 315 A nondispersive infrared (NDIR) instrument. Water vapor was removed prior to entering the instrument because it interferes with the SO_2 analysis. Other constituents in the gas phase do not seriously interfere with the SO_2 readings. Under dry conditions, the SO_2 standards could be reproduced to within ±1 percent. To further substantiate the SO_2 levels recorded by the NDIR method, spot checks were made from time to time using the Goksøyr-Ross method to analyze for SO_2[11]. In this method, the SO_2 is oxidized by hydrogen peroxide to sulfuric acid and the acid is titrated with standard sodium hydroxide solutions.

SO_3. The sulfur trioxide level in the flue gas was determined, after condensation as sulfuric acid, by titration or by a colorimetric method involving barium chloranilate[12]. For low values of SO_3 (<5 ppm) or for short sampling times, the colorimetric method was generally used because considerably smaller quantities of SO_3 are required for this method. Otherwise, a sufficient sample of acid was collected using the Goksøyr-Ross technique and the acid was titrated with standard sodium hydroxide solution.

NO_x. Nitrogen oxides were monitored continuously using an Enviro-Metrics Faristor detector that detects both NO_x and SO_2. To obtain the correct NO_x values in the flue gas, the SO_2 contribution to the total readout values either was subtracted electronically using an additional Faristor specifically for SO_2 or the total readout values were corrected for SO_2 contribution by standardizing the NO_x-SO_2 Faristor with both NO and SO_2 and subtracting the appropriate amount of SO_2. The latter method was used almost exclusively in this program. Instrument specifications indicate a reproducibility of about ±2 percent. However, problems encountered with baseline drift in the instrument probably can account for an additional 10 percent error or more in the NO_x data.

Fuels

Fuels used on this program were three residual oils and three coals. These materials were supplied to Battelle-Columbus by the Sponsors and some were accompanied by analyses. All of the materials were reanalyzed at Battelle-Columbus, and additional checks were obtained from independent analyses by other laboratories. For the residual oils, additional sulfur analyses were obtained from Esso R&E. The three coals were reanalyzed by Bituminous Coal Research, Inc.

Residual Oils. Samples of the three residual oils were analyzed for C, H, N, and S using standard procedures. C, H, and N values were obtained using a microcombustion procedure, and the nitrogen contents of the oils were verified using a micro-Kjeldahl method. The sulfur contents of the oils were determined by the peroxide-bomb and X-ray methods; the latter is probably more accurate. A listing of the results of these analyses is given in Table A-1.

TABLE A-1. RESIDUAL OIL ANALYSES

Oil	Percentage of Elemental Constituents						
	C	H	N[a]	N[b]	S[c]	S[d]	S[e]
V-954[f]	85.1	10.9	0.4	0.44	2.28	2.37	2.43
V-950[g]	86.1	12.2	0.2	0.23	0.82	0.9	0.96
SX-7812[h]	85.3	10.7	0.4	0.38	2.39	2.33	2.64

(a) Microcombustion method.
(b) Kjeldahl method.
(c) Peroxide-bomb method.
(d) Supplier's analysis.
(e) X-ray method by Esso R&E.
(f) Venezuelan oil.
(g) Desulfurized V-954.
(h) Mid-continent oil.

Coals. Samples of the three coals were analyzed for C, H, N, S, ash, and H_2O. C, H, and N values were obtained by a microcombustion procedure using a Perkin Elmer Model 240 Elemental Analyzer; ash content was determined by ashing the coal at 1382 F; H_2O was determined by weight loss at 220 F; and sulfur was determined by the Eschka[13] method. Data obtained by Battelle-Columbus and BCR are listed in Table A-2.

Particulates

Particulate samples were collected using the standard EPA sampling rig[14]. This rig consists of a heated probe and filter assembly followed by a set of Greenburg-Smith impingers immersed in an ice bath. Flue gas is pumped through the sampler at a rate determined to maintain isokinetic sampling, and the flow rate is measured dry by a dry-gas meter. Particulate samples were taken with this apparatus at a point between the boiler/economizer and stack sections of the system when firing with oil (Point P-1 on Figure A-1), and both before and after the precipitator when firing with coal (Points P-1 and P-3 on Figure A-1). In addition, samples were withdrawn by hand from the precipitator catch when firing with coal (Point P-2 on Figure A-1).

Analyses of the particulate samples consisted of separate analyses of probe, filter, and impinger catches. These analyses were carried out using two different procedures. For most of the filter catches, X-ray fluorescence (XRF) by a Norelco X-ray Fluorescence Vacuum Spectrograph was used to determine sulfur content. Probe and impinger samples were analyzed by dissolution of the remaining particulate using an ion-exchange resin followed by barium chloranilate (BCA) colorimetric determination. The BCA data were further checked using a gravimetric precipitation procedure. Results of the XRF, BCA, and gravimetric determinations are listed in Appendix D.

TABLE A-2. COAL ANALYSES

Coal	Percentage Moisture	Percentage Ash[a]	Percentage C[a]	Percentage C[b]	Elemental Constituents H[a]	Elemental Constituents H[b]	Elemental Constituents N[a]	Elemental Constituents N[b]	S[a] Inorganic	S[a] Organic	S[b]	O_2[c]
Unwashed[d]	1.3	15.4	68.8	68.9	5.01	4.7	1.2	1.2	2.82	1.08	3.94	4.37
Washed[e]	1.44	7.3	76.6	77.0	5.46	5.1	1.4	1.3	1.84	1.14	3.04	4.78

(a) Dry basis, determined by Bituminous Coal Research, Inc.
(b) Dry basis, determined by Battelle-Columbus.
(c) By difference.
(d) Raw Pittsburgh-seam coal.
(e) Washed Pittsburgh-seam coal.

APPENDIX B

FURNACE-STACK DATA

TABLE B-1. FURNACE-STACK RUNS WITH RESIDUAL OILS

	Firing and Sampling Conditions						Dry Basis Concentrations, ppm		
Run	Fuel	Furnace Temp, F	Flue Gas Oxygen, percent	Sampling Point	Residence Time from Burner, sec	Sampling Temp, F	SO_2	SO_3	NO_x
1-A	V-954	2840	2.7	2	0.8	2240	880	105	865
1-B	V-954	2840	2.7	3	6.5	~300	1030	9	560
1-C	V-954	2840	2.7	5	11.9	315	1050	23	530
2-A	V-954	2810	3.7	2	1.0	1800	1110	13	480
2-B	V-954	2810	3.7	3	6.7	405	855	6	360
2-C	V-954	2810	3.7	5	12.1	355	900	5	425
3-A	V-954	2770	4.8	2	1.0	1800	1040	17	430
3-B	V-954	2770	4.8	3	6.7	380	910	7	420
3-C	V-954	2770	4.8	5	12.1	340	910	10	430
4-A	V-954	2840	2.6	2	1.0	1920	1190	15	690
4-B	V-954	2840	2.6	3	6.7	400	1080	17	650
4-C	V-954	2840	2.6	5	12.1	355	1100	23	630
4-D	V-954	2880	2.4	2	1.0	1880	1120	12	760
4-E	V-954	2880	2.4	3	6.7	357	1010	11	790
4-F	V-954	2880	2.4	5	12.1	322	1100	12	765
4-G	V-954	2880	2.4	2	1.0	1880	1080	–	960
4-H	V-954	2880	2.4	3	6.7	350	1135	–	810
4-I	V-954	2880	2.4	5	12.1	315	1110	–	780
5-A	V-954	2830	2.4	2	0.9	2000	1180	24	570
5-B	V-954	2830	2.4	3	6.7	350	1115	7	660
5-C	V-954	2830	2.4	5	12.2	350	1080	8	660
6-A	V-954	2850	2.4	2	0.9	1980	1180	33	525
6-B	V-954	2850	2.4	3	6.5	305	1100	12	550
6-C	V-954	2850	2.4	5	11.8	325	1100	13	570
7-A	V-950	2850	2.4	2	0.9	2000	450	10	290
7-B	V-950	2850	2.4	3	6.7	298	380	3	335
7-C	V-950	2850	2.4	5	12.6	314	380	4	345
7-D	V-950	2850	2.4	2	0.9	2000	430	9	470
7-E	V-950	2850	2.4	3	6.7	300	445	4	400
7-F	V-950	2850	2.4	5	12.6	317	390	4	445
8-A	SX-7812	2850	2.4	2	1.1	1750	1425	26	600
8-B	SX-7812	2850	2.4	3	6.8	290	1240	7	610
8-C	SX-7812	2850	2.4	5	12.4	312	1280	6	580
8-D	SX-7812	2850	2.4	2	1.1	1750	1360	18	690
8-E	SX-7812	2850	2.4	3	6.8	290	1085	6	710
8-F	SX-7812	2850	2.4	5	12.4	312	1160	7	745
9-A	SX-7812	2850	2.5	2	1.1	1680	1370	21	570
9-B	SX-7812	2850	2.5	3	6.9	325	1190	8	630
9-C	SX-7812	2850	2.5	5	12.4	348	1190	9	690
10-A	V-954	2830	2.6	2	1.1	1910	1150	–	412
10-B	V-954	2830	2.6	3	6.7	320	1124	–	404
10-C	V-954	2830	2.6	5	12.3	325	1137	–	408
11-A	V-954	2830	2.7	2	1.0	1930	1133	–	423
11-B	V-954	2830	2.7	3	6.8	320	1102	–	456
13-A[a]	V-954	2736	2.7	5	12.7	305	973	–	456
13-B	V-954	2825	2.7	5	12.7	305	973	–	563
13-C	V-954	2835	2.7	5	12.7	320	–	–	623
13-D	V-954	2850	2.7	5	12.7	320	1044	–	581
14-A	SX-7812	2800	2.7	2	1.0	1860	1345	–	607
14-B	SX-7812	2800	2.7	5	12.9	320	1217	–	650

(a) Samples 13A through D used to check reproducibility of results; samples 13A and B taken in morning, 13C and D in afternoon.

TABLE B-2. FURNACE-STACK RUNS WITH COALS

Run	Fuel	Firing and Sampling Conditions: Furnace Temp, F	Flue Gas Oxygen, percent	Sampling Point	Residence Time from Burner, sec	Sampling Temp, F	Dry Basis Concentrations, ppm: SO_2	SO_3	NO_x
1-A	Unwashed	2730	3.2	5	15.2	–	3350	–	440
2-A	Unwashed	2900	3.5	2	1.02	1860	3525	–	290
2-B	Unwashed	2900	3.5	3	8.4	305	3450	–	437
2-C	Unwashed	2900	3.5	5	13.5	278	3450	–	537
2-D	Unwashed	2860	3.5	2	1.05	1860	3310	–	405
2-E	Unwashed	2860	3.5	3	–[a]	294	3100	–	495
2-F	Unwashed	2860	3.5	5	–	270	3200	–	554
2-G	Unwashed	2860	3.5	2	1.05	1750	3475	–	561
2-H	Unwashed	2860	3.5	3	–	280	3070	–	595
2-I	Unwashed	2860	3.5	5	–	265	3010	–	593
2-J[b]	Unwashed	2860	3.5	5	–	240	3200	–	494
2-K	Unwashed	2850	3.4	2	1.05	1800	4100	–	369
2-L	Unwashed	2850	3.4	3	7.2	285	3850	–	506
2-M	Unwashed	2850	3.4	5	11.4	260	4050	–	587
3-A	Unwashed	2740	2.9	2	1.01	1900	2850	–	459
3-B	Unwashed	2740	2.9	3	10.1	287	2500	–	618
3-C	Unwashed	2740	2.9	5	16.5	260	2470	–	736
4-A	Unwashed	2800	3.5	2	1.03	1900	3275	–	433
4-B	Unwashed	2800	3.5	3	–	262	2610	–	649
4-C	Unwashed	2800	3.5	5	–	245	2470	–	696
5-A	Unwashed	2840	3.0	2	1.04	1995	3220	–	475
5-B	Unwashed	2840	3.0	3	8.1	305	2950	–	625
5-C	Unwashed	2840	3.0	5	12.7	285	2800	–	676
5-O	Unwashed	2880	3.4	2	1.05	2065	3050	–	972
5-P	Unwashed	2880	3.4	3	–	257	2680	–	904
5-Q	Unwashed	2880	3.4	5	–	243	2600	–	910
5-R	Unwashed	2800	3.4	2	1.03	1930	3200	–	406
5-S	Unwashed	2800	3.4	3	9.3	270	3040	–	498
5-T	Unwashed	2800	3.4	5	14.9	250	3140	–	481
6-A	Unwashed	2770	3.4	2	1.02	1830	3570	7.4	362
6-B	Unwashed	2770	3.4	3	7.6	308	3650	16.5	516
6-C	Unwashed	2770	3.4	5	11.9	282	3770	13.0	566
6-M	Unwashed	2720	4.0	2	1.01	1860	2360	–	626
6-N	Unwashed	2720	4.0	3	–	295	2740	–	685
6-O	Unwashed	2720	4.0	5	–	270	2800	–	730
6-P	Unwashed	2720	7.1	2	1.01	1860	3200	15.8	718
6-Q	Unwashed	2720	7.1	3	–	303	2875	24.6	687
6-R	Unwashed	2720	7.1	5	–	272	2975	16.1	708
6-D′	Unwashed	2730	7.2	2	1.01	–	3500	–	523
6-E′	Unwashed	2730	7.2	3	7.4	–	3000	–	601
6-F	Unwashed	2730	7.2	5	11.6	–	3050	–	625

TABLE B-2. (Continued)

Run	Fuel	Firing and Sampling Conditions: Furnace Temp, F	Flue Gas Oxygen, percent	Sampling Point	Residence Time from Burner, sec	Sampling Temp, F	Dry Basis Concentrations, ppm: SO_2	SO_3	NO_x
7-A	Unwashed	2800	3.8	2	1.03	1710	5500	10	208
7-B	Unwashed	2800	3.8	3	10.1	265	5450	0.78	357
7-C	Unwashed	2800	3.8	5	16.3	255	5210	0.35	414
7-D[b]	Unwashed	2850	3.8	5	–	–	3650	–	632
7-N	Unwashed	2850	3.8	2	–	1800	3000	–	679
8-A	Washed	2880	3.2	2	1.04	1900	2360	–	689
8-B	Washed	2880	3.2	3	18.7	290	2070	–	730
8-C	Washed	2880	3.2	5	30.5	265	2070	–	750
8-D[b]	Washed	2880	3.2	2	–	1900	2300	–	798
8-N	Washed	2840	3.4	2	1.04	1920	1900	–	673
8-O	Washed	2840	3.4	3	15.0	275	1750	–	666
8-P	Washed	2840	3.4	5	24.5	250	1750	–	686
9-A	Washed	2800	3.7	2	1.02	1880	1960	–	439
9-B	Washed	2800	3.7	3	9.5	305	1825	–	519
9-C	Washed	2800	3.7	5	15.0	345	1775	–	548
9-K	Washed	2850	3.6	2	1.04	1880	2000	–	575
9-L	Washed	2850	3.6	3	–	275	1875	–	569
9-M	Washed	2850	3.6	5	–	270	1850	–	584
9-N	Washed	2850	3.4	2	1.04	1885	2060	–	438
9-O	Washed	2850	3.4	3	13.1	270	1875	–	469
9-P	Washed	2850	3.4	5	21.4	250	1700	–	578
9-A'[b]	Washed	2890	3.6	3	–	260	1850	–	211
10-A	Washed	2790	3.7	2	1.02	1805	1950	–	663
10-B	Washed	2790	3.7	3	11.2	275	1800	–	904
10-C	Washed	2790	3.7	5	18.0	270	1750	–	938
10-D	Washed	2800	3.8	2	1.03	1822	2060	–	457
10-E	Washed	2800	3.8	3	9.2	283	2010	–	399
10-F	Washed	2800	3.8	5	14.8	285	2060	–	457
11-A	Washed	2780	3.4	2	1.02	1840	2550	–	–
11-B	Washed	2780	3.4	3	8.6	275	2300	–	–
11-C	Washed	2780	3.4	5	13.6	265	2125	–	–
11-I	Washed	2800	3.4	2	1.03	1820	2490	–	–
11-J	Washed	2800	3.4	3	7.9	235	2550	–	–
11-K	Washed	2800	3.4	5	12.7	233	2300	–	–
11-P	Washed	2800	3.4	2	1.03	–	2190	–	–
11-Q	Washed	2800	3.4	3	8.7	–	2420	–	–
11-R	Washed	2800	3.4	5	14.1	–	2700	–	–
11-S[b]	Washed	2800	3.4	2	–	–	2500	–	–
12-A	Unwashed	2780	3.6	2	1.02	1900	3340	–	–
12-B	Unwashed	2780	3.6	3	7.8	260	3200	–	–
12-C	Unwashed	2780	3.6	5	12.6	270	3200	–	–
12-F	Unwashed	2910	3.6	2	1.04	1900	3550	–	–
12-G	Unwashed	2910	3.6	3	7.1	305	3650	–	–
12-H	Unwashed	2910	3.6	5	11.2	280	3600	–	–

(a) Residence times not reported in a given series within residence times reported at beginning and end of a series for each sampling point.

(b) Repeat of a previous sample (in same series) taken under similar sampling conditions.

APPENDIX C

PLUME-CHAMBER DATA

TABLE C-1. PLUME-CHAMBER RESULTS WITH RESIDUAL OILS

Run No.	Fuel	Temp, F	Residence[a] Time, sec	Dilution Ratio	Relative[b] Humidity, percent	SO_2 Concentration, ppm Bottom	Center	Top
1-D	V-954	~325	57	0	NA	1010	–	1050
2-D	V-954	320	58	0	NA	900	–	980
2-E	V-954	215	–	3:1		325	–	320
4-H	V-954	325	58	0	NA	1090	–	1070
5-D	V-954	350	55	0	NA	1162	–	1162
5-E	V-954	255	10	5:1	<40	233	229	229
6-D	V-954	272	55	0	NA	1030	994	1003
6-E	V-954	205	10	5:1	<40	238	220	211
6-F	V-954	145	4	15:1	<40	75	70	75
6-G	V-954	173	10	5:1	<40	224	–	–
6-H	V-954	184	10	5:1	>90	224	211	216
6-I	V-954	131	4	15:1	>90	79	79	77
6-J	V-954	109	4	15:1	>90	85	85	85
6-K	V-954	109	4	15:1	<40	90	–	–
6-L	V-954	135	10	5:1	<40	207	211	213
6-M	V-954	186	55	0	NA	1074	–	1056
7-D	V-950	242	55	0	NA	374	374	374
7-E	V-950	240	178	0	NA	387	–	–
7-F	V-950	175	12	15:1	>90	29	28	26
7-G	V-950	180	25	7:1	>90	82	82	82
7-H[c]	V-950	180	25	7:1	>90	82	–	–
7-I	V-950	180	178	0	NA	380	–	–
8-G	SX-7812	253	55	0	NA	1280	–	1219
8-H[c]	SX-7812	264	55	0	NA	1188	–	1157
8-I	SX-7812	201	10	5:1	<40	249	–	262
8-J	SX-7812	150	4	15:1	<40	95	–	95
8-K	SX-7812	144	4	15:1	>90	92	–	95
8-L	SX-7812	152	10	5:1	>90	253	–	253
9-D	SX-7812	268	55	0	NA	1214	–	1214
9-E	SX-7812	217	10	5:1	<40	161	–	161
9-F	SX-7812	175	4	15:1	<40	99	–	99
9-G	SX-7812	195	10	5:1	<40	223	–	–
9-H	SX-7812	165	10	5:1	>90	223	216	209
9-I	SX-7812	154	10	5:1	>100[d]	–	–	209
9-J	SX-7812	154	>15	<5:1	>100[d]	152	–	161
10-D	V-954	150	1920	0	NA	403	–	336
10-F	V-954	145	320	5:1	<40	104	–	104
10-H	V-954	150	120	15:1	<40	31	35	34

Footnotes appear at end of table.

TABLE C-1. (CONTINUED)

Run No.	Fuel	Temp, F	Residence[a] Time, sec	Dilution Ratio	Relative[b] Humidity, percent	SO_2 Concentration, ppm Bottom	Center	Top
10-J	V-954	155	320	5:1	>90	93	–	111
10-L	V-954	155	320	5:1	<40	97	–	–
11-C	V-954	195	1920	0	NA	403	–	327
11-E	V-954	185	320	5:1	>70	111	142	124
11-F[c]	V-954	180	320	5:1	>70	115	133	–
11-G	V-954	165	120	15:1	>70	49	49	49
11-I	V-954	160	320	5:1	>70	119	–	142
12-D	SX-7812	160	1920	0	NA	938	885	872
12-K[c]	SX-7812	–	1920	0	NA	827	752	743
12-M	SX-7812	150	320	5:1	<40	93	128	128
12-P	SX-7812	–	320	5:1	<40	73	–	–
12-Q	SX-7812	150	320	5:1	>70	75	95	84
12-T	SX-7812	190	320	5:1	>>100[d]	77	59	–
13-E	V-954	130	1920	0	NA	735	699	690
13-G	V-954	175	1920	0	NA	752	681	673
13-I	V-954	170	320	5:1	<40	124	137	135
13-K	V-954	160	120	15:1	<40	52	52	52
13-L	V-954	158	120	15:1	>70	52	52	–
13-N	V-954	152	320	5:1	>70	131	131	–
13-P	V-954	–	320	5:1	>>100[d]	137	–	–
13-Q	V-954	–	320	5:1	<40	127	–	–
14-C	SX-7812	196	1920	0	NA	938	788	–
14-D[c]	SX-7812	196	1920	0	NA	947	–	–
14-E	SX-7812	203	1920	0	NA	1018	805	–

(a) Residence time for full-chamber length.
(b) Relative humidity of dilution air; NA means no dilution air.
(c) Repeat of previous samples under similar operating conditions.
(d) Excess steam injected with dilution air.

TABLE C-2. PLUME CHAMBER RESULTS WITH COALS

Run No.	Fuel	Temp, F	Residence[a] Time, sec	Dilution Ratio	Relative[b] Humidity, percent	SO_2 Concentration, ppm Bottom	Center	Top
1-B	Unwashed	–	640	0	NA	1050	–	–
1-C	Unwashed	–	640	0	NA	1400	–	–
1-D	Unwashed	–	640	0	NA	1650	–	–
2-N	Unwashed	213	1920	0	NA	2050	1925	1925
2-O[c]	Unwashed	238	1920	0	NA	2150	–	–
2-P	Unwashed	–	384	5:1	<40	300	–	–
2-Q	Unwashed	210	1920	0	NA	2110	1610	1610
2-R[c]	Unwashed	238	1920	0	NA	2100	–	–
3-D	Unwashed	130	1920	0	NA	2350	2270	2250
3-E[c]	Unwashed	220	1920	0	NA	2250	–	–
3-F	Unwashed	–	384	5:1	<40	290	–	–
5-D	Unwashed	258	1920	0	NA	2740	2550	1700
5-E	Unwashed	256	1920	0	NA	2420	1875	1750
5-F[c]	Unwashed	280	1920	0	NA	2490	–	–
5-G	Unwashed	243	384	5:1	<40	450	510	460
5-H[c]	Unwashed	260	384	5:1	<40	410	–	–
5-I	Unwashed	230	128	15:1	<40	145	135	125
5-J[a]	Unwashed	225	128	15:1	<40	140	–	–
5-K	Unwashed	218	384	5:1	>70	370	380	385
5-L[c]	Unwashed	230	384	5:1	>70	365	–	–
5-M	Unwashed	–	384	5:1	<40	300	–	–
5-N	Unwashed	240	1920	0	NA	2360	–	–
5-U	Unwashed	232	1920	0	NA	2275	1650	1625
5-V[c]	Unwashed	245	1920	0	NA	2280	–	–
5-W	Unwashed	232	384	5:1	<40	305	380	365
5-X[c]	Unwashed	248	384	5:1	<40	360	–	–
5-Y	Unwashed	221	128	15:1	<40	105	95	92
5-Z[c]	Unwashed	208	128	15:1	<40	90	–	–
5-A	Unwashed	214	384	5:1	>70	300	300	315
5-B[c]	Unwashed	–	384	5:1	>70	295	–	–
5-C	Unwashed	–	384	5:1	<40	265	–	–
5-D	Unwashed	–	1920	0	NA	2330	–	–
6-D	Unwashed	225	1920	0	NA	3275	2650	2610
6-E[c]	Unwashed	257	1920	0	NA	3200	–	–
6-F	Unwashed	221	384	5:1	<40	550	560	550
6-G[c]	Unwashed	240	384	5:1	<40	565	–	–
6-H	Unwashed	208	128	5:1	<40	185	200	205
6-I	Unwashed	226	384	5:1	<40	415	–	–
6-J	Unwashed	210	384	5:1	>70	380	440	435
6-K[c]	Unwashed	224	384	5:1	>70	385	–	–
6-L	Unwashed	224	384	5:1	<40	390	–	–

Footnotes appear at end of table.

TABLE C-2. (Continued)

Run No.	Fuel	Temp, F	Residence[a] Time, sec	Dilution Ratio	Relative[b] Humidity, percent	SO_2 Concentration, ppm Bottom	Center	Top
6-R	Unwashed	220	1920	0	NA	2260	1700	1675
6-T[c]	Unwashed	240	1920	0	NA	2275	–	–
6-U	Unwashed	220	384	5:1	<40	400	450	425
6-V[c]	Unwashed	235	384	5:1	<40	375	–	–
6-W	Unwashed	210	128	15:1	<40	155	150	145
6-X[c]	Unwashed	–	128	15:1	<40	145	–	–
6-Y	Unwashed	220	384	5:1	<40	370	–	–
6-Z	Unwashed	204	384	5:1	>70	340	385	370
6-A'[c]	Unwashed	217	384	5:1	>70	340	–	–
6-B'	Unwashed	217	384	5:1	<40	340	–	–
6-C'	Unwashed	–	1920	0	NA	2060	–	–
7-E	Unwashed	223	1920	0	NA	2740	2530	2510
7-F[c]	Unwashed	250	1920	0	NA	2610	–	–
7-G	Unwashed	226	384	5:1	<40	450	420	365
7-I	Unwashed	220	128	15:1	<40	105	100	95
7-J[c]	Unwashed	208	128	15:1	<40	95	–	–
7-K	Unwashed	–	384	5:1	<40	270	–	–
7-L	Unwashed	210	384	5:1	>70	270	285	270
8-E	Washed	220	1920	0	NA	1125	1125	1100
8-F[c]	Washed	247	1920	0	NA	1350	–	–
8-G	Washed	218	384	5:1	<40	300	335	355
8-I[c]	Washed	234	384	5:1	<40	365	–	–
8-J	Washed	208	128	15:1	<40	165	180	205
8-K[c]	Washed	200	128	15:1	<40	215	–	–
8-L	Washed	205	384	5:1	>70	320	355	380
8-M[c]	Washed	–	1920	0	NA	1290	–	–
9-D	Washed	145	1920	0	NA	1225	1050	1025
9-E[c]	Washed	234	1920	0	NA	1150	–	–
9-F	Washed	170	384	5:1	<40	150	180	160
9-G	Washed	170	128	15:1	<40	55	50	45
9-H	Washed	160	384	5:1	>70	110	120	115
9-I[c]	Washed	210	384	5:1	>70	85	–	–
9-J	Washed	210	384	5:1	<40	85	–	–
9-Q	Washed	250	1920	0	NA	1280	1020	810
9-R[c]	Washed	240	1920	0	NA	1210	1000	830
9-T	Washed	233	384	5:1	<40	150	162	177
9-U[c]	Washed	241	384	5:1	<40	145	–	–
9-V	Washed	215	128	15:1	<40	45	40	37
9-W[c]	Washed	214	128	15:1	<40	35	–	–
9-X	Washed	215	384	5:1	>70	110	115	110
9-Y[c]	Washed	218	384	5:1	>70	105	–	–
9-Z	Washed	218	384	5:1	<40	100	–	–
10-G	Washed	185	1920	0	NA	1550	1185	1150
10-H[c]	Washed	183	1920	0	NA	1490	–	–
10-I	Washed	187	384	5:1	<40	200	210	200
10-J	Washed	180	384	5:1	>70	165	170	160
10-K[c]	Washed	225	384	5:1	>70	150	170	160

Footnotes appear at end of table.

TABLE C-2. (Continued)

Run No.	Fuel	Temp, F	Residence[a] Time, sec	Dilution Ratio	Relative[b] Humidity, percent	SO_2 Concentration, ppm Bottom	Center	Top
11-D	Washed	264	873	0	NA	1375	1375	1200
11-E[c]	Washed	264	873	0	NA	1375	–	–
11-F	Washed	241	175	5:1	<40	200	200	200
11-G	Washed	232	175	5:1	>70	120	140	140
11-L	Washed	256	800	0	NA	1890	1910	1700
11-M	Washed	227	160	5:1	<40	360	350	360
11-N	Washed	208	160	5:1	>70	400	360	350
12-D	Unwashed	256	800	0	NA	2550	2490	2040
12-E	Unwashed	237	160	5:1	<40	–	425	440
12-I	Unwashed	230	800	0	NA	2740	2550	2550
12-J	Unwashed	214	160	5:1	<40	440	430	420
12-K[c]	Unwashed	–	800	0	NA	2370	–	–
12-L	Unwashed	230	160	5:1	>70	440	400	400
12-M[c]	Unwashed	–	160	5:1	>70	460	–	–
12-O[c]	Unwashed	–	800	0	NA	2360	–	–

(a) Residence time for full-chamber length.
(b) Relative humidity of dilution air; NA means no dilution air.
(c) Repeat runs.

TABLE C-3. SUMMARY OF SO_2 LOSSES OBSERVED IN THE PLUME CHAMBER

Fuel	Run	Residence Time, sec	Relative[a] Humidity, percent	SO_2, ppm Input	SO_2, ppm Output	k, min^{-1}
Coal	2-n	1920	NA	2050	1925	2.0×10^{-3}
"	2-q	1920	NA	2110	1610	8.4×10^{-3}
"	3-d	1920	NA	2350	2250	1.4×10^{-3}
"	5-d	1920	NA	2740	1700	1.5×10^{-2}
"	5-e	1920	NA	2420	1750	1.0×10^{-2}
"	5-i	128	<40	145	125	7.0×10^{-2}
"	5-u	1920	NA	2275	1625	1.1×10^{-2}
"	5-y	128	<40	105	92	6.2×10^{-2}
"	6-d	1920	NA	3275	2610	7.1×10^{-3}
"	6-R	1920	NA	2260	1675	9.4×10^{-3}
"	6-w	128	<40	155	145	3.1×10^{-2}
"	7-e	1920	NA	2740	2510	2.7×10^{-3}
"	7-g	384	<40	450	365	3.3×10^{-2}
"	7-i	128	<40	105	95	4.7×10^{-2}
"	8-e	1920	NA	1250	1100	4.0×10^{-3}
"	9-d	1920	NA	1225	1025	5.6×10^{-3}
"	9-g	128	<40	55	45	9.4×10^{-2}
"	9-q	1920	NA	1280	810	1.4×10^{-2}
"	9-r	1920	NA	1210	830	1.2×10^{-2}
"	9-v	128	<40	45	37	9.2×10^{-2}
"	10-g	1920	NA	1550	1150	9.3×10^{-3}
"	11-d	800	NA	1375	1200	1.0×10^{-2}
"	11-n	800	>70	400	350	1.0×10^{-2}
"	12-d	800	NA	2550	2040	1.7×10^{-2}
"	12-i	800	NA	2740	2550	5.4×10^{-3}
"	12-j	800	<40	440	420	3.5×10^{-3}
"	12-ℓ	800	>70	440	400	7.1×10^{-3}
Oil	4-H	58	NA	1090	1070	1.9×10^{-2}
"	5-E	10	<40	233	229	1.0×10^{-1}
"	6-E	10	<40	238	211	7.2×10^{-1}
"	6-i	4	>90	79	77	3.8×10^{-1}
"	6-M	55	NA	1074	1056	1.8×10^{-2}
"	7-F	12	>90	29	26	5.4×10^{-1}
"	8-G	55	NA	1280	1219	5.3×10^{-2}
"	8-H	55	NA	1188	1157	2.9×10^{-2}
"	9-H	10	>90	223	209	3.9×10^{-1}
"	10-D	1920	NA	403	336	5.7×10^{-3}
"	11-C	1920	NA	403	327	6.5×10^{-3}
"	12-D	1920	NA	938	872	2.2×10^{-3}
"	12-K	1920	NA	827	743	3.3×10^{-3}
"	13-E	1920	NA	735	690	2.0×10^{-3}
"	13-G	1920	NA	752	673	3.5×10^{-3}

(a) Relative humidity of dilution air; NA = no dilution air.

APPENDIX D

PARTICULATE ANALYSES

TABLE D-1. PARTICULATE SAMPLES – BEFORE PRECIPITATOR

Coal	Total, $SO_4^=$ mg[a]	Gas Volume, cu ft at 68 F	Equivalent PPM SO_2
Unwashed	261	16.35	145
Unwashed	224	18.28	111
Washed	190	13.92	124
Washed	271	21.3	115
Washed	165	11.88	126
Washed	72	11.90	55
Washed	110	23.4	42
Washed	170	13.7	112
Washed	114	16.4	88
Washed	165	11.8	126
Washed	274	11.5	102
Washed	180	13.3	118

(a) XRF analysis.

TABLE D-2. PARTICULATE SAMPLES – AFTER PRECIPITATOR

Coal	Total, $SO_4^=$ mg[a]	Gas Volume, cu ft at 68 F	Equivalent PPM SO_2
Washed	48.1	13.525	32
Washed	156.2	19.07	74
Unwashed	183	15.928	104

(a) BCA analysis.

TABLE D-3. PARTICULATE SAMPLES — PRECIPITATOR CATCH

Coal	Percentage $SO_4^=$	Equivalent Percentage of Coal Sulfur
Unwashed	15.9[a] 18.2[b]	20.9
Unwashed	13.3[a]	17.5
Washed	9.7[a]	7.9
Washed	10.9[a] 10.9[b]	8.8

(a) BCA analysis.
(b) Gravimetric analysis after carbonate fusion.

TABLE D-4. PARTICULATE SAMPLES

Oil	$SO_4^=$ Wt, mg	Gas Sample Volume, cu ft at 68 F	Equivalent SO_2 in Gas, ppm
V-954	26.2	10.1	23
SX-7812	25.3	14.7	15