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Analysis of Thermal Decomposition Products of Flue Gas Conditioning Agents

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August 1979

Analysis of Thermal Decomposition Products of Flue Gas Conditioning Agents

by

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ABSTRACT

The reactions of several flue gas conditioning agents were investigated in the laboratory under conditions simulating those in the flue gas train of a coal-burning power plant. The primary purposes of the study were to characterize the chemical species resulting from the addition of conditioning agents to the flue gas of a coal-fired power plant and to identify potentially hazardous chemical species originating from the agents that may be emitted into the environment.

To investigate the flue gas conditioning agents, a laboratory bench-scale facility was constructed that simulated the composition of the flue gas of a coal-fired power plant and the temperature zones and residence times relevant to the injection of conditioning agents.

The compounds investigated were sulfur trioxide, ammonia, triethylamine, sodium carbonate, ammonium sulfate, and diammonium hydrogen phosphate. These compounds were injected into the simulated flue gas train at various gas stream temperatures ranging from 650 to 160 °C, and samples of flue gas were withdrawn at various locations downstream from the points of injection of the agents and were chemically analyzed.

The most prevalent types of reactions observed in these experiments were thermal decomposition at high temperatures, recombination of the decomposition fragments at lower temperatures, and addition and substitution reactions of the agents or their decomposition products with normal components of the flue gas.

With the exception of the organic compound triethylamine, none of the conditioning agents studied appear to be capable of discharging a significant amount of any environmentally unacceptable chemical species into the environment. However, the potent carcinogen N-nitrosodiethylamine was found in trace amounts as a thermal decomposition product of triethylamine when this agent was injected into the flue gas stream at 160 °C. The formation of this nitrosamine thus represents the only significant environmental threat of any decomposition or reaction product identified during this investigation.

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Dr. William J. Barrett, Head of the Analytical and Physical Chemistry Division, served as the overall technical supervisor of this project.

SECTION 1

INTRODUCTION

This report presents the results of a laboratory investigation of reactions of flue gas conditioning agents under conditions simulating those in the gas train of a coal-burning electric power plant. The reactions studied were of three types: thermal decomposition at high temperatures, recombination of the decomposition fragments at lower temperatures, and reactions with normal components of flue gas. The principal purposes of this investigation were to characterize the chemical species resulting from the addition of conditioning agents to the flue gas of a coal-fired power plant and specifically to identify toxic substances originating from the agents that can potentially undergo stack discharge to the environment.

TECHNICAL BACKGROUND

The recent widespread use of low-sulfur coals in electric power production has led to difficulty in achieving efficient collection of fly ash in electrostatic precipitators at temperatures around 150 °C, where most of the older precipitators operate. This difficulty is attributable to an increase in the electric resistivity of the ash, which limits the useful voltage and current that can be maintained in a precipitator. A major reason for the increase in resistivity is the lower rate of production of the vapor of sulfuric acid (H_2SO_4) in the flue gas and the correspondingly smaller quantity of this conductive substance that is adsorbed on the surfaces of fly-ash particles.[1]

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1. Dismukes, E. B. A Study of Resistivity and Conditioning of Fly Ash. EPA-R2-72-087, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1972. 138 pp.

Several approaches may be taken to upgrade precipitator performance.[2] One approach is to enlarge the precipitator and thus increase the electrode collecting area and the residence time of the gas stream during treatment. Another approach is to relocate the precipitator in the gas stream to a position upstream from the air preheater, where the gas temperature is 300 °C or greater and the ash resistivity is low enough without surface conditioning by sulfuric acid. Still other approaches involve steps to alter resistivity when the precipitator operates downstream from the air preheater. The gas temperature may be lowered from 150 °C to around 100 °C to make the water vapor in flue gas more effective as a surface conditioning agent; such a reduction in temperature may be accomplished by increasing the ratio of combustion air to flue gas passing through the air preheater and discarding the excess air. The remaining approach, which was of basic concern in this investigation, involves chemical conditioning of the flue gas: that is, addition of a chemical compound to the gas stream upstream from a precipitator to obtain the resistivity effect normally produced by sulfuric acid or to obtain some other beneficial effect besides the modification of electrical resistivity.

CHOICES OF CONDITIONING AGENTS FOR STUDY

The most widely used method of chemical conditioning is to add sulfuric acid from an external source and supplement the limited quantity of this substance occurring in flue gas.[1,3] The compound may be added as the acid itself or as sulfur trioxide (SO_3); when the latter substance is added, it is converted to sulfuric acid in the gas stream by combination with water vapor. Injection of either substance is normally made between the air preheater and the precipitator, at a location as near as possible to the preheater to allow adequate time for interaction with suspended fly ash. When properly designed, a system injecting either sulfuric acid or sulfur trioxide performs satisfactorily, upgrading precipitator performance if factors other than resistivity do not limit performance.

A wide variety of other chemical conditioning agents have been investigated in the laboratory, in pilot plants, or in full-scale precipitators. Many of the substances, unlike sulfuric

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2. Sparks, L. E. Electrostatic Precipitator Options for Collection of High Resistivity Ash. In: Symposium on Particulate Control in Energy Processes. EPA-600/7-76-010, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1976. pp 127-141.

3. Dismukes, E. B. Conditioning of Fly Ash with Sulfur Trioxide and Ammonia. EPA-600/2-75-015, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1975. 157 pp.

acid, are not normal constituents of flue gas. However, they have usually been expected to give a similar effect on resistivity. In actuality, some of these compounds do alter resistivity, but some operate through different mechanisms that still improve precipitator performance.

After sulfuric acid, ammonia (NH_3) is one of the most popular conditioning agents.[3] It is used with a great deal of success in Australia, for example, where it exceeds or rivals sulfuric acid in importance.[4] Frequently, ammonia is assumed to lower resistivity by adsorption on fly-ash surfaces, but its importance in this connection has not been clearly demonstrated. Available research data have shown that ammonia operates by two entirely different mechanisms: (1) by creating a favorable space-charge effect in the gas stream within a precipitator and (2) by increasing the cohesiveness of fly ash after deposition.[3,5] The first effect gives more efficient collection of ash; the second minimizes loss of collected ash by reentrainment. Conditioning with ammonia may also suppress one of the unfavorable manifestations of high resistivity: back corona or reverse ionization occurring in the collected ash.

Triethylamine, an organic base similar to ammonia ($[C_2H_5]_3N$), has been receiving attention recently. Some investigators argue that the amine acts as an agglomerating agent, increasing the effective average size of fly-ash particles before precipitation occurs and thus helping to overcome the basic difficulty of precipitating small particles.[6] It is probable, however, that the amine acts also or mainly through the mechanisms described for ammonia.

Sodium carbonate (Na_2CO_3) has recently been receiving attention as a conditioning agent for use in plants operating with either a hot-side precipitator (temperature, around 370 °C) or a cold-side precipitator (temperature, around 150 °C). The compound may be added to the boiler along with the coal, in which case

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4. Watson, K. S. Australian Experience with Flue Gas Conditioning. In: Symposium on Particulate Control in Energy Processes. EPA-600/7-76-010, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1976. pp 189-216.

5. Dismukes, E. B. Conditioning of Fly Ash with Ammonia. J. Air Pollut. Contr. Assoc., 25:152-156, 1975.

6. Potter, E. C., and C. A. J. Paulson. Improvement of Electrostatic Precipitator Performance by Carrier Gas Additives and Its Graphical Assessment Using an Extended Deutsch Equation. Chem. Ind., 1974:532-533.

sodium oxide from the carbonate compound is incorporated in the fly ash as a resistivity-lowering constituent.[7] Alternatively, the sodium compound may be added to the flue gas just ahead of the electrostatic precipitator, in which case it is coprecipitated with the ash, serving as a conductive species in a mixture with the relatively nonconductive fly ash.[8]

Still other compounds used for conditioning occur as constituents of proprietary formulations of such companies as Apollo Chemical Corporation. During this research, as described in Section 3, different Apollo formulations were analyzed and found to contain ammonium sulfate ($[NH_4]_2SO_4$), sodium bisulfate ($NaHSO_4$), diammonium hydrogen phosphate ($[NH_4]_2HPO_4$), and urea ($[NH_2]_2$-C=O) as the principal constituents. It is conceivable that each of these compounds may, to a degree, operate through each of the conditioning mechanisms described above.

The conditioning agents selected for study during this investigation were as follows:

- Sulfur trioxide (SO_3)
- Ammonia (NH_3)
- Triethylamine ($[C_2H_5]_3N$)
- Sodium carbonate (Na_2CO_3)
- Ammonium sulfate ($[NH_4]_2SO_4$)
- Diammonium hydrogen phosphate ($[NH_4]_2HPO_4$)

The basis for the selection of each of these compounds except triethylamine was the relatively widespread use known to occur presently. Triethylamine, the only organic compound in this group, was selected because of its potential use and its potential conversion to toxic organic compounds.

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7. Bickelhaupt, R. E. Sodium Conditioning to Reduce Fly Ash Resistivity. EPA-650/2-74-092, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1974. 10 pp.

8. Selle, S. J., and L. L. Hess. Factors Affecting ESP Performance on Western Coals and Experience with North Dakota Lignites. In: Symposium on Particulate Control in Energy Processes. EPA-600/7-76-010, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1976. pp 105-125.

DESIGN AND FABRICATION OF APPARATUS FOR REACTION STUDIES

The first task completed during this investigation was the design and fabrication of a laboratory-scale gas train simulating pertinent components of the flue gas train in a full-scale electric power station. Requirements of this train were that it should simulate the temperature-time profile of an actual flue gas train extending from the highest temperature at which a conditioning agent might be added to the lowest temperature reached in the stack prior to gas emission to the environment. Accordingly, an apparatus with temperatures decreasing in steps from 650 to 90 °C was fabricated. This simulated flue gas train is described in Section 4.

The gas stream maintained in this apparatus simulated the composition of flue gas from the combustion of low sulfur coal. The most fundamental and consistently used gas-phase components were 76% nitrogen, 12% carbon dioxide, 4% oxygen, and 8% water vapor. As dictated by the objectives of individual experiments, the following additional components were added on occasion: up to 500 or 600 ppm of sulfur dioxide, up to 25 ppm of sulfur trioxide, 100 ppm of nitrogen dioxide, and 1000 ppm of nitric oxide. In one important aspect, however, no attempt was made to simulate the composition of flue gas; no attempt was made to include suspended fly ash as a constituent of the flue gas because of technical problems.

KINETIC STUDIES OF CONDITIONING AGENTS

The simulated flue gas train was fitted with ports through which conditioning agents could be injected at various temperatures and through which the reaction products could be withdrawn for analysis at various locations downstream from the injection sites. A variety of devices for sampling the reaction products was employed. The choices of sampling devices and the methods of analysis depended upon the type of conditioning agent injected and the type of reaction product expected. Details of the experimental procedures and results with the individual conditioning agents are subsequently described in Section 5.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

The principal conclusions reached during this research program are discussed below under headings for each of the conditioning agents studied.

Sulfur Trioxide

This agent was investigated mainly in control experiments to determine whether this highly reactive substance could be maintained in the flue gas stream and its loss by wall effects minimized. It was injected only at 370 °C. The compound was presumably quantitatively converted to sulfuric acid vapor by reaction with water vapor; however, no evidence of loss by other chemical reactions was detected, and indications of wall losses were overcome by taking the necessary experimental precautions.

Sulfur trioxide represents an environmental threat by its escape from the stack of a power plant as a condensed mist of sulfuric acid or as a sulfate coating on fly ash particles. The distribution of the agent between these two forms was not determined in this investigation inasmuch as fly ash was absent from the experimental system. However, previous investigations[3,9] have shown that the distribution probably will be controlled by the alkalinity of the ash; at high alkalinity sulfate on the ash will predominate, and at low alkalinity sulfuric acid mist will predominate.

Ammonia

This agent was injected at temperatures of 650, 370, and 160 °C. It was found to participate in reactions with sulfuric acid and nitrogen oxides that are normally present in flue gas.

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9. Dismukes, E. B., and J. P. Gooch. Fly Ash Conditioning with Sulfur Trioxide. EPA-600/2-77-242, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1977. 65 pp.

The reaction with sulfuric acid leads to the formation of bisulfate and sulfate salts, which are solids. The reactions with nitrogen oxides were not fully characterized, but they apparently lead to the formation of solid nitrate salts among other possible products.

Depending upon the stoichiometry of ammonia and its reactants present in the flue gas, ammonia may be largely converted to solid compounds. The products may then be effectively removed from the gas stream by collection in the electrostatic precipitator. The collection of bisulfate and sulfate salts in this manner has been previously demonstrated.[3] However, if there is not a molar equivalence of sulfuric acid present, the excess ammonia will not react with sulfur dioxide (as an alternative to sulfuric acid) to produce a bisulfite or sulfite salt. In this event, some stack loss of ammonia to the environment may occur.

Triethylamine

This compound decomposes extensively if injected into the flue gas stream at 650 °C. Only traces of the reaction products thus produced were observed, however. The compounds observed were ammonia, hydrogen cyanide, nitrogen dioxide, and nitric oxide; no organic residue was identified.

It is thus practical to inject triethylamine only at a temperature of about 370 °C or less. Under these conditions, the compound remains largely intact molecularly, but it is capable of reacting with either sulfur dioxide or sulfuric acid to form the bisulfite, sulfite, bisulfate, or sulfate salt.

The most noteworthy product of decomposition of triethylamine is the carcinogen N-nitrosodiethylamine.[10] It appears that diethylamine—either a primary decomposition product of triethylamine or an impurity in the injected agent—is a precursor of the N-nitroso compound. The concentrations of the N-nitroso compound were low, only 70 to 200 ppb, compared with the injected concentration of triethylamine of about 25 ppm. Even so, the formation of the N-nitroso compound appears to represent the most significant environmental threat of any decomposition or reaction product identified during this investigation.

Sodium Carbonate

This agent was injected only into the 160 °C reaction zone, as in the current field investigation of this compound under Environmental Protection Agency Contract 68-02-2656. The molar

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10. Magee, P. N., and J. M. Barnes. Carcinogenic Nitroso Compounds. In: Advances in Cancer Research, Vol. 10, A. Haddow and S. Weinhouse, Eds. Academic Press, New York, New York. pp 163-246.

components of this compound—sodium oxide and carbon dioxide—exist in such a stable state that no thermal fragmentation of the compound occurred at 160 °C. However, reactions of sodium carbonate occurred with acidic flue gas—sulfur dioxide and sulfuric acid—leading to the formation of sodium sulfite and sodium sulfate and the evolution of carbon dioxide. The environmental impact of sodium carbonate and its reaction products should be minimized by the collection of the solid reaction products in the electrostatic precipitator.

Ammonium Sulfate

This compound was injected at 650 °C in either of two ways—as ordinary ammonium sulfate in aqueous soltuion or as the proprietary product of Apollo Chemical Corporation known as Coaltrol LPA-40 (also an aqueous solution). The high injection temperature was selected because of Apollo's practice of injecting LPA-40 ahead of the economizer in a full-scale plant. To the extent that comparisons were made between the two forms of the conditioning agent, the results seemed to be identical.

At 650 °C, ammonium sulfate decomposed primarily into its constituent compounds: ammonia, sulfur trioxide, and water. Upon cooling of the flue gas to 160 or 90 °C, recombination of the molecular fragments occurred. Ammonium bisulfate appeared to be the principal recombination product at 160 °C, and ammonium sulfate seemed to be predominant at 90 °C.

The implications of these results with respect to stack emissions are that some ammonia may be present in the stack emissions and ammonium salts may also be present if these solids are not effectively removed in the electrostatic precipitator.

Diammonium Hydrogen Phosphate

This compound was injected only as the commercial form sold by Apollo Chemical Corporation as Coaltrol LPA-445. It was injected at 650 °C, inasmuch as Apollo recommends high temperature injection to produce thermal decomposition of the compound.

Decomposition of the compound to ammonia and unidentified phosphoric acid species appeared to occur at 650 °C. Ammonia and the phosphoric acid species that were found analytically were not in the expected 2:1 mole ratio. In part, the discrepancy was due to the experimental failure to inject the compounds in the correct 2:1 stoichiometric ratio; the injection rate of ammonia was more than twice that of the phosphoric acid species on the mole basis. However, the ratios of ammonia and phosphoric acid concentrations found were even higher than the ratios injected. This observation is tentatively explained as the result of wall losses of orthophosphoric acid, condensed phosphoric acids, or perhaps even phosphorus pentoxide.

Recombination of the high temperature fragmentation products was observed at 160 to 90 °C. The most logical explanation for the mechanism of recombination was that ammonia and phosphoric acid recombined principally as ammonium dihydrogen phosphate (with the mole ratio of ammonia to phosphoric acid being 1:1 rather than 2:1 as at the beginning). A considerable excess of ammonia vapor remained in the gas stream after the solid phosphate was removed by filtration.

It thus appears that ammonia will be emitted from the stack of a power plant when diammonium hydrogen phosphate is used for conditioning. If not removed by electrostatic precipitation, ammonium dihydrogen phosphate particles will also be emitted.

RECOMMENDATIONS

Experimental studies of the type described in this report should be pursued as new agents are brought into use. Representatives of Apollo Chemical Corporation state that new proprietary agents are being developed by that company. Nalco Chemical Corporation reportedly is active in the development of new conditioning agents, and Betz Laboratories has disclosed its activity in this area over the past 2 yr. Particular attention should be paid to any formulation that contains an organic compound.

Further work should be done to confirm the most crucial finding of the present investigation: that N-nitrosodiethylamine is produced from triethylamine. Additional work should also be done to determine how the operation of an electrostatic precipitator or the presence of fly ash in the flue gas influences the formation and removal of the N-nitroso compound.

Efforts should be made to modify the present laboratory facility simulating the flue gas train of a power plant in such a way that fly ash can be introduced and kept in suspension. If these efforts are successful, then the system including fly ash should be used to generate particulate samples treated by a variety of conditioning agents. Such samples should be screened for biological activity by the Ames mutagenesis assay technique[11] and perhaps by other screening techniques for biological activity.

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11. Ames, B., J. McCann, and E. Yamasaki. Methods for Detecting Carcinogens and Mutagens with the Salmonella/Mammalian-Microsome Mutagenicity Test. Mutation Res., 31:347-364, 1975.

SECTION 3

ACQUISITION AND ANALYSIS OF CONDITIONING AGENTS FOR EXPERIMENTAL STUDY

The chemical conditioning agents acquired for study during this investigation can best be categorized as either proprietary or nonproprietary agents. Although both classes of conditioning agents are obtained commercially for use in coal-burning power plants, some of the additives used are standard industrial chemicals, whereas others are proprietary formulations that are both sold and injected by commercial vendors.

NONPROPRIETARY AGENTS

Five commercially available chemicals were acquired for study during this investigation based on either their current widespread use or their potential use as flue gas conditioning agents. All of the commercial chemicals studied in this investigation were reagent-grade chemicals. The chemicals used, their purities, and their commercial sources are as follows:

- Sulfur trioxide (SO_3)—Sulfuric acid, fuming (oleum), 18-24%, reagent ACS, Fischer Scientific Company, Fair Lawn, New Jersey.

- Ammonia (NH_3)—ammonium hydroxide, (NH_4OH) approximately 58%, Mallinkrodt analytical reagent, Mallinkrodt, Inc., St. Louis, Missouri.

- Ammonia (NH_3)—1.0% anhydrous ammonia (gas) in nitrogen, Linde Division, Union Carbide Corporation, Birmingham, Alabama.

- Triethylamine ($[C_2H_5]_3N$)—99% minimum purity (assayed by GLC), Eastman Organic Chemicals, Eastman Kodak Company, Rochester, New York.

- Sodium carbonate (Na_2CO_3)—Anhydrous powder, 'Baker Analyzed' Reagent, J. T. Baker Company, Phillipsburg, New Jersey.

- Ammonium sulfate ($[NH_4]_2SO_4$)—Granular, 'Baker Analyzed' Reagent, J. T. Baker Company, Phillipsburg, New Jersey.

PROPRIETARY AGENTS

All of the proprietary conditioning agents acquired for use in this investigation were obtained from the Apollo Chemical Corporation of Whippany, New Jersey. Samples representing two series of additives were obtained from Apollo, the LPA series and the LAC series. The LPA series of additives are for "high temperature" applications, where the conditioning agent is injected at gas stream temperatures up to 900 °C.[12-14] The LAC series of additives are for "low temperature" applications, where the conditioning agent is injected at some point between the air preheater and the electrostatic precipitator (personal communication with Dr. R. P. Bennett of Apollo Chemical Corporation). This corresponds to gas stream temperatures of approximately 160 °C.

The agents obtained from Apollo Chemical Corporation were Coaltrol LPA-40, Coaltrol LPA-410, Coaltrol LPA-445, Coaltrol LAC-50, and Coaltrol LAC-51B. The compositions of these formulations were not revealed to us by Apollo Chemical Corporation, but some indication of the compositions was available from a series of U. S. patents granted to Apollo in 1977 and 1978[12-15] and from the analyses of some of the formulations by independent laboratories. The compositions of these proprietary formulations supplied to us by Apollo were investigated in our laboratories by several analytical techniques. The description and results of these analyses are presented in the following sections.

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12. Bennett, R. P., and M. J. O'Connor. Method of Conditioning Flue Gas to Electrostatic Precipitator. U. S. Patent 4 043 768, August 23, 1977. Assigned to Apollo Chemical Corporation, Whippany, New Jersey.

13. Bennett, R. P., M. J. O'Connor, A. E. Kober, and I. Kukin. Method of Conditioning Flue Gas to Electrostatic Precipitator. U. S. Patent 4 042 348, August 16, 1977. Assigned to Apollo Chemical Corporation, Whippany, New Jersey.

14. Bennett, R. P., and A. E. Kober. Method of Conditioning Flue Gas. U. S. Patent 4 113 447, September 12, 1978. Assigned to Apollo Chemical Corporation, Whippany, New Jersey.

15. Kober, A. E., and I. Kukin. Method of Agglomerating Particles in Gas Stream. U. S. Patent 4 070 162, January 24, 1978. Assigned to Apollo Chemical Corporation, Whippany, New Jersey.

Coaltrol LPA-40

Coaltrol LPA-40 (Batch No. A217-44A) is a light brown solution with a density of 1.27 g/mL and a pH of 3.9. The qualitative identification of the primary components was performed by infrared spectroscopy and ion chromatography.[16] The solid material resulting from the evaporation of the water from the formulation possessed an infrared spectrum that was identical to that of ammonium sulfate, ($[NH_4]_2SO_4$). Analysis of the formulation by ion chromatography revealed that sulfate ion was the only anion of a strong acid that was present in significant amounts.

The LPA-40 formulation was quantitatively analyzed for ammonium ion by the phenol-hypochlorite colorimetric method[17] and by acid-base titration with sodium hydroxide solution, and the sulfate concentration was determined by titration with barium perchlorate solution using Thorin as an indicator.[18] The ammonium ion concentration was found to be 5.9 mmol/g and the sulfate concentration 3.0 mmol/g. Within the experimental error of these determinations, there were found twice as many millimoles of ammonium ion as sulfate ion, consistent with the identification of the solid residue from the evaporation of the formulation as ammonium sulfate. The LPA-40 formulation thus consists of about 40% w/w ammonium sulfate, with water accounting for the remaining 60%.

A reddish-brown solid gradually precipitated from the LPA-40 formulation on standing. The precipitate was filtered from a portion of the formulation and found to contain iron amounting to 30% w/w of the precipitate. The filtrate was found to contain 2.6 mg/mL iron in solution. The original formulation, after being shaken well to suspend the solid material, was found to contain 2.7 mg/mL iron. The concentration of iron in the original solution was, therefore, about 0.2% w/w. Little of the iron appeared to be lost from solution by precipitation. By spot tests with ferrocyanide and ferricyanide,[19] both ferrous and ferric ions were identified in the formulation. No attempt was made to determine their relative amounts.

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16. Small, H., T. S. Stevens, and W. C. Bauman. Novel Ion Exchange Chromatographic Method Using Conductimetric Detection. Anal. Chem., 47:1801-1809, 1975.

17. Harwood, J. E., and A. L. Kühn. A Colorimetric Method for Ammonia in Natural Waters. Water Res., 4:805-811, 1970.

18. Fritz, J. S., and S. S. Yamamura. Rapid Microtitration of Sulfate. Anal. Chem., 27:1461-1464, 1955.

19. Sorum, C. H. Introduction to Semimicro Qualitative Analysis. Prentice Hall, Inc., Englewood Cliffs, New Jersey, 1967. 277 pp.

Coaltrol LPA-410

Coaltrol LPA-410 (Batch No. A217-44B) is a clear, light blue-green solution with a density of 1.33 g/mL and an apparent pH of about zero. The identities of the primary components of the formulation were suggested from a prior chemical analysis performed by an independent laboratory for a confidential source. This analysis indicated that LPA-410 was a rather complex aqueous solution including sulfuric acid, sodium sulfate (or sodium bisulfate), and sodium benzenesulfonate. The formulation was qualitatively analyzed at Southern Research Institute by infrared spectroscopy and ion chromatography, and sulfate (or bisulfate) ion was identified as the only anion present in significant amounts in the solution.

The concentration of hydrogen ion in LPA-410 was found to be 3.16 mmol/g by acid-base titration. The total sulfate concentration was determined to be 3.05 mmol/g by titration with barium perchlorate using Thorin as an indicator.[18] The concentration of sodium ion was found to be 3.39 mmol/g by atomic emission spectroscopy. The weight percent of water in the formulation was determined physically from the loss in weight of a known volume of LPA-410 that was evaporated to dryness in an oven at 150 °C.

Within the experimental error, the molar ratio of sodium to hydrogen to sulfate was about 1:1:1. Thus, it appears that the major component of LPA-410 is sodium bisulfate, $NaHSO_4$. The formulation may be prepared by dissolving sodium bisulfate or an equimolar mixture of sulfuric acid and sodium sulfate. The approximate concentration of sodium bisulfate is 35 to 40% w/w. No evidence of sodium benzenesulfonate was found, contrary to earlier results found elsewhere.

The LPA-410 formulation was also analyzed by atomic absorption spectroscopy for iron and found to contain approximately 0.2% w/w iron. Ferrocyanide and ferricyanide spot tests[19] on the formulation indicated the presence of both ferrous and ferric ions in the solution. Unlike the iron content of the LPA-40 formulation, however, the iron species in LPA-410 were all in solution. Finally, the LPA-410 formulation was analyzed by atomic emission spectroscopy specifically for cobalt, chromium, potassium, sodium, nickel, tin, and zinc; measurable signals were obtained only for sodium and potassium.

Coaltrol LPA-445

Coaltrol LPA-445 is a clear, colorless liquid with a distinct ammoniacal odor. Its density is 1.14 g/mL, and its pH is approximately 8.2. Mass spectrometric analysis of the solid residue remaining after evaporation of the formulation to dryness indicated that the solid residue was an ammonium phosphate salt.

LPA-445 was identified as an aqueous solution of diammonium hydrogen phosphate ($[NH_4]_2HPO_4$) and the concentration of the solution determined by analyzing the formulation for ammonium ion by the phenol-hypochlorite colorimetric method[17] and for orthophosphate ion by ion chromatography[16] and by the vanadomolybdophosphoric acid colorimetric method.[20] The ammonium ion concentration in the solution was found to be 3.71 mmol/g and the phosphate ion concentration 1.87 mmol/g. Within the experimental error of these determinations, there are twice as many millimoles of ammonium ion as there are of phosphate ion. This corresponds to an empirical formula of $(NH_4)_2HPO_4$ for the LPA-445 solute. Analysis of the formulation by ion chromatography[16] also revealed the presence of trace amounts of sulfate ion (approximately 7.30 µmol/g or 0.08% w/w) as the only other anion of measurable concentration in LPA-445. The LPA-445 formulation thus consists of about 24% w/w diammonium hydrogen phosphate, with water accounting for the remaining 76% of the weight.

Two separate samples of LPA-445 were used during the investigation of this conditioning agent (Sample No. A217-9916 and Sample No. A217-9831). Each of the samples was analyzed individually, and the two samples were found to be identical within the experimental limits of error of the chemical methods used in the analyses.

Coaltrol LAC-50

Coaltrol LAC-50 (Sample No. A217-9915) is a clear, colorless, odorless aqueous liquid with a density of 1.09 g/mL and a pH of approximately 4.2. The solid residue resulting from the evaporation of the water from the formulation was analyzed qualitatively by infrared spectroscopy and mass spectrometry. Both the infrared and mass spectra of the solid residue were identical to the corresponding spectra of pure urea. Thus, Coaltrol LAC-50 was qualitatively identified as an aqueous solution of urea.

The LAC-50 formulation was quantitatively analyzed by the urea-specific p-dimethylaminobenzaldehyde colorimetric method.[21] The concentration of urea in the LAC-50 solution was found to be 5.43 mmol/g (326 mg/g). Within the experimental error, this concentration of urea was identical to the concentration of solute found in the solution after evaporation of the LAC-50 formulation to dryness (338 mg/g). These results indicate that LAC-50 consists of approximately 33% w/w of urea in water.

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20. Kitson, R. E., and M. G. Mellon. Colorimetric Determination of Phosphorus as Molybdivanodophosphoric Acid. Ind. Eng. Chem., 16:379-383, 1944.

21. Watt, G. W., and J. D. Chrisp. Spectrophotometric Method for Determination of Urea. Anal. Chem., 26:452-453, 1954.

Coaltrol LAC-51B

Coaltrol LAC-51B (Sample No. A217-9922) is a clear, colorless solution with a distinct ammoniacal odor. Its density is 1.14 g/mL, and its pH is approximately 8.3. Both the mass spectrum and infrared spectrum of the solid residue remaining after evaporation of the formulation to dryness were identical to the corresponding spectra of the evaporative residue of LPA-445. These results indicate that LAC-51B, like LPA-445, is an aqueous solution of diammonium hydrogen phosphate.

The LAC-51B formulation was quantitatively analyzed for ammonium ion by the phenol-hypochlorite colorimetric method[17] and for orthophosphate ion by ion chromatography[16] and by the vanadomolybdophosphoric acid colorimetric method.[20] The ammonium ion concentration in the solution was found to be 3.71 mmol/g and the phosphate ion concentration 1.89 mmol/g. Within the experimental error, there is thus a 2:1 mole ratio of ammonium ion to phosphate ion in the formulation, corresponding to an empirical formula of $(NH_4)_2HPO_4$ for the LAC-51B solution. No other anion of measurable concentration other than orthophosphate was found in the formulation by ion chromatography. Thus, with the exception of the absence of trace amounts of sulfate ion, the LAC-51B formulation is identical to LPA-445, consisting of a 24% w/w solution of diammonium hydrogen phosphate in water.

SECTION 4

DESIGN AND FABRICATION OF A LABORATORY-SCALE FLUE GAS TRAIN

GENERAL CONSIDERATIONS

For the investigation of reactions of flue gas conditioning agents, a laboratory bench-scale facility was constructed to simulate the pertinent components of the flue gas train in a full-scale coal-burning power plant. Hardware components of the laboratory facility represented components of a full-scale flue gas train extending from a point upstream from the economizer to the outlet of the stack, ranging from a maximum temperature of 650 °C to a minimum of 90 °C. The gas mixture flowing through the train simulated the composition of flue gas produced from the combustion of coal. The sizes of the hardware components of the laboratory train and the flow rate of simulated flue gas were selected to give residence times of the gas at various locations in the train that approximated those in a full-scale power plant. Originally, the plans were to suspend fly ash in the gas stream to simulate the particulate produced from the combustion of coal. However, the anticipation of technical difficulties associated with maintaining fly ash in suspension and interpreting the results of reaction studies in a heterogeneous system led to abandonment of efforts to include fly ash in the system.

Flue gas conditioning agents may be injected into the gas stream in a full-scale plant at various points upstream from the electrostatic precipitator. At the time the design of the laboratory train was being developed, it was assumed that 650 °C—representative of a point upstream from the economizer—would be the highest temperature required for injection. Later, several patents appeared,[12-14] indicating that temperatures up to 900 °C may sometimes be used in full-scale practice. The information contained in these patents, however, became available after the laboratory facility with a maximum temperature of 650 °C had been fabricated and placed in use.

Flue gas undergoes varying degrees of cooling in traversing the components of a flue gas train leading ultimately to the outlet of the stack. These components include mainly the economizer and the air preheater. Some degree of cooling may occur also in

the stack; for the purpose of this investigation, a final temperature of 90 °C at the outlet of the stack was assumed to be applicable.

Figure 1 shows the principal components of the laboratory train in a schematic diagram. These components are itemized and described briefly as follows:

- An electric heater for raising the temperature of the synthetic flue gas to 650 °C.
- A heated quartz cylinder maintaining a portion of the gas stream at 650 °C, a representative gas temperature in the duct upstream from the economizer.
- A Pyrex heat exchanger representing the economizer.
- A heated Pyrex cylinder maintaining a portion of the gas stream at about 370 °C, a representative gas temperature in the duct between the economizer and the air preheater.
- A Pyrex heat exchanger representing the air preheater.
- A heated Pyrex cylinder maintaining a portion of the gas stream at about 160 °C, representing the temperature in the duct between the air preheater and the electrostatic precipitator.
- A small wire-and-pipe electrostatic precipitator (ESP) maintained at a temperature of about 160 °C.
- A Pyrex heat exchanger simulating cooling near the stack exit.
- A heated Pyrex cylinder maintaining a portion of the gas stream at about 90 °C, a representative temperature of the gas stream near the top of the stack.

The dimensions of the cylinders were chosen to provide gas residence times of 2 s within each cylinder except the heat exchangers and the ESP. The gas residence time within each of the heat exchangers was a fraction of a second. The gas residence time within the ESP was about 7 s. The gas residence times are based on the flow rate of the simulated flue gas that was normally used, about 35 L/min as calculated for 25 °C.

The major components of the synthetic flue gas were nitrogen, oxygen, carbon dioxide, and water vapor. Approximate concentrations of these components were as follows:

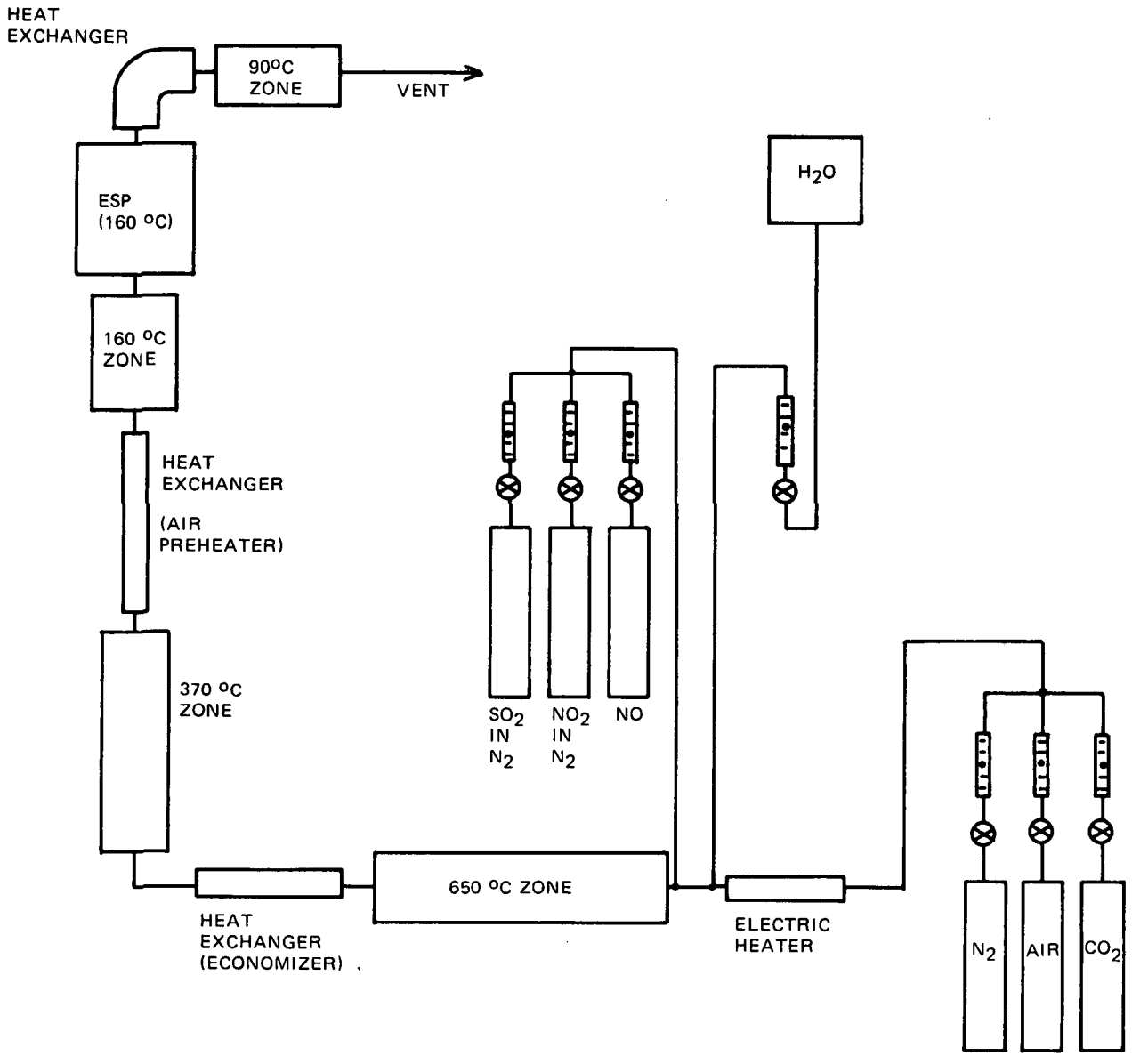

Figure 1. Schematic diagram of flue gas train.

Component	Concn, % v/v
Nitrogen	76
Carbon dioxide	12
Water vapor	8
Oxygen	4

In addition, low concentrations of sulfur dioxide, nitric oxide, and nitrogen dioxide were added individually or in combinations. The approximate concentration of sulfur dioxide was 600 ppm v/v,* as produced from a low sulfur coal. The typical concentrations of the nitrogen oxides were 1000 ppm for nitric oxide and 100 ppm for nitrogen dioxide. In some experiments, up to 30 ppm of sulfur trioxide (sulfuric acid vapor) was included in the flue gas composition. The purpose of these experiments was either to study the behavior of sulfur trioxide as a conditioning agent or to study the reactions of sulfur trioxide with other conditioning agents. At a concentration of 30 ppm, however, sulfur trioxide was well above the level to be expected in flue gas from a low sulfur coal.

DESIGN OF THE FLUE GAS TRAIN

Heater for the Flue Gas Mixture

The synthesized gas mixture was electrically heated to 650 °C before it entered the 650 °C constant temperature zone by means of a small, efficient GTE-Sylvania electrical heater (Sylvania Emissive Products, Exeter, New Hampshire). The GTE-Sylvania fluid heater consisted of an approximately 20-cm length of a patented ferrous alloy heating element in a serpentine configuration installed in a stainless steel pipe. The heating element came in direct contact with the gas mixture and heated it quickly and efficiently to 650 °C. The fluid heater was powered by a West 20-A silicon controlled rectifier power supply and controlled with a West analog set point, solid-state temperature controller (West Instruments Division of Gulton Industries, Inc., East Greenwich, Rhode Island). A stainless steel ball-joint socket was connected to the outlet end of the heater by means of a pipe fitting to enable the heater to be connected to the 650 °C constant temperature zone.

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* All flue gas concentrations given subsequently in this report in parts per million or in parts per billion are on the volume basis (v/v), unless otherwise specified.

Constant Temperature Zones*

The four constant temperature zones designed for the apparatus were intended to maintain temperatures of about 650, 370, 160, and 90 °C. These constant temperature zones corresponded to the duct upstream from the economizer, the duct between the economizer and the air preheater, the duct leading to the electrostatic precipitator plus the precipitator itself, and a portion of the stack near the outlet, respectively.

With the exception of the 650 °C zone and the electrostatic precipitator, the containment vessels of the flue gas at the different temperatures were constructed of interconnected Pyrex glass cylinders. The containment vessel for the gas at 650 °C was initially constructed of borosilicate glass as well, but it was found to devitrify and break into pieces at the intermittent temperatures needed to maintain the gas stream at 650 °C. Thus, reconstruction of this vessel from quartz proved to be necessary. The electrostatic precipitator was constructed of stainless steel, as described later in this report.

The significant dimensions of the constant temperature zones are listed in Table 1. This table includes the inside diameters of the quartz and glass cylinders used as containment vessels for the constant temperature zones, the distance between the injection and sampling ports of each zone, the calculated residence time of the gas stream at the indicated temperatures at a total gas flow of 35 L/min (expressed for 25 °C) in each zone, and the inside diameter of the sampling tube in each reaction zone. Thermocouple wells were made of either quartz (in the 650 °C zone) or Pyrex; the thermocouple wells extended into the center of each reaction zone and were connected to the reaction zones near each injection or sampling port to measure the temperature in the center of the gas stream near the ports. Each injection port was a side arm ending in a ground-glass spherical ball-joint socket (S 35/20). Each sampling port was a quartz or glass tube with a stopcock valve (except for the 650 °C zone) that extended to the center of the gas stream and then turned 90° to face the flow of gas. The diameter of each sampling tube was chosen to provide isokinetic sampling of the gas stream at a flow rate equivalent to 1 L/min at 25 °C.

To compensate for the loss of heat as the gas moved through the train, the 650 °C quartz constant temperature zone was wrapped with two 3.66-m long beaded heaters (Nichrome resistance wire insulated with ball-and-socket ceramic beads), and the Pyrex cylinders were wrapped with electrical heating tapes. The quartz

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* In later sections of this report, the constant temperature zones are frequently referred to as "reaction zones."

TABLE 1. DIMENSIONS OF CONSTANT TEMPERATURE ZONES

Temperature of zone, °C	Inside diameter, cm	Length,* cm	Approximate residence time,† s	Inside diameter of sampling tube, cm
650	7.0	91.4	2	1.3
370	7.5	61.0	2	1.4
160	8.5	30.5	2	1.6
160 (ESP)‡	15.2	33.0	7	2.4
90	7.6	30.5	2	1.4

* This is the length between the injection port and the sampling port.

† The calculated residence time is based on a total gas flow of 35 L/min expressed for 25 °C.

‡ The electrostatic precipitator was maintained at a constant temperature around 160 °C.

and Pyrex cylinders were then insulated with several layers of Fiberfrax sheet, a fibrous ceramic material. Despite the insulation, however, the maximum power output of the beaded heaters and the heating tapes were chosen to be high enough to compensate for the heat loss estimated if the quartz and Pyrex cylinders were not insulated.

A detailed drawing of the quartz cylinder used to maintain a gas temperature of 650 °C is given in Figure 2. This illustration is also applicable to the cylinders used to maintain lower temperatures except for the difference in dimensions given in Table 1 and for the insertion of a stopcock valve in the sampling ports of the Pyrex cylinders.

Electrostatic Precipitator

A small, single-stage wire-and-pipe electrostatic precipitator was designed for insertion into the flue gas train just downstream from the Pyrex cylinder used for the 160 °C constant temperature zone. The flue gas in the precipitator was also maintained near 160 °C, a temperature typical of the flue gas temperature in a "cold-side" electrostatic precipitator.

The electrostatic precipitator was housed in a Pyrex cylinder wrapped with heating tapes and insulation. The precipitator consisted of a 0.02-cm negative corona discharge wire mounted along the axis of a stainless steel cylinder that served as the

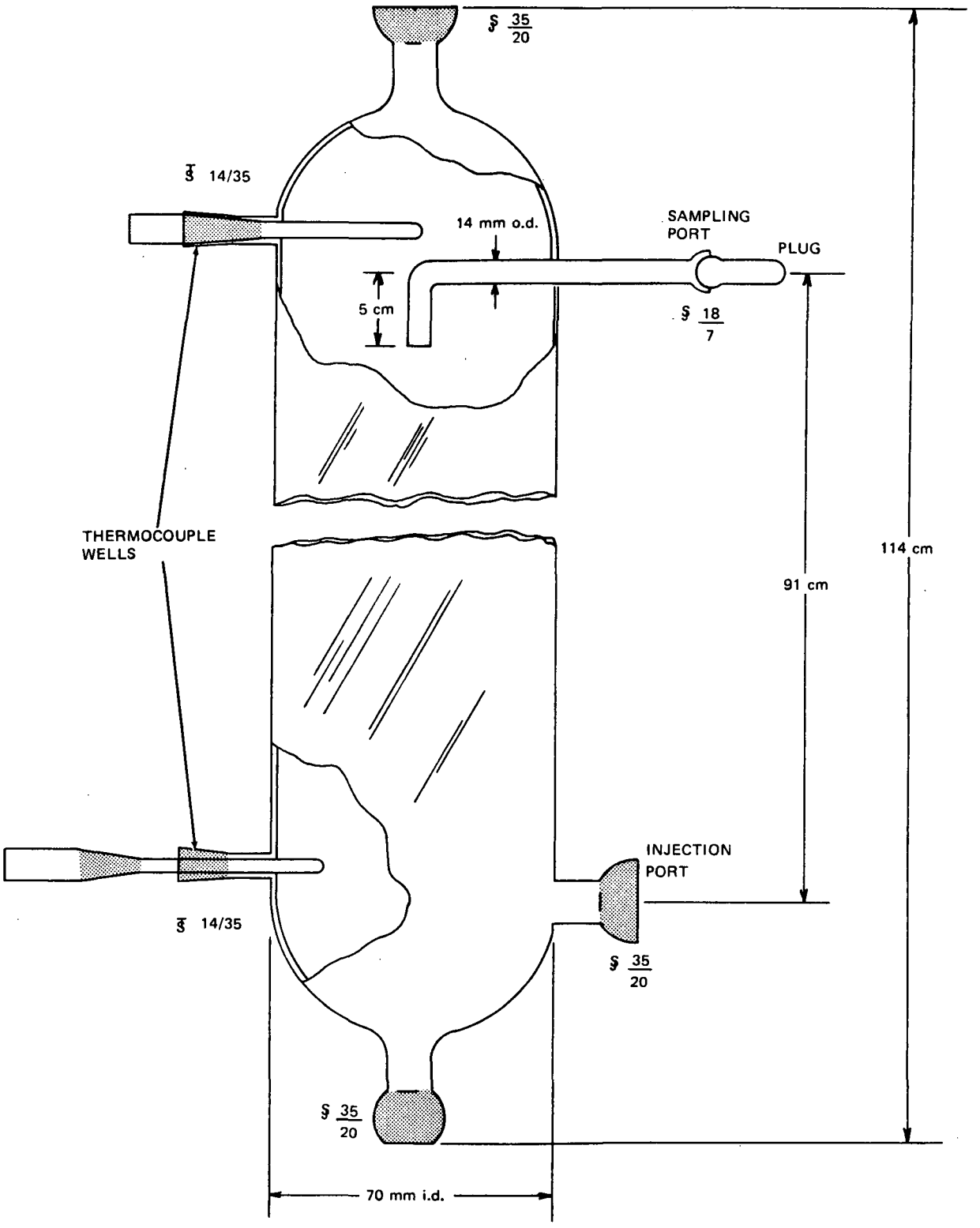

Figure 2. Detailed illustration of the quartz 650 °C constant temperature zone.

positive collection electrode. The cylinder had an inside diameter of 13.6 cm and was 33.0 cm long. The area of the inside surface of the stainless steel cylinder was thus 1410 cm^2.

The dimensions of the precipitator were chosen to provide a residence time of the flue gas inside the precipitator of 6 to 7 s at a volume flow rate of 51 L/min at 160 °C (equivalent to 35 L/min at 25 °C) and, at the same time, to provide a high collection efficiency at a reasonable operating power. From the Deutsch equation,[22] the efficiency of collection and the "slip" were computed for a range of migration velocities of 1 to 7 cm/s. The power densities required to produce this range of velocities were then estimated from an empirically derived linear relationship between these two variables for the collection of fly ash.[22] From the surface area of the collection electrode of the wire-and-pipe precipitator, the corona power was then estimated. These quantities are presented in Table 2. The values predict that a collection efficiency of about 99% would require a corona power of 270 mW.

TABLE 2. COLLECTION EFFICIENCY AND CORONA POWER FOR VARIOUS MIGRATION VELOCITIES

Migration velocity, cm/s	Collection efficiency, %*	"Slip", %†	Power density, mW/cm^2	Corona power, mW
1	81	19	0.06	90
2	96.4	3.6	0.13	180
3	99.32	0.68	0.19	270
4	99.87	0.13	0.25	360
5	99.975	0.025	0.31	440
6	99.9954	0.0046	0.38	530
7	99.99912	0.00088	0.44	620

* The collection efficiency, C. E., is given according to the Deutsch equation as follows:

$$C.E. = 100\ (1 - \exp(-WA/V))$$

where W = effective migration velocity
A = collection electrode surface area
V = volume flow rate

† "Slip" = 100 - C.E.

22. Oglesby, S., and G. B. Nichols. A Manual of Electrostatic Precipitator Technology, Part 1—Fundamentals. PB-196 380, National Air Pollution Control Administration, Cincinnati, Ohio, 1970. 322 pp.

The corona power requirement was also estimated by another approach. For a coal-burning power plant precipitator, the ratio of power to gas flow rate corresponding to a collection efficiency of 99% was estimated to be about 0.30 mW/(cm^3/s).[22] The power required for a total flow rate of 51 L/min was therefore estimated to be about 250 mW, a value in good agreement with the first estimate. It thus appears that the laboratory-scale precipitator would be capable of efficient collection of fly ash when operating at relatively low power—for example, at an applied voltage of 10 kV and a total current of 25 μA or a current density of 18 nA/cm^2.

The calculated value of the specific collecting area—SCA (the ratio of collection area to volume flow rate)—was 166 m^2/(m^3/s) or 842 ft^2/(1000 ft^3/min) at the usual value of the flow rate. The SCA value would be characteristic of a full-size unit operating with very high efficiency of dust collection.

Heat Exchangers

Heat exchangers were required to make three reductions in flue gas temperature: from 650 to 370 °C, from 370 to 160 °C, and from 160 to 90 °C. These devices corresponded to the economizer, the air preheater, and the stack, respectively.

A simple but effective heat exchanger was designed to cool the temperature of the flue gas stream rapidly from 650 to 370 °C. This simulated economizer consisted simply of two 30 cm lengths of borosilicate glass tubing of 2 cm i.d. that were connected to each other and to the containment vessels of the 650 and 370 °C constant temperature zones by means of ball-and-socket joints. The tube connected to the 650 °C zone was loosely wrapped with a thin layer of insulation, while the tube connected to the 370 °C zone was wrapped with heating tape and thinly insulated. Heat from the 650 °C gas stream was lost to the ambient air surrounding the tubes by free convection, and excessive heat loss was compensated for by electrical heating (with the heating tape).

The design of a heat exchanger to cool the flue gas stream from 370 to 160 °C rapidly and efficiently (and thus simulate the action of the air preheater in a coal-burning power plant) was based on the design of a similar heat exchanger used in a previous project for an industrial sponsor. The heat exchanger consisted of a modified, commercially available Allihn condenser that was 500 mm long with an outside diameter of 40 mm. The water jacket of this condenser was filled with glycerol, and the entire condenser was tightly wrapped with a coil of 0.32-cm o.d. copper tubing. An unmetered flow of cold tap water through the coiled copper tubing counter-current to the direction of flow of the gas stream was used to dissipate heat from the glycerol. The glycerol was heated by the gas stream and served as a uniform heat transfer

medium, minimizing the possibility of overcooling the gas stream or the formation of "cold spots" on the inside walls of the heat exchanger.

The heat exchanger designed for lowering the temperature of the gas stream from 160 to 90 °C was a 30 cm length of uninsulated process pipe (thick-walled glass tubing) of 7.6 cm i.d. A 90° short-radius elbow process pipe connected the vertically aligned electrostatic precipitator to the horizontally aligned 90 °C constant temperature zone. The pipe was wrapped with a small heating tape so that excessive gas cooling could be compensated for by electrical heating.

Gas Mixing and Delivery System

Nitrogen and carbon dioxide from regulated, compressed gas cylinders and regulated, charcoal-filtered compressed house air were combined in a stainless steel Swagelok union-cross compression tube fitting (Crawford Fitting Company, Cleveland, Ohio). The union-cross fitting was connected to the inlet of the gas heater through a short length of 0.16-cm i.d. stainless steel tubing by means of a compression fitting. The gases were individually metered through Matheson flowmeters (Matheson Gas Products, Morrow, Georgia). The inlet pressure of the flue gas train was measured just downstream from the point of mixing of the nitrogen, air, and carbon dioxide cylinder gases with a Magnehelic differential pressure gauge (Dwyer Instruments, Inc., Michigan City, Indiana). The combination of nitrogen, carbon dioxide, and air was then passed through the heater previously described and raised to a temperature of about 650 °C.

Distilled, deionized water was fed by gravity through a Gilmont flowmeter (Roger Gilmont Instruments, Inc., Great Neck, New York) and through a stainless steel "tee" joint, at which point the liquid water entered the hot mixture of gases emerging from the heater. Water vapor was thus added to the flue gas stream by flash evaporation of liquid water.

Sulfur dioxide, nitrogen dioxide, and nitric oxide cylinder gases were added to the gas mixture, when needed, through a union-cross tube fitting and a "tee" joint into the hot, humidified gas mixture just downstream from the point of injection of water. The sulfur dioxide flow rate was measured with a Matheson flowmeter, and the nitrogen dioxide and nitric oxide flow rates were measured with Gilmont flowmeters. Teflon tubing was used to transfer the sulfur dioxide and water. Nylon and stainless steel tubing were used for the other gases.

In instances when sulfur trioxide was added to the gas stream, the addition was made into the 370 °C constant temperature zone. The procedure used for this addition is described later in this report.

A schematic presentation of the gas mixing and delivery system is included in Figure 1, which appeared earlier in this report. A tabulation of representative flow rates of the individual gases and of liquid water is presented in Table 3.

TABLE 3. REPRESENTATIVE FLOW RATES OF THE INDIVIDUAL GASES IN THE SIMULATED FLUE GAS TRAIN

Metered component	Corrected flow rate,* L/min	Component in gas mixture	Flow rate,† L/min	Concn
N_2(g)	18.76	N_2	25.65	75.6%
Air(g)	6.64	O_2	1.39	4.1%
CO_2(g)	4.01	CO_2	4.05	11.9%
SO_2-N_2(g)	1.35	SO_2	0.02	595 ppm
NO(g)	0.04	NO	0.04	1107 ppm
NO_2-N_2(g)	0.34	NO_2	0.003	100 ppm
H_2O(l)	2.05×10^{-3}	H_2O	2.79	8.2%

* Measured flow rate corrected for gas density and pressure and expressed as liters per minute at 25 °C and 760 mmHg pressure.

† Flow rate expressed in units of liters per minute at 25 °C and 760 mmHg pressure.

Electrical Control and Measurement Devices

Temperature Control and Measurement--

Chromel-alumel thermocouples were inserted into the quartz or Pyrex wells located near the inlet and outlet of each constant temperature zone to monitor the temperature of the gas stream at these points. Each set of thermocouple wires was connected to one of the binding posts of a mechanical selector switch, which in turn was connected to the input jack of one channel of a Hewlett-Packard Model 7128-A Dual Channel Recorder (Hewlett-Packard Company, San Diego, California). A thermocouple inserted into a stainless steel thermocouple well mounted at the outlet of the gas heater was connected to the other channel of the Hewlett-Packard recorder to monitor the temperature of the heated gas mixture. The thermoelectric output of each thermocouple was read directly from the recorder.

The temperature at the inlet of the 650 °C constant temperature zone was manually controlled by regulating the voltage applied to the appropriate beaded heater with a variable autotransformer. The voltage applied to the beaded heater that

controlled the temperature near the outlet of the 650 °C zone was manually controlled with a solid-state voltage controller (Cole-Parmer Instrument Company, Chicago, Illinois).

The voltages applied to the heating tapes around the heat exchangers simulating the economizer and the gas stack were also manually controlled with solid-state voltage controllers. The temperatures at the inlet and outlet of the 370 °C zone, the inlet of the 160 °C zone, the inlet and outlet of the electrostatic precipitator, and the outlet of the 90 °C zone were controlled by means of temperature controllers with thermistor sensors (Thermalogic Division of Dytron, Inc., Waltham, Massachusetts), which automatically adjusted the voltage from a solid-state voltage controller applied to the appropriate heating tape to maintain the required temperature.

Electrostatic Precipitator Electronics--

The electronic equipment used in conjunction with the electrostatic precipitator consisted mainly of a commercially available power supply unit and electrical measurement devices. A Peschel Model H20-Y Standard Hipot Tester (Peschel Instruments, Inc., Cape Coral, Florida) was used to supply the negative potential to the corona discharge wire, and a Hipotronics Model 100 High Voltage Meter (Hipotronics, Inc., Brewster, New York) was used to monitor the applied voltage. The plate current was measured with a Keithley 610C Electrometer (Keithley Instruments, Inc., Cleveland, Ohio). The electrometer was protected from current surges by means of a simple "homemade" spark protector inserted in the measuring circuit between the collecting electode and the electrometer.

FABRICATION OF THE FLUE GAS TRAIN

Quartz and Glass Components

The quartz and glass components of the flue gas train, including the cylinders for the constant temperature zones, the heat exchangers, and the ESP housing, were fabricated by Mr. M. B. Watson of the University of Alabama in Tuscaloosa, Alabama. They were then wrapped with the required heating tapes and insulation and assembled by Institute personnel.

Physical Configuration

The physical configuration of the flue gas train was dictated by the dimensions of the major components of the gas train (particularly the dimensions of the constant temperature zones) and the size of the laboratory in which the apparatus was installed. The ideal configuration would have been a linear, vertical alignment of all of the constant temperature zones. The

ceiling of the laboratory was not high enough, however, to accommodate this configuration. The major components of the flue gas train were thus aligned as follows:

- The gas heater, the 650 °C constant temperature zone, and the heat exchanger simulating the economizer were all aligned horizontally just above the floor of the laboratory.

- The 370 °C constant temperature zone, the 160 °C constant temperature zone, the heat exchanger simulating the air preheater, and the electrostatic precipitator were all aligned vertically from near the floor of the laboratory to near the ceiling.

- The 90 °C constant temperature zone was aligned horizontally near the ceiling of the laboratory.

- The heat exchanger between the electrostatic precipitator and the 90 °C zone was bent at a 90° angle to join the vertical portion of the gas train to the upper horizontal portion.

- A short 2-cm i.d. borosilicate glass tube with ball-and-socket joints at each end formed a 90° elbow to connect the simulated economizer to the bottom of the 370 °C zone, thus joining the lower horizontal portion of the flue gas train to the vertical portion.

Support Frame

A steel frame for mounting the components of the flue gas train was fabricated by Gregory-Salisbury Metal Products, Inc., of Birmingham, Alabama, and shipped to the laboratory in three parts: a section (3.0 m x 0.5 m x 0.5 m) to be mounted horizontally on the floor, a section (2.4 m x 0.5 m x 0.5 m) to be mounted horizontally on the ceiling, and a section (3.0 m x 0.5 m x 0.5 m) to be mounted vertically between the floor and the ceiling. The sections of the frame were bolted to the laboratory floor and ceiling. Shelves were attached to the frame to accommodate sampling from the flue gas train. A plywood panel (1.2 m x 1.8 m) was also attached to provide a support for the temperature controllers, voltage regulators, flowmeters, valves, and recorder.

A phtograph of the completely assembled apparatus is reproduced in Figure 3.

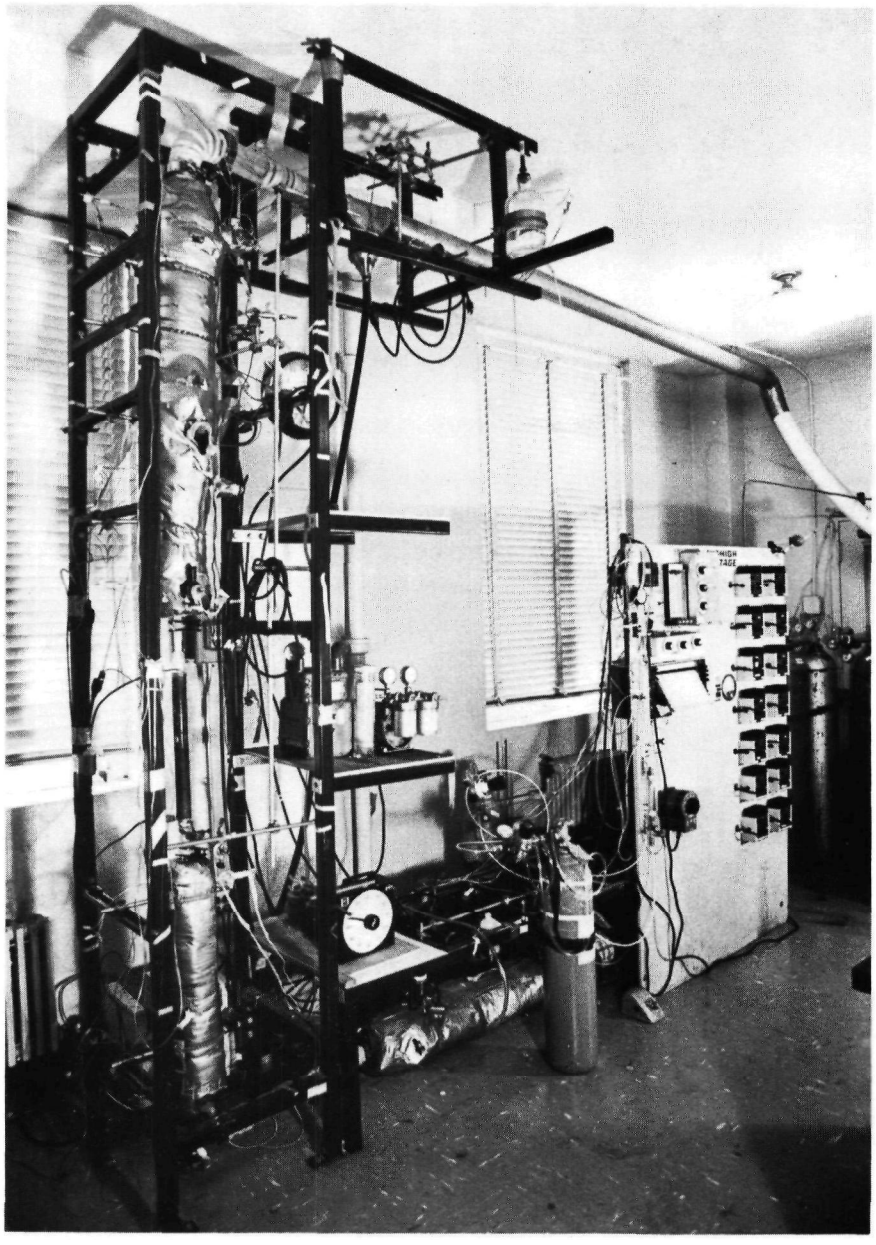

Figure 3. Photograph of assembled laboratory-scale flue gas train.

SECTION 5

INVESTIGATION OF INDIVIDUAL CONDITIONING AGENTS IN THE FLUE GAS TRAIN

SULFUR TRIOXIDE

Sulfur trioxide was selected as the first agent to be investigated. The main objective in the study of this agent was to determine how efficiently the agent could be recovered from the flue gas train at different sampling temperatures.

Sulfur trioxide was injected into the flue gas train at the inlet of the 370 °C zone and sampled at the outlet of this zone and other zones of lower temperatures. No reaction of sulfur trioxide other than that with water vapor to produce sulfuric acid was expected.

$$SO_3(g) + H_2O(g) \rightarrow H_2SO_4(g) \qquad (1)$$

Sulfur trioxide and sulfuric acid were indistinguishable by the analytical methods used; thus, no detectable change in the chemical state of the injected conditioning agent was anticipated. However, sulfur trioxide or sulfuric acid was expected to undergo wall losses as the result of adsorption or condensation. Knowledge of the extent of wall losses was expected to be of value in interpreting the results of experiments with other conditioning agents, such as ammonium sulfate, that thermally decompose to produce sulfur trioxide at high temperatures.

Injection Procedure

To add sulfur trioxide to the flue gas train, dry nitrogen was flushed at a controlled rate over the surface of oleum (a solution of sulfur trioxide in sulfuric acid) in a round bottom flask. The temperature of the oleum was maintained at 33 °C by placing the flask in a Styrofoam box containing a 60-W light bulb as a heater; the light bulb was activated as necessary by means of a temperature-sensitive switch. The sulfur trioxide vapor entrained in the nitrogen was passed through a Teflon tube to a glass probe extending into the center of the 370 °C zone of the

flue gas train near the inlet of this zone. A side arm from the connecting tubing permitted sampling to determine the output concentration of sulfur trioxide from the oleum source.

The concentration of sulfur trioxide in the oleum was 20% w/w. The vapor pressure of the sulfur trioxide over the source was calculated to be 0.9 mmHg, which corresponds to a concentration of about 1200 ppm.[23] Observed concentrations in the effluent stream, however, were below this equilibrium value.

Determinations of the concentration of sulfur trioxide evolved from the vapor generator were made by passing the effluent stream through a bubbler containing 80% w/w isopropanol in water and then through a glass fiber filter, which retained sulfuric acid mist formed in the bubbler. The bubbler solution and a filter wash were titrated with 0.1 N sodium hydroxide with bromphenol blue as the indicator. Observed sulfur trioxide concentrations in the injection line with different rates of nitrogen flow over the oleum were as follows: about 600 ppm at a flow rate of 0.6 L/min or about 500 ppm at a flow rate of 1.0 L/min. Reasonably constant sulfur trioxide concentrations were observed for about 20 h of operating time; after then, the output began to decrease, and the generator was recharged.

Analytical Procedures

The flue gas stream was analyzed for sulfur oxides by two procedures. The first procedure gave the total concentration of sulfur oxides, whereas the second procedure gave the concentrations of sulfur trioxide and sulfur dioxide individually.

The first procedure involved sampling the flue gas at the rate of 1 L/min through a bubbler containing 3% w/w hydrogen peroxide in water. The glass sampling line was maintained above 150 °C to avoid loss of sulfur trioxide as condensed sulfuric acid. The acid collected in the peroxide solution was titrated with 0.1 N sodium hydroxide, and the concentration of sulfur oxides in the gas stream was calculated from the observed amount of acid titrated and the volume of flue gas sampled.

The second procedure was based on collecting sulfur trioxide from a sample stream in a condenser maintained at a temperature between 60 and 90 °C and then passing the sample stream through a bubbler containing 3% w/w hydrogen peroxide in water to collect the sulfur dioxide as sulfuric acid. The controlled-

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23. Washburn, E. W., Ed. International Critical Tables of Numerical Data, Physics, Chemistry, and Technology. McGraw-Hill Book Company, Inc., New York, New York, 1928. Volume III, p. 304.

temperature condensation of sulfur trioxide as sulfuric acid was based on the collection principle usually ascribed to Goksøyr and Ross;[24] however, in our work the condenser was based on a design developed by Maddalone.[25] Sulfuric acid from the condenser was titrated with dilute barium perchlorate using Thorin as an indicator.[18] Sulfuric acid in the peroxide bubbler was titrated with 0.1 N sodium hydroxide with bromphenol blue as the indicator.

In some of the sampling experiments, particularly at the lower flue gas temperatures, a particulate filter was incorporated in the sampling train ahead of the condenser. The purpose was to remove any sulfuric acid present in the gas stream as the condensed acid. A Teflon filter with a 2- to 5-μm pore size was employed for this purpose in a heated Pyrex filter holder. Similar fibrous fluorocarbon filters have reported collection efficiencies of about 90% for particles as small as 0.03 μm,[26] and the Teflon filter was thus expected to be adequate for the removal of sulfuric acid mist. Sulfuric acid was removed from the particulate filter by drawing 80% w/w isopropanol through the filter under vacuum; the acid was then titrated by the barium perchlorate-Thorin method.

Experimental Results

Baseline Studies without Sulfur Trioxide Injection--

The first determinations of sulfur oxides in the flue gas were made without the injection of sulfur trioxide. The purpose of these experiments was to determine how closely the sulfur dioxide concentration agreed with the level anticipated from the makeup procedure for the flue gas and to determine how much oxidation of sulfur dioxide to sulfur trioxide occurred in the flue gas train. In all of the experiments, the anticipated concentration of sulfur dioxide was 590 ppm, assuming a negligible degree of oxidation to the trioxide.

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24. Goksøyr, H., and K. Ross. The Determination of Sulfur Trioxide in Flue Gases. J. Inst. Fuel, 35:177-179, 1962.

25. Maddalone, R. L. Guidelines for Combustion Source Sulfuric Acid Emission Measurements. TRW Document No. 28055-6005-RU-00 (prepared under U. S. Environmental Protection Agency Contract No. 68-02-2165). TRW Defense and Space Systems Group, Redondo Beach, California, 1977. 14 pp.

26. Liu, B. Y. H., and K. W. Lee. Efficiency of Membrane and Nuclepore Filters for Submicrometer Aerosols. Environ. Sci. Technol., 10:345-350, 1976.

In the initial series of experiments, the total concentration of sulfur oxides was determined. The average result obtained by sampling at various points in the flue gas train was 630 ppm with a relative standard deviation of 2%. This average result was about 7% higher than the anticipated value.

In the second series of experiments, sulfur dioxide and sulfur trioxide were collected independently. The results of these experiments are listed in Table 4. The results for sulfur dioxide were again higher than the expected value. The results for sulfur trioxide ranged from values below the detection limit (i.e., <0.1 ppm) to a value as high as 2.0 ppm. It seems reasonable to conclude, however, that the representative background level of sulfur trioxide was less than 1 ppm.

TABLE 4. DETERMINATION OF SULFUR OXIDES WITHOUT INJECTED SULFUR TRIOXIDE

Sampling temp, °C	SO_2,* ppm	SO_3,† ppm
370	654	1.6
160	615	0.1
	642	0.3
	672	<0.1
	637	0.2
160 (ESP)	664	<0.1
	654‡	2.0‡
	609	0.1
	598‡	<0.1‡
90	626	0.7
	616	0.1

* The average result was 635 ppm; the expected value was 590 ppm.

† Determined without a particulate filter.

‡ These results were obtained with the ESP energized: applied voltage (V), 7.5 kV; current density (j), ca. 30 nA/cm^2.

Baseline Studies with Sulfur Trioxide Injection--

A substantial amount of experimentation was required before the observed concentrations of sulfur trioxide in the flue gas train approximated the levels predicted from the injection rate. One result of this experimentation was the finding that silicone

or Apiezon grease could not be used as a lubricant for the stopcocks in the sampling ports; instead of these lubricants, a light coating of colloidal Teflon was found to be suitable. Another result was the finding that additional insulation and heating tapes around the sampling ports were required. Still another result was the finding that a period of conditioning of the system—up to 1 h—was required before the expected sulfur trioxide concentrations could be obtained.

After the need for certain precautions as described above was recognized, reasonably satisfactory results for the concentration of sulfur trioxide were obtained. The results of two series of experiments are presented in Tables 5 and 6. Table 5 gives the results at two sampling locations as determined without a filter for the removal of sulfuric acid particulate. Table 6 gives the results at five sampling locations, sometimes as determined with the particulate filter. The average of the absolute differences between observed and expected sulfur trioxide concentrations in these two tables is 2 ppm.

TABLE 5. DETERMINATION OF SULFUR OXIDES WITH INJECTED SULFUR TRIOXIDE

Sampling temp, °C	Observed SO_2,* ppm	Observed SO_3,† ppm	Expected SO_3, ppm
370	668	4	9
	680	6	11
	686	7	11
	726	16	12
	753	8	5
	765	7	5
160 (ESP)	614	5	6
	619	10	12
	623	7	7
	637	5	5
	673	5	6
	673	6	7
	702	9	12
	717	9	10

* The average value was 681 ppm; the expected value was about 600 ppm.

† Determined without a particulate filter.

TABLE 6. DETERMINATION OF INJECTED SULFUR TRIOXIDE

Sampling temp, °C	Observed SO_3, ppm	Expected SO_3, ppm
370	9	8
	9	8
160	5	6
	6	5
	6	6
	7	6
	10	9
	11	10
	11	10
	11	9
	11	9
	12	13
	8*	13
	10*	16
	11*	9
	15*	18
	17*	16
160 (ESP)	11†	16
	11†	10
	12†	13
	14†	17
	15	16
	16	16
90	8	14
	8	14
	8	10
	8*	14

* In five experiments with sampling at 160 °C, about 2 ppm of the total sulfur trioxide concentration was found on the particulate filter. In one experiment with sampling at 90 °C, virtually all of the sulfur trioxide was found in the particulate filter.

† These results were obtained with the ESP energized: applied voltage (V), 7.5 kV; current density (j), 28 nA/cm^2.

Special attention is directed to the results in Table 6 that were obtained with a particulate filter in the sampling line or with the ESP energized. A relatively small fraction of the sulfur trioxide was found on the filter at a sampling temperature of 160 °C, but virtually all of the substance was found on the filter at a sampling temperature of 90 °C. These results are as expected from the acid dew point data; that is, 160 °C was above the dew point, whereas 90 °C was below the dew point.[27] Significant losses of sulfur trioxide at a sampling temperature of 90 °C are also suggestive of condensation of the acid and deposition of acid mist on the walls of the gas train. Energization of the ESP at the operating temperature of 160 °C caused little apparent loss of the sulfur trioxide. This finding is also consistent with the predicted absence of sulfuric acid mist at 160 °C.

AMMONIA

Ammonia was injected into the flue gas stream at the inlet of the 650, 370, or 160 °C constant temperature zone and sampled at the outlet of the 650, 370, 160, or 90 °C zone, depending upon the injection temperature. Ammonia has typically been introduced into power plant flues at temperatures of 150 to 370 °C. But it was considered important to include injection at 650 °C in this investigation, since ammonia is likely to be a decomposition product of an agent such as ammonium sulfate or ammonium phosphate, which are sometimes injected into the gas stream at temperatures around 650 °C.

In the presence of sulfur oxides in the flue gas, ammonia was expected to react mainly by combination with sulfur trioxide and water at temperatures below 200 °C to form particulate ammonium sulfate, $(NH_4)_2SO_4$, or ammonium bisulfate, NH_4HSO_4:[3,5]

$$2NH_3(g) + SO_3(g) + H_2O(g) \rightarrow (NH_4)_2SO_4(s) \qquad (2)$$

$$NH_3(g) + SO_3(g) + H_2O(g) \rightarrow NH_4HSO_4(l \text{ or } s) \qquad (3)$$

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27. Banchero, J. T., and F. H. Verhoff. Evaluation and Interpretation of the Vapour Pressure Data for Sulphuric Acid Aqueous Solutions with Application to Flue Gas Dewpoints. J. Inst. Fuel, 48:76-80, 1975.

The corresponding reaction to produce the sulfite or bisulfite was not expected because of unfavorable thermodynamic conditions.[28] Additionally, there was the possibility that ammonia might thermally decompose to some extent to yield nitrogen and hydrogen or that it might be oxidized to nitrogen or nitric oxide and water:

$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g) \quad (4)$$

$$4NH_3(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(g) \quad (5)$$

$$4NH_3(g) + 5O_2(g) \xrightarrow{Pt} 4NO(g) + 6H_2O(g) \quad (6)$$

With nitrogen oxides as well as sulfur oxides in flue gas, ammonia may react with either or both nitric oxide and nitrogen dioxide to form nitrogen and water:

$$4NH_3(g) + 6NO(g) \rightarrow 5N_2(g) + 2H_2O(g) \quad (7)$$

$$8NH_3(g) + 6NO_2(g) \rightarrow 7N_2(g) + 12H_2O(g) \quad (8)$$

In addition to those reactions given by Equations 7 and 8, ammonia can also react with nitrogen dioxide at temperatures below the melting point of ammonium nitrate (170 °C) to give mainly nitrogen, water, and ammonium nitrate, and it can react at higher temperatures to produce mainly nitrogen, nitric oxide, and water.[29] Ammonia can react with nitric oxide at 100 °C to give nitrogen and traces of ammonium nitrate and ammonium nitrite.[30] In general, ammonia is stable in the presence of nitric oxide in the absence of catalytic surfaces;[31] however, in the presence of catalytic

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28. St. Clair, H. W. Vapor Pressure and Thermodynamic Properties of Ammonium Sulphites. In: Report of Investigations 3339. U. S. Bureau of Mines, Washington, D. C., 1937. pp 19-29.

29. Rosser, W. A., and H. Wise. Gas-Phase Oxidation of Ammonia by Nitrogen Dioxide. J. Chem. Phys., 25:1078-1079, 1956.

30. Gehlen, H. Reactions and Properties of Nitric Oxide and Its Compounds. III. The Reaction Between Nitric Oxide and the Alkali Salts of Nitrodisulfonic Acid. Chem. Ber., B66:292-297, 1933.

31. Wise, H., and M. F. Frech. Kinetics of Oxidation of Ammonia by Nitric Oxide. J. Chem. Phys., 22:1463-1464, 1954.

surfaces such as platinum and other transition metals or their oxides ammonia is known to react readily with nitric oxide at elevated temperatures, and such catalytic reactions have been patented for the removal of nitric oxide from industrial stack gases.[32-34]

Since the inside surfaces of the flue gas train (with the possible exception of the electrostatic precipitator) were not expected to catalyze the reactions of ammonia with oxygen or nitrogen oxides, we were unable to predict with any certainty whether or not ammonia would react with oxygen or nitrogen oxides, particularly at 650 °C. Consequently, knowledge of the occurrence and extent of such reactions could be obtained only through experimentation.

Injection Procedure

Three types of ammonia generators were used in this study. Initially, a solution of ammonium hydroxide was injected with a syringe pump into a stream of hot nitrogen, where the solution was volatilized and flushed into a sidearm of the flue gas train. Considerable variation in ammonia concentration was experienced, and thus other techniques were tried and evaluated. As one technique, pure anhydrous ammonia was injected into the flue gas with a syringe pump. Finally, a mixture of ammonia with nitrogen certified to contain 1.1% v/v of ammonia was metered into the flue gas at a rate of 100 or 200 mL/min. The injection of the certified gas mixture was the most convenient, accurate, and reproducible method and was consequently the method of choice for ammonia injection.

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32. Cohn, J., D. R. Steele, and H. C. Anderson. Selective Removal of Nitrogen Oxides from Oxygen-Containing Gases Especially from Nitric Acid Production from Ammonia. U. S. Patent 2 975 025, March 14, 1961. Assigned to Engelhard Industries, Inc.

33. Anderson, H. C., and C. D. Keith. Removal of Nitric Oxide from Tail Gas after Oxidation of Ammonia to Nitric Acid. U. S. Patent 3 008 796, November 14, 1961. Assigned to Engelhard Industries, Inc.

34. Nonnenmacher, H., and K. Katte. Selective Removal of Oxides of Nitrogen from Gas Mixtures Containing Oxygen. U. S. Patent 3 279 884, October 18, 1966. Assigned to Badische-Anilin- & Soda-Fabrik, AG, Germany.

Analytical Procedures

During the investigation of ammonia, the flue gas stream was sampled and analyzed for ammonia, sulfur trioxide, ammonium ion, sulfate ion, nitrogen dioxide, and nitric oxide. Not all of these species were sampled or determined in every experiment. For example, no attempt was made to determine the nitrogen oxides as reaction products when these gases were included in the makeup of the flue gas.

Ammonia was determined by sampling flue gas through two bubblers in series containing 0.02 N sulfuric acid and by analysis of the bubbler solutions by one of two methods. In one method, ammonia levels were determined with an ammonia-specific electrode (Orion Research Inc., Cambridge, Massachusetts). The other method, the phenol-hypochlorite colorimetric procedure,[17] was preferred because of its better sensitivity and reproducibility. The detection limit of the colorimetric method was estimated to be about 5×10^{-6} M in 100 mL of sample solution, or 0.08 ppm in a 15-L sample of flue gas.

Sulfur trioxide (or sulfuric acid vapor) was sampled with the controlled condensation coil and the resulting sulfate determined, as described earlier in this report.

The collection and determination of ammonium and sulfate salts formed in the gas stream was carried out in the following way. To remove the particulate material from the gas stream, a Teflon filter in a heated Pyrex holder was placed in the sampling line in a location upstream from the bubblers that were to collect ammonia. The filter was maintained at about 150 °C except when samples were taken from the 90 °C zone; here it was maintained at 90 °C. Exposed filters were extracted by vacuum filtration with either 0.02 N sulfuric acid for the determination of ammonium ion or distilled water for the determination of both ammonium ion and sulfate. The acid extract was analyzed for ammonium ion by the phenol-hypochlorite method. To determine the ammonium ion in the water extract, dilute sulfuric acid was added to a portion of the extract, and the colorimetric procedure for ammonia was carried out. To determine sulfate, isopropyl alcohol was added to a portion of the water extract and the sulfate was determined by the barium-Thorin titration, as described earlier.

Nitrogen dioxide was absorbed from the gas stream in Greiss-Saltzman reagent in a bubbler and determined by colorimetry.[35] The sum of both nitrogen dioxide and nitric oxide was determined

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35. Recommended Method of Analysis for Nitrogen Dioxide Content of the Atmosphere (Greiss-Saltzman Reaction). In: Methods of Air Sampling and Analysis, M. Katz, Ed. American Public Health Association, Washington, D. C., 1977. pp 527-534.

by oxidizing the nitric oxide in the gas stream to nitrogen dioxide with chromium trioxide impregnated on firebrick and then determining the total nitrogen dioxide.[36]

Experimental Results

Injection of Ammonia into Flue Gas Containing No Added Oxides of Sulfur or Nitrogen--

Ammonia was initially injected into the flue gas mixture containing no added oxides of sulfur or nitrogen. The purpose of these experiments was to determine the agreement between the concentration of injected ammonia in the gas stream and the concentration anticipated and to determine the extent of thermal decomposition and oxidation of ammonia that occurred in the flue gas train.

Ammonia was injected near the inlet of the 650, 370, or 160 °C constant temperature zone. When ammonia was injected at 650 °C, samples were taken near the outlet of the 370 °C zone, the ESP (160 °C), or the 90 °C zone. When ammonia was injected at 370 or 160 °C, samples were taken near the outlet of the 90 °C zone.

The results of the ammonia determinations are presented in Table 7. This table lists the ammonia concentrations found at various sampling locations in the flue gas train and compares the observed concentrations with the values anticipated from the makeup procedure for the flue gas and the rate of ammonia injection. In some experiments the total observed ammonia concentration was composed of the ammonia found on a Teflon filter in the sampling train and the ammonia found in bubblers of sulfuric acid solution. The filter catch represented the adsorbed ammonia recovered from the filter and filter holder inlet. The bubbler catch represented the ammonia gas trapped in the bubbler, the filter holder outlet, and the glass connecting lines from the filter holder to the bubbler.

The tabulated results show that when ammonia was injected near the inlet of the 650 °C constant temperature zone, the amounts recovered decreased slightly as the sampling temperature was lowered and the location of the sampling point was farther removed from the point of injection. Injection of the ammonia at 370 °C did not improve the recovery at 90 °C, but injection at 160 °C improved the recovery significantly. This general trend suggests that, while most of the ammonia (>85% of that injected)

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36. Tentative Method of Analysis for Nitric Oxide Content of the Atmosphere. In: Methods of Air Sampling and Analysis, M. Katz, Ed. American Public Health Association, Washington, D. C., 1977. pp 524-526.

TABLE 7. DETERMINATION OF AMMONIA IN FLUE GAS CONTAINING NO SULFUR OR NITROGEN OXIDES

Injection temp, °C	Sampling temp, °C	Sample No.	Observed $[NH_3]$, ppm Filter catch	Bubbler catch	Total	Av	Expected $[NH_3]$, ppm
650	370	1	-*	29.3	29.3		
		2	-	28.8	28.8		
		3	-	27.8	27.8		
		4	-	26.2	26.2	27.2	28.8
		5	-	25.7	25.7		
		6	-	27.5	27.5		
		7	-	27.1	27.1		
		8	-	25.5	25.5		
	160 (ESP)	1	0.5	28.2	28.7		
		2	1.2	21.0	22.2		
		3	1.0	17.8	18.8		
		4	2.2	22.4	24.6	25.2	28.8
		5	-	23.4	23.4		
		6	-	33.2	33.2		
		7	-	25.5	25.5		
	90	1	-	23.9	23.9		
		2	-	26.4	26.4	25.6	28.8
		3	0.8	23.3	24.1		
		4	1.0	27.0	28.0		
370	90	1	0.8	26.2	27.0		
		2	0.8	24.7	25.5	26.2	30.6
160	90	1	0.9	29.6	30.5		
		2	0.7	28.2	28.9	29.7	30.6

* A dash indicates that no filter was included in the sampling train.

passed through the flue unchanged, small amounts were lost by adsorption on the walls of the train or by reaction at the higher temperatures.

Since the background concentration of nitrogen was so great in the flue gas mixture, no attempt was made to analyze the gas stream for the small additional amounts of nitrogen that may have been formed from the thermal decomposition of ammonia at 650 °C. However, the concentration of nitrogen oxides in the flue gas was determined from gas stream samples recovered from the 90 °C zone when ammonia was injected at 650 °C. The nitrogen dioxide levels found ranged from 0.11 to 0.18 ppm. With the nitric oxide oxidizer in the sampling line, the results ranged from 0.14 to

0.25 ppm of nitrogen oxides. Without the injection of ammonia, the background concentration of nitrogen oxides was 0.01 ppm. Thus, ammonia was apparently oxidized to nitrogen oxides at 650 °C to some extent, but the extent of reaction was not large.

Injection of Ammonia into Flue Gas Containing Sulfur Dioxide but No Added Sulfur Trioxide or Nitrogen Oxides--

To investigate the reactivity of ammonia in the presence of sulfur dioxide, ammonia was added to flue gas containing about 600 ppm of sulfur dioxide but no added sulfur trioxide or nitrogen oxides. Although sulfur trioxide was not added to the flue gas mixture, the background concentration of this constituent was found to be 1 to 2 ppm. Ammonia was injected near the inlet of the 650 to 160 °C constant temperature zone and sampled at selected points downstream.

The results of the experiments are given in Table 8. The principal aspect of these results differentiating them from the results obtained in the absence of sulfur dioxide was the recovery of a higher fraction of the ammonia on the filter of the sampling train. The ammonia on the filter possibly may have been present as the solid sulfate or bisulfate salt resulting from the reaction of ammonia with the low background concentration of sulfur trioxide; some of the experimental information is not consistent with this hypothesis, however, as discussed in the next paragraph. In any event, the experimental results give no indication of an appreciable reaction of ammonia with sulfur dioxide to form the solid sulfite or bisulfite salt.

The activation of the ESP in one experiment yielded results that were not consistent with the occurrence of suspended ammonium sulfate or bisulfate in the flue gas train. No space charge effect* was observed; also, no substantial reduction in the amount of ammonia on the filter of the sampling train was observed. Conceivably, the reaction of ammonia with sulfur trioxide to produce a solid product occurred mainly on the filter rather than in the flue gas train.

Injection of Ammonia into Flue Gas Containing Added Sulfur Dioxide and Sulfur Trioxide but No Added Nitrogen Oxides--

With both sulfur dioxide (600 ppm) and sulfur trioxide (approximately 30 ppm) added to the flue gas, experiments were carried out to investigate the formation of ammonium sulfate or ammonium bisulfate salt at the lower temperatures in the flue gas train. To minimize complications involving the formation and deposition of salts in the gas train, ammonia was injected near

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* A space charge effect is indicated by a shift in current density to higher values at a specified applied voltage. Such an effect is subsequently illustrated in Figure 4.

TABLE 8. DETERMINATION OF AMMONIA IN FLUE GAS CONTAINING SULFUR DIOXIDE BUT NO ADDED SULFUR TRIOXIDE* OR NITROGEN OXIDES

Injection temp, °C	Sampling temp, °C	Sample No.	Observed $[NH_3]$, ppm Filter catch	Bubbler catch	Total	Expected $[NH_3]$, ppm
650	160 (ESP)	1	2.1	9.8	11.9	14.7
		2	2.8	16.8	19.6	29.4
		3†	3.1	21.3	24.4	29.4
170‡	100‡	1	1.3	28.1	29.4	30.6
		2	1.0	30.7	31.7	30.6
		3	1.8	29.4	32.2	30.6
		4	1.5	31.4	32.9	30.6

* The background concentration of sulfur trioxide was 1 to 2 ppm.

† This result was obtained with the ESP energized: applied voltage (V), 10 kV; current density (j), 60 to 65 nA/cm².

‡ Actual temperatures of the constant temperature zones nominally held at 160 and 90 °C.

the inlet of the 160 °C zone (maintained at an actual temperature of 175 °C in these experiments), and sulfur trioxide was introduced near the inlet of the 370 °C zone. Samples were taken for analysis at the outlets of the 160 and 90 °C zones.

The results of these experiments are presented in Table 9. Analysis of the gas samples withdrawn at 175 °C revealed that essentially all of the ammonia was collected on the filter apparently as a salt, which appeared to be ammonium bisulfate since the ratios of sulfate to ammonium ion were just slightly greater than the one-to-one ratio expected. Excess sulfur trioxide passed through the filter, presumably as sulfuric acid vapor.

The results from the samples taken from the 90 °C zone (actually at 100 °C) disclose the drastic effect that the activation of the ESP had upon the passage of the ammonium salts out of the stack. With the ESP not energized, recoveries of ammonia and sulfur trioxide were high, indicating that ammonium salts and perhaps some excess sulfuric acid aerosol were leaving the flue gas train. With the ESP energized, recoveries were low, apparently because the particulate material was collected by the ESP.

TABLE 9. DETERMINATION OF AMMONIA AND SULFATE IN FLUE GAS CONTAINING ADDED SULFUR DIOXIDE AND SULFUR TRIOXIDE BUT NO ADDED NITROGEN OXIDES

Sampling temp, °C	Sample No.	Observed concentrations,* ppm: Filter catch NH_3	Filter catch SO_3	Bubbler catch NH_3	Bubbler catch SO_3	Total NH_3	Total SO_3	Expected concn, ppm NH_3	Expected concn, ppm SO_3
175†	1	24.8	26	1.9	-	26.7	26	29.2	26
	2	19.8	25	0.1	2‡	19.9	27	29.2	27
	3	17.7	22	0.4	7‡	18.1	29	29.2	24
100†	1§	0.9	0	0.3	-	1.2	0	29.2	24
	2§	1.5	0	0.2	-	1.7	0	29.2	24
	3	19.7	25	0.3	-	20.0	25	29.2	30
	4	29.9	27	0.3	-	30.2	27	29.2	30

* The NH_3 and SO_3 on the filter presumably occurred as NH_4^+ and SO_4^{-2} ions.

† Actual temperatures of the constant temperature zones nominally held at 160 and 90 °C.

‡ The sulfate found was extracted from the filter holder outlet and was counted as part of the bubbler catch since it probably represents sulfuric acid vapor.

§ The ESP was energized: V = 10 kV, j = 41 nA/cm^2.

The addition of about 30 ppm of ammonia to flue gas containing about 26 ppm of sulfur trioxide produced a space charge effect in the ESP. The current-voltage curves demonstrating the shift are presented in Figure 4. One interesting aspect of the curves is that they merge at applied potentials near the point where sparking occurred.

Injection of Ammonia into Flue Gas Containing Added Sulfur Dioxide and Nitrogen Oxides--

To investigate the possible reactions of ammonia with nitrogen oxides, ammonia was injected into the flue gas mixture containing 600 ppm of added sulfur dioxide (plus approximately 2 ppm of background sulfur trioxide), first in the presence and then in the absence of approximately 1000 ppm of added nitrogen oxides in the gas stream. The added nitrogen oxides consisted of approximately 100 ppm of nitrogen dioxide and 900 ppm of nitric oxide. Ammonia was injected near the inlet of the 650 °C constant temperature zone in all of the experiments at a rate estimated to give an

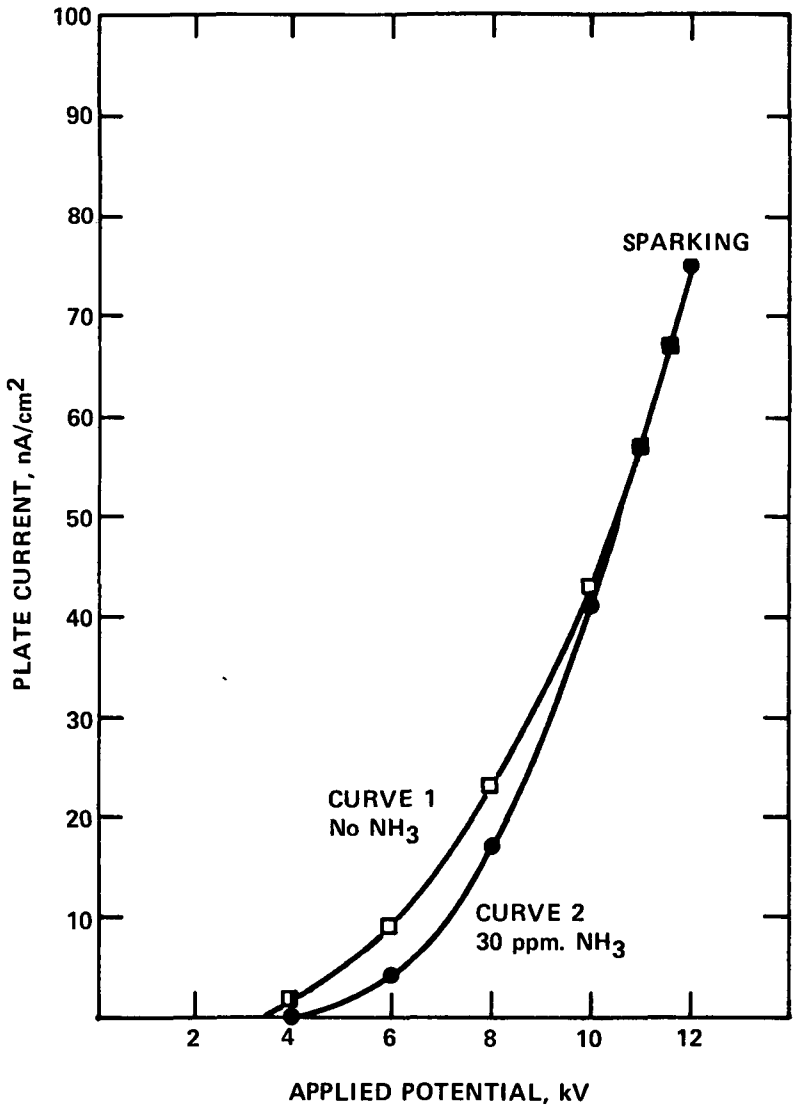

Figure 4. Current-voltage relationship for the ESP reflecting the space charge effect from the combination of ammonia and sulfur trioxide.

ammonia concentration of 63 ppm. The gas stream was sampled from the outlets of all of the various reaction zones downstream from the point of injection.

The results of the ammonia determinations in the presence and absence of added nitrogen oxides to the flue gas stream are given in Table 10. This table indicates that most of the ammonia injected was recovered at all of the sampling points when the nitrogen oxides were not present. The average of all the observed ammonia concentrations in the absence of added nitrogen oxides was 64 ppm, in excellent agreement with the anticipated concentration of 63 ppm. In the presence of added nitrogen oxides, however, the observed ammonia concentrations at all sampling temperatures averaged only 36 ppm. This represents a 44% decrease in the average ammonia recovery observed in the absence of nitrogen oxides. The observed ammonia concentrations in the absence of added nitrogen oxides were approximately the same at all sampling temperatures. Thus, the reaction of ammonia with nitrogen oxides appears to have occurred predominantly at 650 °C.

TABLE 10. DETERMINATION OF AMMONIA IN FLUE GAS CONTAINING ADDED SULFUR DIOXIDE AND NITROGEN OXIDES

	Observed $[NH_3]$,* ppm			
	Without added NO_x		With added NO_x	
Sampling temp, °C	Individual experiments	Av	Individual experiments	Av
650	64			
	63		40	
	59		33	37
	70			
	70	65		
370	57		40	
	74		44	
	75	69	43	42
160	51		25	
	62		32	
	56	56	30	29
90	70			
	57	63	36	36

* The expected $[NH_3]$ was 63 ppm.

No ammonia determinations were made in the presence of nitric oxide or nitrogen dioxide alone. And since the major reaction products of ammonia with either nitric oxide or nitrogen dioxide are the same (nitrogen and water), only speculation can be offered for the exact nature of the reactions between ammonia and nitrogen oxides in the flue gas stream.

One other possible cause for the observed effect of nitrogen oxides on ammonia is interference by nitrogen oxides in the chemical determination of ammonia. No mention of such an interference was made in the original reference to the determination of ammonia by the phenol-hypochlorite method;[17] and no mention is made of interference by ammonia in the standard analytical methods for the determination of nitrogen oxides.[35-37] Nevertheless, a brief experiment was conducted at the conclusion of the investigation of ammonia to determine whether or not nitrogen oxides may have interfered with the determination of ammonia. A series of ammonium chloride standards equivalent to a concentration of ammonia in the flue gas stream of approximately 55 ppm were analyzed by the phenol-hypochlorite method. To some of these standards, various concentrations of sodium nitrite (up to an equivalent concentration of NO_x in the gas stream of 600 ppm) and sodium nitrate (equivalent to an NO_x concentration in the gas stream of 600 ppm) were added. No measurable difference in the determined ammonia concentration was observed whether or not nitrite ion had been added to the ammonia standard. The observed concentration of ammonia was, however, approximately 30% greater in the presence of added nitrate ion than in its absence, but the effect of this interference was opposite in direction to an interference that would result in an artificially low observed ammonia concentration. Thus, chemical reaction appears to be the most probable cause for the apparent disappearance of ammonia when nitrogen oxides were added to the flue gas stream.

Summary and Discussion of the Results

The addition of ammonia to flue gas that contained no added sulfur oxides or nitrogen oxides indicated that the ammonia passed essentially unchanged through the gas stream. The loss of some ammonia was attributed to adsorption on the walls of the flue gas train. The injection of ammonia at 650 °C produced traces of nitrogen oxides (0.1 to 0.2 ppm) that were detected near the outlet of the train.

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37. Tentative Method of Analysis for Total Nitrogen Oxides as Nitrate (Phenoldisulfonic Acid Method). In: Methods of Air Sampling and Analysis, M. Katz, Ed. American Public Health Association, Washington, D. C., 1977. pp 534-538.

The injection of ammonia into flue gas that contained about 600 ppm of sulfur dioxide and about 1 to 2 ppm of sulfur trioxide but no added nitrogen oxides gave some evidence of a reaction of the ammonia with sulfur trioxide. However, there was no indication of a reaction between ammonia and sulfur dioxide, as predicted from thermodynamic data.[28]

When sulfur trioxide was added to the flue gas to produce a concentration of about 30 ppm, all of the ammonia injected (about 30 ppm) appeared to be converted to the bisulfate salt. The ammonium aerosol was collected by the ESP, and a space charge effect was observed.

The addition of ammonia to flue gas that contained both added sulfur dioxide and nitrogen oxides indicated that ammonia reacted extensively with the added nitrogen oxides at 650 °C, resulting in the destruction of over 40% of the injected ammonia.

From a strictly thermodynamic point of view, the reactions of ammonia with nitric oxide and nitrogen dioxide are both highly favorable energetically.[38] Both of the reactions have very large negative free energy changes, which give extremely large values for the equilibrium constants of these reactions.* The free energy of reaction of ammonia with nitric oxide (Equation 7) ranges from -436.22 kcal at 25 °C to -445.27 kcal at 627 °C, with corresponding equilibrium constant values ranging from 10^{320} to 10^{108} over the same temperature interval. The reaction of ammonia with nitrogen dioxide (Equation 8) has free energy values ranging from -697.72 to -792.39 kcal and equilibrium constants ranging from 10^{512} to 10^{192} over the temperature interval 25 to 627 °C. From a comparison of the magnitudes of these calculated thermodynamic quantities, the reaction of ammonia with nitrogen dioxide is seen to be more energetically favorable than the reaction of ammonia with nitric oxide and would be expected to proceed preferentially when in competition with the ammonia-nitric oxide reaction.

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38. Stull, D. R., and H. Prophet, Eds. JANAF Thermochemical Tables, 2nd ed. National Bureau of Standards, Washington, D. C., 1971.

* Calculated from the standard free energies of formation of the reactants and products in Equations 7 and 8 that are tabulated in Reference 38.

Kinetically, the rate of disappearance of ammonia in the reaction of ammonia with nitrogen dioxide has been found to follow the rate expression:[29,39]

$$-\frac{d[NH_3]}{dt} = k[NH_3][NO_2] \tag{9}$$

where $k = 10^{12.7}e^{-27500/RT}$ cc/(mol s) and the constant 27500 is given in cal/mol. (10)

The rate expression given in Equation 9 was roughly evaluated by use of the specific values of the rate constant calculated from Equation 10 and the concentration of ammonia and nitrogen dioxide found experimentally in this investigation.

The results of the calculations indicate that the reaction of ammonia with nitrogen dioxide can account for only a small fraction of the ammonia loss observed experimentally. Thus, ammonia may react with nitric oxide as well as with nitrogen dioxide. A rate expression for the reaction of ammonia with nitric oxide that could be evaluated with the data obtained under the conditions of this investigation could not be found during a brief review of the literature. Thus, the extent of reaction of ammonia with nitric oxide in the flue gas stream could not be estimated.

TRIETHYLAMINE

Triethylamine was injected into the flue gas train near the inlet of the 650, 370, or 160 °C constant temperature zone. The gas stream was sampled near the outlet of the ESP (160 °C) or the 90 °C zone.

Triethylamine was expected to undergo several routes of thermal decomposition or chemical reaction. At high temperatures, the expected thermal degradation products of triethylamine included monoethyl- and diethylamines, ammonia, hydrogen cyanide, and hydrocarbons. These fragments were potentially capable of interacting or combining with components of the flue gas to produce such compounds as alkyl cyanides, hydrazines, and nitrosamines. Another possible reaction expected was the oxidation of triethylamine to carbon dioxide, water vapor, nitrogen, and nitrogen oxides. Finally, there were the possibilities of triethylamine reacting with water in the flue gas mixture to form ethanol

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39. Bedford, G., and J. H. Thomas. Reaction Between Ammonia and Nitrogen Dioxide. J. Chem. Soc., Faraday Trans. 1, 68: 2163-2170, 1972.

and primary and secondary amines or producing solid salts from the combination of triethylamine with sulfur dioxide, sulfur trioxide, and water.

Injection Procedure

Triethylamine vapor was generated by bubbling dry nitrogen through a reservoir of the liquid amine maintained at 0 °C in an ice bath. At a nitrogen flow rate of 30 mL/min and the usual flow rate in the flue gas train, the expected triethylamine concentration in the flue gas was 27 ppm (based on the vapor pressure of the compound at 0 °C). The actual concentrations in the flue gas were calculated by analyzing the generator effluent and correcting the results for the dilution factor in the flue gas. The results ranged from 14 to 36 ppm but were reasonably constant during a given day of experimentation.

Traces of diethylamine were present along with triethylamine in the generator effluent. Analysis of the liquid triethylamine showed that diethylamine was present at a concentration of about 0.15% w/w; analysis of the vapor showed that diethylamine was added to the flue gas at a concentration of about 80 ppb when triethylamine was added at 21 ppm. The indicated diethylamine concentration was 0.27% w/w of the triethylamine concentration in the vapor state. Thus, the value was higher in the vapor state than in the liquid state, as expected, because of the higher volatility of diethylamine.

Analytical Procedures

During the investigation of triethylamine, the flue gas was analyzed for a variety of substances based on the possible reactions of triethylamine in the flue gas train. These substances included triethylamine, other organic amines, other organic compounds (including N-nitrosodiethylamine), sulfur oxides, nitrogen oxides, hydrogen cyanide, ammonia, and salts of protonated amines. All of these substances were not determined in every experiment, as indicated by the experimental results presented later in this report.

Organic Amines--

Organic amines were collected from the flue gas in bubblers containing 0.1 N sulfuric acid solution. An aliquot of an exposed bubbler solution was made alkaline with sodium hydroxide solution to regenerate the free amine, and the basic solution was then analyzed by gas chromatography (GC).

Two GC procedures were used for the determination of organic amines. In one method, a stainless steel column (4 m by 2 mm i.d.) packed with 10% Carbowax 20M-5% potassium hydroxide on 60/80-mesh Chromosorb W was coupled with a flame ionization detector. The injection port was maintained at 110 °C, the column at 110 °C, and

the detector at 250 °C. The helium carrier gas flow rate was 50 mL/min. The detection limit was estimated to be about 1 ppm triethylamine in a 15-L sample of flue gas. This column, however, would not separate diethylamine from triethylamine.

In the second GC method, which did allow the separation and determination of mono-, di-, and triethylamines,[40] the GC column was a stainless steel tube (0.6 m by 2 mm i.d.) packed with 60/80-mesh Chromosorb 103. A glass precolumn (10 cm by 2 mm i.d.) containing 20/30-mesh Ascarite was attached to the analytical column. The injection port, precolumn, and analytical column were held at 170 °C, and the thermionic detector was maintained at 275 °C. The nitrogen carrier gas flow rate was 50 mL/min. The detection limit for triethylamine was estimated to be less than 0.5 ppm in a 15-L sample; for diethylamine, less than 1 ppb in a 15-L sample. The detection limit for monoethylamine was not determined.

General Types of Organic Compounds--

In some experiments, a nonspecific sampling and analytical procedure for organic compounds was followed. Two different sampling devices were employed:

(1) A cartridge containing Amberlite XAD-2 porous polymer maintained at about 30 °C. The dimensions of the 1-g sorbent bed provided a gas residence time comparable to that in the organic module of the SASS sampling train.[41]

(2) A cold trap at 0 °C followed by a trap at -78 °C.

The exposed sorbent material was extracted with methylene chloride with a Soxhlet extractor, and the extract was concentrated to about 2 mL with a Kuderna-Danish evaporator. The concentrate was then analyzed by GC. After flue gas was sampled through the cold traps, the traps were first rinsed with distilled, deionized water and then with methylene chloride. The water rinse was extracted with methylene chloride. The methylene chloride extract and rinse were then combined and concentrated prior to GC analysis. In one experiment after the flue gas was sampled, gas samples were taken from the trap at -78 °C with a gastight syringe and injected into a GC.

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40. Taylor, D. G., Ed. NIOSH Manual of Analytical Methods, Vol. 1, 2nd ed. National Institute for Occupational Safety and Health, Cincinnati, Ohio, April, 1977. pp 221-1 to 221-9.

41. Blake, D. Operation and Service Manual, Source Assessment Sampling System. AEROTHERM Report UM-77-80, ACUREX Corporation, Mountain View, California, March, 1977.

Both liquid and gas samples were analyzed by GC with a glass column packed with 3% OV-1 on 40/60-mesh Chromosorb W. The column dimensions were 2 m by 2 mm i.d. The carrier gas was helium with a flow rate of 75 mL/min. Temperatures of the injection port, column, and flame ionization detector were all in the range 250 to 260 °C. The detection limit for most organic compounds was expected to be in the sub-parts-per-million range. A few samples were also analyzed on the OV-1 column coupled to a thermionic detector, which increased the sensitivity for compounds containing nitrogen to the parts-per-billion range.

N-Nitrosodiethylamine--

Although the nonspecific sampling procedures for organic compounds were applicable to the determination of N-nitrosodiethylamine, a separate sampling as well as a separate analytical procedure was also used for this compound. Flue gas was sampled through bubblers containing 1 N sodium hydroxide.[42] The alkaline solutions were extracted with methylene chloride and the extracts were concentrated prior to analysis by GC with thermionic detection. The GC column was a stainless steel tube packed with 10% Carbowax 20M-TPA on 60/80-mesh Chromosorb W. The carrier gas was nitrogen, and its flow rate was 50 mL/min. The injection port temperature was 230 °C, the column temperature 150 °C, and the thermionic detector temperature 230 °C. Four-microgram amounts of N-nitrosodiethylamine added to alkaline bubblers could be determined before or after exposure of bubblers to flue gas. In a 50-L gas sample, 4 μg of the compound corresponds to about 20 ppb. The detection limit was estimated to be considerably less.

Other Flue Gas Components--

Other components of the flue gas were determined as follows:

- Sulfur oxides, by methods previously described in this report.
- Nitrogen oxides, by methods previously described, or on occasion, the total of nitrogen oxides by the phenoldisulfonic acid method.[37]
- Hydrogen cyanide, by collection in a solution of 0.1 N sodium hydroxide and quantification with a cyanide-specific electrode (Orion Research Inc., Cambridge, Massachusetts).
- Ammonia, by the phenol-hypochlorite colorimetric method.[17]

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42. Fine, D. H., D. P. Rounbehler, E. Sawicki, and K. Krost. Determination of Dimethylnitrosamine in Air and Water by Thermal Energy Analysis: Validation of Analytical Procedures. Environ. Sci. Technol., 11:577-580, 1977.

- Salts formed by reaction of amines with sulfur oxides, by collection on a Teflon filter, extraction into water, and quantification of organic ammonium ions by GC or sulfate by oxidation with hydrogen peroxide and titration by the barium perchlorate-Thorin method described earlier.

Experimental Results

Injection of Triethylamine into Flue Gas Containing No Added Sulfur Oxides or Nitrogen Oxides--

In the absence of reactive oxides of sulfur and nitrogen in the flue gas, triethylamine was injected into the gas stream near the inlet of the 650, 370, or 160 °C constant temperature zone. The gas stream was sampled near the outlet of the ESP (160 °C) or the 90 °C zone.

When triethylamine was injected at 650 °C, most of it appeared to decompose. Samples taken from the flue gas stream at the outlet of the ESP indicated a 2 to 10% recovery of the triethylamine injected. These results, along with others, are presented in Table 11.

There was evidence that diethylamine was one product of the degradation process. In Sample No. 5 taken at an injection temperature of 650 °C, the concentration of diethylamine was found to be 600 ppb, while that of triethylamine was only 400 ppb. In Sample No. 8 taken at this injection temperature, small amounts of an unidentified compound containing nitrogen with a GC retention time between that of monoethylamine and diethylamine was found; the level of diethylamine in this sample was 60 ppb. No other organic compound that could be associated with the decomposition of triethylamine was found when samples were taken with cold traps or a cartridge of XAD-2 resin.

Some inorganic compounds were also found in the flue gas at the outlet of the ESP when triethylamine was injected at 650 °C. Ammonia was found at concentrations averaging about 2 ppm; hydrogen cyanide averaged about 1 ppm. The nitrogen dioxide level was found to be about 0.05 ppm, and the nitric oxide level was about 1 ppm.

When triethylamine was injected into the flue gas at 370 or 160 °C, the recovery at the outlet of the ESP (160 °C) or the 90 °C zone was considerably higher than that found when the amine was injected at 650 °C (see Table 11). Although there was some variation in results, the data indicate that most of the triethylamine passed through the flue gas train unchanged.

TABLE 11. DETERMINATION OF TRIETHYLAMINE* IN FLUE GAS CONTAINING NO SULFUR OR NITROGEN OXIDES

Injection temp, °C	Sampling temp, °C	Sample No.	Observed [TEA], ppm Filter catch	Bubbler catch	Total	Expected [TEA], ppm	Recovery, %
650	160	1	-	0.0	0.0	36.3	0
	(ESP)	2	-	0.0	0.0	36.3	0
		3	0.0	0.0	0.0	13.6	0
		4	0.0	0.2	0.2	33.4	1
		5	0.1	0.3	0.4	20.0	2
		6	0.0	1.6	1.6	33.4	5
		7	0.0	2.8	2.8	33.4	8
		8	<0.1	1.9	1.9	19.5	10
370	160	1	0.0	16.4	16.4	20.3	81
	(ESP)						
160	160	1	-	15.1	15.1	27.8	54
	(ESP)	2	-	17.7	17.7	27.8	64
		3	-	18.4	18.4	27.8	66
		4	-	20.5	20.5	22.3	92
		5	-	20.2	20.2	21.8	93
	90	6	0.0	11.5	11.5	14.7	78
		7	-	11.8	11.8	14.7	80
		8	-	11.9	11.9	14.7	81
		9	0.0	24.8	24.8	29.0	86

* Abbreviated as TEA in this table.

Injection of Triethylamine into Flue Gas Containing Added Sulfur Dioxide but No Added Sulfur Trioxide or Nitrogen Oxides--

To investigate the reaction of triethylamine with sulfur dioxide in the flue gas train, triethylamine was injected near the inlet of the 160 °C zone into a flue gas mixture containing about 600 ppm of sulfur dioxide but no other added oxides of sulfur or nitrogen. The flue gas was sampled at the outlet of the ESP (160 °C) or the 90 °C zone.

The results of the analyses of the flue gas samples, which are presented in Table 12, indicate that much of the triethylamine passed unchanged through the flue gas train. The recovery of triethylamine was usually less and the variation in results greater, however, than those observed without sulfur dioxide in the flue gas. There was evidence for the formation of diethylamine in the flue gas. The diethylamine level in Sample No. 3 of Table 12, which was collected at the ESP outlet at 160 °C, was found to be about 700 ppb. This value is considerably higher than the 80 to 100 ppb expected to result from the operation of the triethylamine generator.

TABLE 12. DETERMINATION OF TRIETHYLAMINE* IN FLUE GAS CONTAINING ADDED SULFUR DIOXIDE BUT NO ADDED SULFUR TRIOXIDE OR NITROGEN OXIDES

Sampling temp, °C†	Sample No.	Observed [TEA], ppm Filter catch	Bubbler catch	Total	Expected [TEA], ppm	Recovery, %
160 (ESP)	1	0.0	14.2	14.2	27.9	51
	2	1.5	17.2	18.7	27.9	67
	3	0.4	19.8	20.2	27.9	72
90	4	3.1	11.1	14.2	27.9	51
	5	4.5	15.0	19.5	27.9	70
	6	8.4	19.7	28.1	29.0	97

* Abbreviated as TEA in this table.

† Injection temperature, 160 °C.

There was one finding in these experiments that differed significantly from the results obtained with no sulfur dioxide in the flue gas. Some triethylamine, presumably present as triethylammonium ion, was collected by the filter in the sampling train. In samples taken at the ESP, 8% or less of the total triethylamine recovered was found on the filter; but in samples taken from the 90 °C zone 22 to 30% was collected on the filter. After portions of the water washes of the filters were treated with hydrogen peroxide to oxidize any sulfite present to sulfate, sulfate was found to be present in amounts that provided a molar excess with respect to the amounts of triethylamine present. The results appear to confirm the presence of sulfur-containing salts in the filter catch of samples taken from both the ESP and the 90 °C zone and suggest the formation of triethylammonium sulfite or bisulfite by the reaction of triethylamine and sulfur dioxide in the flue gas.

Injection of Triethylamine into Flue Gas Containing Added Sulfur Dioxide and Sulfur Trioxide but No Added Nitrogen Oxides--

When triethylamine was injected into flue gas containing about 600 ppm sulfur dioxide and about 20 ppm sulfur trioxide, the total recoveries of triethylamine were comparable to the results obtained with samples taken from flue gas containing sulfur dioxide but no added sulfur trioxide (see Table 13). However, the fraction of the triethylamine that was trapped by the filter, presumably as triethylammonium ion, was larger than that found with no sulfur trioxide in the flue gas. The filter catch amounted to 67 to 80% of the triethylamine recovered at the ESP outlet and 92 to 95% of that recovered from the 90 °C zone. It is likely that the salt formed in the gas stream was triethylammonium bisulfate

TABLE 13. DETERMINATION OF TRIETHYLAMINE* IN FLUE GAS CONTAINING ADDED SULFUR DIOXIDE AND SULFUR TRIOXIDE BUT NO ADDED NITROGEN OXIDES

Sampling temp, °C†	Sample No.	Observed [TEA], ppm Filter catch	Bubbler catch	Total	Expected [TEA], ppm	Recovery, %
160	1	9.8	2.5	12.3	23.4	53
(ESP)	2	9.0	4.5	13.5	23.4	56
90	3	17.3	1.5	18.8	25.0	75
	4	18.8	1.0	19.8	25.0	79

* Abbreviated as TEA in this table.

† Injection temperature, 160 °C.

because the amounts of sulfate that were determined from filter washes were in molar excess of the amounts of triethylamine determined.

A surprising result was that the level of diethylamine apparently formed in the flue gas by decomposition of triethylamine was greater than the amounts found in the earlier experiments with no sulfur trioxide in the flue gas. The determination of triethylamine in Sample No. 1 of Table 13 indicated a level of 3.1 ppm. Of this amount, 3.0 ppm was collected by the filter, presumably as the diethylammonium ion. Diethylamine was also found in a syrupy residue that collected and charred on the glass surfaces of the flue gas train at temperatures near and below 160 °C. Analysis of the substance by mass spectrometry revealed not only the presence of diethylamine but also triethylamine, sulfur trioxide, and diethylsulfamic acid.

The addition of 28 ppm of triethylamine to flue gas containing 600 ppm of sulfur dioxide and 20 ppm of sulfur trioxide produced a space charge effect at applied voltages just above the potential required for the initiation of corona in the ESP (see Figure 5). At higher voltages, the curve was shifted to higher current densities relative to those obtained with no triethylamine in the flue gas.

Injection of Triethylamine into Flue Gas Containing Added Sulfur Dioxide, Nitric Oxide, and Nitrogen Dioxide--

When triethylamine was added to flue gas at 160 °C containing about 600 ppm of sulfur dioxide, 1000 ppm of nitric oxide, and 100 ppm of nitrogen dioxide, the overall recovery of triethylamine was around 50% of the amount injected (see Table 14). A significant fraction (18 to 41%) of the total amount recovered

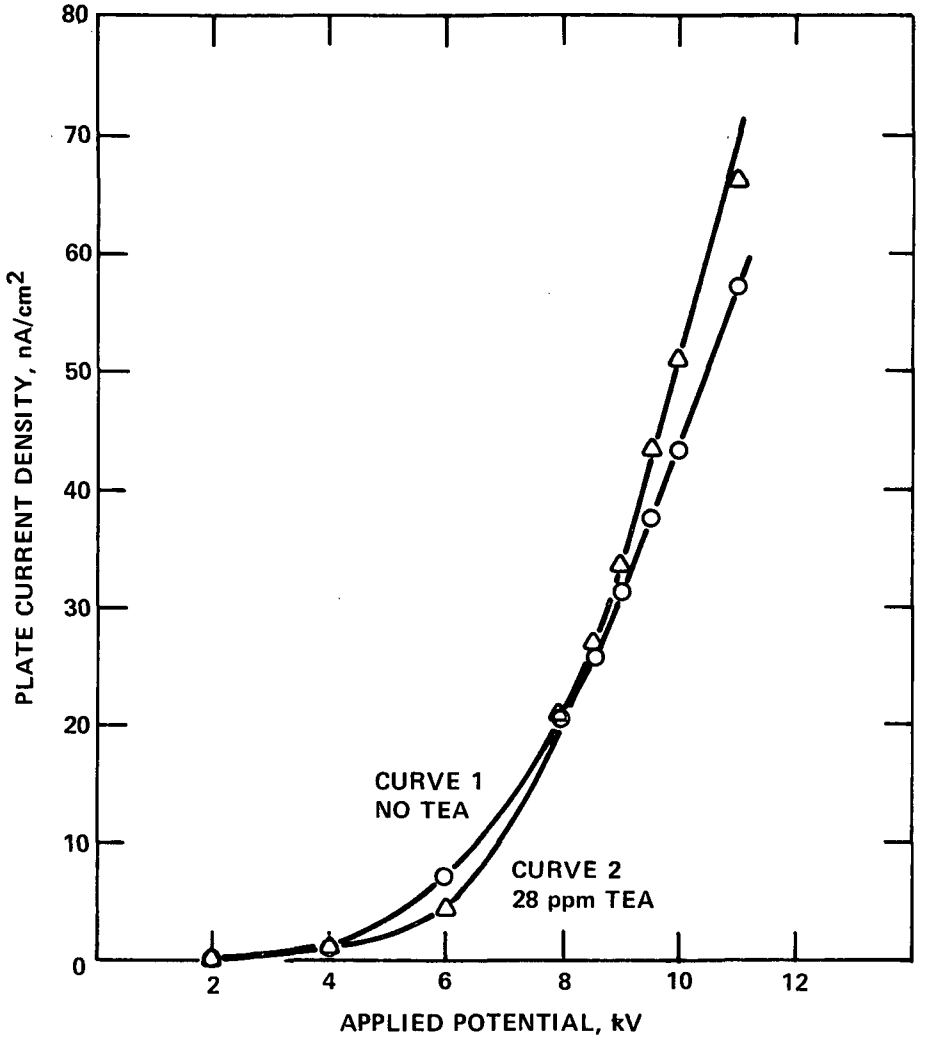

Figure 5. Current-voltage relationship for the ESP reflecting the space charge effect from the combination of triethylamine and sulfur trioxide.

TABLE 14. DETERMINATION OF TRIETHYLAMINE* IN FLUE GAS CONTAINING ADDED SULFUR DIOXIDE† AND NITROGEN OXIDES

Sample No.	Observed [TEA], ppm Filter catch	Bubbler catch	Total	Expected [TEA], ppm	Recovery, %
1	2.2	10.2	12.4	20.9	59
2	5.6	8.0	13.6	20.9	65

* Abbreviated as TEA in this table; injected and sampled at 160 °C.

† The background concentration of sulfur trioxide was found to be 3 to 6 ppm, although this substance was not added to the flue gas. The high background level is attributed to the oxidation of sulfur dioxide by the nitrogen oxides.

was found in the filter catch, presumably as triethylammonium bisulfate. The assumed source of the bisulfate was the 3 to 6 ppm of sulfur trioxide that was present in the flue gas, apparently as the result of the oxidation of sulfur dioxide by nitrogen dioxide.

As in the experiments discussed earlier, there was evidence for the formation of diethylamine in the flue gas although the levels observed were not as high as those measured in flue gas containing 20 ppm of sulfur trioxide. The total level of diethylamine determined in Sample No. 1 of Table 14 was 170 ppb with 60 ppb of that amount in the filter catch. In Sample No. 2, the total concentration was 210 ppb with about 100 ppb found on the filter. The results indicate that about one-third to one-half of the diethylamine determined was present as a diethylammonium salt, probably as the bisulfate or sulfate.

Perhaps the most interesting finding in the investigation of triethylamine was the discovery of organic compounds containing nitrogen (other than triethylamine and diethylamine) in methylene chloride extracts of the 1 M sodium hydroxide, XAD-2 sorbent, and cold traps that were used to sample organic matter in the flue gas at the ESP outlet. One of the compounds was identified as N-nitrosodiethylamine. The GC retention time of the unknown on two different analytical columns was identical with that of N-nitrosodiethylamine. The concentrations of the unknown in methylene chloride solution were near the detection limit of the mass spectrometer, but the identity was tentatively confirmed with gas chromatography coupled with mass spectrometry by monitoring the molecular ion at m/e 102. A complete mass spectrum was not obtained.

Although only a few samples were taken from flue gas containing added sulfur dioxide and oxides of nitrogen, the results appeared to give some insight into a possible mechanism for the formation of the nitrosamine. It was observed that a concentration of N-nitrosodiethylamine of 67 ppb was found in flue gas containing no nitric oxide, and a comparable concentration (89 ppb) was found with 750 ppm of nitric oxide in the flue gas. In both instances, the nitrogen dioxide concentration was about 100 ppm. Another observation was that an increase in the concentration of diethylamine vapor in the flue gas from 60 to 110 ppb at comparable levels of triethylamine produced an increase in the amount of nitrosamine found from 89 to 211 ppb. The results appear to indicate that the level of nitrosamine was more related to the concentrations of diethylamine and nitrogen dioxide than to the concentrations of triethylamine and nitric oxide. These observations seem to support a mechanism involving the reaction of diethylamine with nitrogen dioxide to produce N-nitrosodiethylamine.

In subsequent tests, it was observed that some, but apparently not all, of the N-nitrosodiethylamine found in the bubblers was formed during sampling. When bubblers were spiked with triethylamine and diethylamine and then exposed to flue gas, some N-nitrosodiethylamine formed in the bubblers. The results indicated, however, that the bubblers had to be spiked with many times the amounts of amine vapors actually sampled from the flue gas to produce amounts of N-nitrosodiethylamine comparable to those found in unspiked bubblers.

Summary and Discussion of the Results

The addition of triethylamine to flue gas that contained no added oxides of sulfur or nitrogen revealed that the amine passed essentially unchanged when injected at temperatures no higher than 370 °C. A significant degradation of triethylamine occurred when the compound was injected at temperatures near 650 °C. One decomposition product was diethylamine; it was found at levels of 60 to 600 ppb in the flue gas. No other organic decomposition products were identified. However, traces of ammonia (2 ppm), hydrogen cyanide (1 ppm), nitrogen dioxide (50 ppb), and nitric oxide (1 ppm) were found. No compounds were found in sufficient amounts to account for all of the triethylamine that was decomposed.

The principal products of the thermal decomposition of triethylamine eluded detection. In a past study of the degradation of triethylamine in a closed reactor at temperatures from 470 to 500 °C, a mechanism was proposed that involved the formation of butane and hydrazine as intermediate products with subsequent

decompositon chiefly to methane and nitrogen.[43] Methane would not have been trapped in the sampling trains employed in this investigation. Detection of the small amounts of nitrogen that would have been produced would have been prohibited by the high background concentration of nitrogen in the flue gas. Butane and hydrazine, if present, should have been collected by the cold traps and resin; however, they were not observed in the analyses.

When triethylamine was added to flue gas containing 600 ppm of sulfur dioxide, the most interesting result was the finding that as much as 30% of the amine in the flue gas reacted at 90 °C to form a bisulfite salt. At 160 °C, only 8% or less of the amine reacted. The bisulfite (or sulfite) ion was not identified, but sulfate was found in the filter extracts after the extracts were treated with hydrogen peroxide. The ability of triethylamine to produce bisulfite or sulfite under conditions where ammonia does not produce these compounds is consistent with the higher base strength of triethylamine.

One possible mechanism for the reaction of sulfur dioxide with triethylamine is that expressed by Bateman et al.[44] According to this mechanism, sulfur dioxide reacts to form a one-to-one addition product with triethylamine that rapidly absorbs water on exposure to moist air to form triethylammonium bisulfite with a melting point of about 75 °C. The bisulfite slowly absorbs oxygen to produce chiefly the bisulfate salt with a melting point of about 115 °C. If the addition product only exists as an unstable intermediate in the presence of the water in the flue gas, then the resulting bisulfite would be expected to slowly absorb oxygen to produce the bisulfate. Samples taken from the flue gas would contain the bisulfite, the bisulfate, or a mixture of both.

When triethylamine was injected into flue gas containing both 600 ppm of sulfur dioxide and 20 ppm of sulfur trioxide, most of the triethylamine reacted to form the sulfate or bisulfate salt. As in the previous experiments, the salt amounted to a greater fraction of the triethylamine injected when sampled at 90 °C than when sampled at 160 °C at the ESP outlet.

An unexpected finding was that as much as 3 ppm of diethylamine was produced in the gas stream. The diethylamine was converted chiefly to a salt, presumably bisulfate, that was collected at 160 °C at the ESP outlet.

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43. Taylor, H. A., and E. E. Juterbock. The Thermal Decomposition of Triethylamine. J. Phys. Chem., 39:1103-1110, 1935.

44. Bateman, L. C., E. D. Hughes, and C. K. Ingold. Molecular Compounds Between Amines and Sulfur Dioxide. A Comment on Jander's Theory of Ionic Reactions in Sulfur Dioxide. J. Chem. Soc., 1944:243-247.

Diethylamine was also found along with triethylamine, sulfur trioxide, and diethylsulfamic acid in a viscous residue that was observed to collect and char in the gas train after the introduction of sulfur trioxide. The discovery of diethylsulfamic acid in the residue (mp 89 °C) was totally unexpected.

The injection of triethylamine into flue gas containing sulfur dioxide, nitric oxide, and nitrogen dioxide also gave interesting results. A compound identified as N-nitrosodiethylamine was found in samples taken from the ESP outlet. The compound was found at concentrations of 67 to 211 ppb. Some of the compound was apparently produced during the sampling process; but the amount thus produced was minor compared to the total found.

Although only a few experiments were carried out with oxides of nitrogen in the flue gas, a mechanism for the formation of N-nitrosodiethylamine can be proposed from the data available. The concentration of the nitrosamine appeared to be more dependent upon the concentration of nitrogen dioxide and diethylamine than nitric oxide or triethylamine in the flue gas. The mechanism of formation of the nitrosamine therefore appeared to involve the reaction of nitrogen dioxide and diethylamine. Because the degradation of triethylamine or diethylamine in the flue gas was evident, triethylamine might also be considered a precursor of the nitrosamine.

SODIUM CARBONATE

The investigation of sodium carbonate was undertaken to complement plans of the Environmental Protection Agency to test the effectiveness of sodium carbonate as a conditioning agent in field studies (Contract 68-02-2656). The main objectives in the laboratory experiments were directed toward the identification of reaction products of sodium carbonate with acidic flue gas components such as sulfur and nitrogen oxides. Examples of the reactions expected with sulfur oxides to produce sodium sulfite and sodium sulfate are indicated below:

$$Na_2CO_3(s) + SO_2(g) \rightarrow Na_2SO_3(s) + CO_2(g) \qquad (11)$$

$$Na_2CO_3(s) + SO_3(g) \rightarrow Na_2SO_4(s) + CO_2(g) \qquad (12)$$

In the laboratory experiments, sodium carbonate was injected near the inlet of the 160 °C constant temperature zone, and the flue gas was then sampled near the outlet of the ESP (160 °C) or the outlet of the 90 °C zone. Initial experiments were carried out with no reactive oxides in the flue gas to determine the

losses of sodium carbonate on the walls of the flue gas train. Reactive sulfur oxides and nitrogen oxides were then added in later experiments.

Injection Procedure

It was considered desirable in our laboratory experiments to simulate the injection conditions of sodium carbonate into the flue gas train that were proposed by the EPA for field tests. The EPA plans called for the injection of sodium carbonate powder with a mass median diameter of approximately 10 μm into flue gas upstream from the electrostatic precipitator at a temperature of 160 °C. The rate of injection of the powder would correspond to 2.5 g of sodium oxide for every 100 g of fly ash. For a typical fly ash concentration of 9 g/m^3 (4 gr/ft^3), the appropriate concentration of sodium carbonate would be 370 mg/m^3 (at 25 °C).

In the laboratory tests, most of these conditions were reproduced. A dry aerosol of sodium carbonate was produced by nebulizing an aqueous solution of sodium carbonate into a quartz tube heated with resistance wire to 200 °C. The solution was nebulized with a Retec X70/N nebulizer assembly obtained from the Burton Division of Cavitron Corporation, Van Nuys, California. The nebulizer was activated with dry nitrogen gas. The dry aerosol was injected into the center of the flue gas stream near the inlet of the 160 °C constant temperature zone. Nebulization conditions were optimized to produce sodium carbonate concentrations equivalent to 180 to 340 mg/m^3 (expressed for 25 °C). These conditions corresponded to 3.40 to 6.57 x 10^{-3} meq/L (at 25 °C).

The greatest apparent discrepancy between the injection method proposed for the field tests and the laboratory injection technique was that the particles injected by the nebulization method were probably significantly smaller than 10 μm. Although the particle size distribution of the liquid aerosol produced by the nebulizer was not measured, the manufacturer's description indicated that the mass median diameter of the liquid aerosol generated was about 5 μm. If it is assumed that one liquid particle produced one salt particle when the water was evaporated, then the calculated mass median diameter of the particles generated in this investigation was approximately 0.6 μm.

Analytical Procedures

The sampling and analytical methods employed for the determination of sulfur dioxide, sulfur trioxide, nitrogen dioxide, and nitric oxide have been described and referenced earlier in this report, and descriptions of these methods will therefore not be repeated here.

Particulate material was collected from the flue gas with a heated Teflon filter as also previously described, but the procedures for analyzing the collected solids were modified in these experiments. In some experiments, filters exposed to flue gas were washed with distilled and deionized water, and the wash was analyzed for one or more of the following ions: sodium, carbonate, sulfate, sulfite, nitrite, and nitrate. Sodium ion was determined by atomic emission spectroscopy. Carbonate ion (in the filter wash and in the nebulizer solutions) was determined by titration with dilute hydrochloric acid solutions. All of the other anions were analyzed as a mixture by ion chromatography.[16]

In other experiments, filters were analyzed individually for sulfite, nitrite, or nitrate ions. Sulfite was determined by the West-Gaeke colorimetric procedure.[45] The exposed filter was washed with tetrachloromercurate solution, and the resulting dichlorosulfitomercurate was then treated with pararosaniline to yield the colored product.

Nitrite and nitrate were determined by modification of the colorimetric methods used for determining oxides of nitrogen in the flue gas.[35,37] To analyze for nitrite, the filter was washed with the absorbing reagent for the Greiss-Saltzman reaction. The sum of nitrite and nitrate collected on a filter was determined by first washing the filter with a solution of hydrogen peroxide and sulfuric acid to oxidize nitrite to nitrate and then treating the nitrate ion with phenoldisulfonic acid. The amount of nitrate present in the original filter wash was determined by difference.

Since sulfite and nitrite salts are easily oxidized in humid air, it was considered important to test the validity of the sampling method for sodium sulfite and sodium nitrite to insure that oxidation did not occur during sampling. Teflon filters were impregnated with sodium sulfite or sodium nitrite and exposed to flue gas containing added sulfur dioxide, nitrogen dioxide, and nitric oxide. At a filter temperature of 160 °C, neither the sulfite nor the nitrite was stable, although a significant amount of each salt was recovered when filters were spiked with several hundred micrograms. At a filter temperature of 90 °C, on the other hand, both sodium sulfite and sodium nitrite in amounts as low as 35 μg (5×10^{-4} meq) were stable.

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45. West, P. W., and G. C. Gaeke. Fixation of Sulfur Dioxide as Sulfitomercurate III and Subsequent Colorimetric Determination. Anal. Chem., 28:1816-1818, 1956.

Experimental Results

Injection of Sodium Carbonate into Flue Gas Containing No Added Sulfur Oxides or Nitrogen Oxides--

Sodium carbonate was first injected into a flue gas stream containing no added reactive oxides. The salt was injected near the inlet of the 160 °C constant temperature zone, and the flue gas was sampled near the outlet of the ESP (160 °C) or the 90 °C zone. The purpose of these experiments was to determine the recovery of sodium carbonate under conditions unfavorable to reaction.

The results of the experiments are presented in Table 15. Approximately 60 to 80% of the injected sodium carbonate was recovered from the outlet of the electrostatic precipitator at 160 °C and approximately 60 to 65% was recovered from the 90 °C zone. The low recoveries were mainly due to losses of sodium carbonate on the walls of the flue gas train. A significant accumulation occurred on the walls downstream from the injection point.

TABLE 15. DETERMINATION OF ANIONS IN FLUE GAS CONTAINING SODIUM CARBONATE BUT NO ADDED REACTIVE GASES

Sampling temp, °C	Sample No.	Anions, meq/L x 1000* Observed CO_3^{-2}	$SO_4^{-2} + SO_3^{-2}$	Total	CO_3^{-2} injected
160	1	3.77	0.04	3.81	6.51
	2	2.66	0.02	2.68	3.34
90	3	2.86	-†	2.86	4.74
	4	3.06	-†	3.06	4.74

* Expressed for 25 °C; converted to the hypothetical parts-per-million basis (gas by volume) by multiplying by the factor 12.2.

† Not determined.

Little or no reaction of sodium carbonate was observed during the tests with sulfur and nitrogen oxides absent from the flue gas. Very small amounts of sulfate and sulfite were found in two samples, apparently as the result of sulfur oxides still being present in the gas stream after previous experiments. No detectable amount of nitrite or nitrate was observed. No other anion was found at significant levels by ion chromatography. The sodium ion concentrations were found to correspond to the carbonate concentrations.

Injection of Sodium Carbonate into Flue Gas Containing Added Sulfur Dioxide and Nitrogen Oxides--

Sodium carbonate was next injected into flue gas containing approximately 600 ppm of sulfuric dioxide, 100 ppm of nitrogen dioxide, and 1000 ppm of nitric oxide. This mixture of reactive gases produced a background sulfur trioxide concentration of about 6 ppm (0.5×10^{-3} meq/L at 25 °C) in the gas stream. The sodium carbonate was again injected at the inlet of the 160 °C zone, and the gas stream was again sampled at the outlet of the ESP or the 90 °C zone.

The primary reaction products found when sodium carbonate was added to the flue gas were sodium sulfate and sodium sulfite. The amounts of carbonate and the total amounts of sulfate plus sulfite recovered are presented in Table 16. The sulfite concentrations determined in separate experiments at similar injection rates of sodium carbonate are given in Table 17. The sulfate and sulfite salts comprised 50 to 80% of the solids recovered. Sulfite levels were usually comparable to sulfate levels. However, in Sample No. 2 of Table 17, it appears that almost all of the sample was sulfite. The concentrations of nitrite and nitrate found were detectable but insignificant relative to the sulfite and sulfate levels. The highest nitrite concentration was 2×10^{-5} meq/L (expressed for 25 °C), and the highest nitrate concentration was 3×10^{-5} meq/L (expressed for 25 °C). The sodium ion concentrations corresponded to the total anion concentrations.

The low recoveries of the salts in gas samples with respect to the sodium carbonate added to the flue gas stream were principally the result of wall losses. Analyses of water washes of the flue gas train after the experiments cited in Tables 16 and 17 revealed that significant quantities of sodium carbonate, sodium sulfite, and sodium sulfate had accumulated. The mole fractions of these compounds in the residue from the walls of the 160 °C constant temperature zone and the electrostatic precipitator were 0.36 sodium carbonate, 0.05 sodium sulfite, and 0.59 sodium sulfate. The mole fractions in the residue from the walls of the 90 °C zone were 0.36 sodium carbonate, 0.55 sodium sulfite, and 0.09 sodium sulfate.

Summary and Discussion of the Results

In summary, sodium carbonate reacted extensively with the sulfur oxides in the flue gas. The location of the reaction—in the flue gas or on the collection medium—could not be identified; but similar reactions in a power plant flue would be expected to occur on precipitator electrodes, on the walls of the gas train, and possibly on the surface of fly ash particles.

The formation of some of the sodium sulfate found in flue gas samples was undoubtedly the result of the reaction of sodium carbonate with sulfur trioxide (6 ppm was present as sulfuric

TABLE 16. DETERMINATION OF ANIONS IN FLUE GAS CONTAINING SODIUM CARBONATE AND REACTIVE GASES

Sampling temp, °C	Sample No.	Anions, meq/L x 1000* Observed CO_3^{-2}	$SO_4^{-2} + SO_3^{-2}$	Total	CO_3^{-2} injected
160	1	0.74	0.80	1.54	3.60
	2	0.29	1.37	1.66	3.40
	3	0.60	1.31	1.91	4.26
	4	0.91	2.26	3.17	5.71
	5	1.49	1.54	3.03	5.23
90	6	1.80	1.03	2.83	4.74
	7	1.49	1.03	2.52	6.57

* Expressed for 25 °C; converted to the hypothetical parts-per-million basis (gas by volume) by multiplying by the factor 12.2.

TABLE 17. DETERMINATION OF SULFITE IN FLUE GAS CONTAINING SODIUM CARBONATE AND REACTIVE GASES

Sampling temp, °C	Sample No.	SO_3^{-2} observed, meq/L x 1000*	CO_3^{-2} injected, meq/L x 1000
160	1	0.54	5.66
	2	1.86†	5.66
	3	0.44†	5.66
90	4	0.14	4.74
	5	0.17	6.57

* Expressed for 25 °C; converted to the hypothetical parts-per-million basis (gas by volume) by multiplying by the factor 12.2.

† Total $SO_3^{-2} + SO_4^{-2} = 1.93 \times 10^{-3}$ meq/L expressed for 25 °C.

acid vapor at 160 °C). The remainder of the sulfate found at 160 °C must have been produced by the oxidation of sodium sulfite. The presence of sulfite in some of the samples withdrawn from the gas stream and on the walls of the flue gas train shows clearly that sulfur dioxide reacted with sodium carbonate. Nitrogen dioxide and nitric oxide were found to undergo no significant reaction with sodium carbonate.

AMMONIUM SULFATE

Ammonium sulfate is the primary component of the first proprietary conditioning formulation studied in this investigation, Apollo Chemical Corporation's Coaltrol LPA-40. Ammonium sulfate was always injected into the flue gas train at 650 °C in these experiments, either as an aqueous solution of reagent-grade ammonium sulfate or as the aqueous proprietary formulation LPA-40. The compound was injected at such a high temperature because Apollo normally injects LPA-40 ahead of the economizer in full-scale power plants. The gas stream was sampled at 650, 160, or 90 °C. The primary objective in the study of this agent was to identify and quantitate (if possible) the thermal decomposition products and recombination products of ammonium sulfate in the flue gas stream in both the absence and presence of added reactive sulfur and nitrogen oxides.

The probable decomposition products at 650 °C were the gases shown in the following equation:

$$(NH_4)_2SO_4(s) \rightarrow 2NH_3(g) + H_2O(g) + SO_3(g) \qquad (13)$$

The occurrence of this reaction is consistent with the thermodynamic data of Kelley et al.[46] and Scott and Cattell.[47] Stepwise reversal of this reaction was expected with decreasing temperature:

$$SO_3(g) + H_2O(g) \rightarrow H_2SO_4(g) \qquad (1)$$

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46. Kelley, K. K., C. H. Shomate, F. E. Young, B. F. Naylor, A. E. Salo, and E. H. Huffman. Thermodynamic Properties of Ammonium and Potassium Alums and Related Substances with Reference to Extraction of Alumina from Clay and Alunite. Technical Paper 688. U. S. Bureau of Mines, Washington, D. C., 1946. pp 66-69.

47. Scott, W. D., and F. C. R. Cattell. Vapor Pressure of Ammonium Sulfates. Atmos. Environ., 13:307-317, 1979.

$$NH_3(g) + H_2SO_4(g) \rightarrow NH_4HSO_4(l \text{ or } g) \quad (14)$$

$$NH_3(g) + NH_4HSO_4(l \text{ or } g) \rightarrow (NH_4)_2SO_4(s) \quad (15)$$

Decomposition products accompanying those shown in Equation 13 were expected to include nitrogen, nitrogen oxides, and sulfur dioxide. This statement is based on the findings of Halstead[48] in an investigation of the decomposition products of ammonium sulfate.

Injection Procedure

An aqueous solution of ammonium sulfate or a filtered solution of LPA-40 was nebulized with a Retec X70/N nebulizer assembly (Burton Division, Cavitron Corporation, Van Nuys, California). The nebulizer was activated with dry nitrogen gas, and the ammonium sulfate aerosol resulting from the nebulization process was introduced into the 650 °C constant temperature zone through a quartz tube that extended to the center of the flue gas stream. The rate of injection was chosen so that the concentration of ammonium sulfate in the flue gas did not exceed 41 μg/L at 650 °C, a concentration corresponding to the upper limit specified by Apollo.[12,13] To achieve levels below this limit in the laboratory flue gas train, a dilute solution of LPA-40 was injected. As discussed in Section 3 of this report, the LPA-40 formulation contained small quantities of an uncharacterized insoluble iron compound. The formulation was filtered to remove this compound and diluted by a factor of two. This dilute solution was injected at a nebulization rate of 0.2 mL/min. The measured concentrations of ammonium sulfate injected into the flue gas streams ranged from 9 to 41 μg/L at 650 °C, which is equivalent to 4.2×10^{-4} to 19×10^{-4} meq/L at 25 °C.

The average injection rate of ammonium sulfate was usually determined by measuring the amount of sulfate in the nebulizer before and after the nebulization period and by calculating the amount of sulfate lost. Frequently, however, the injection rate was found by determining the amount of ammonium ion lost during the nebulization period. In some experiments, the rates determined by the two methods agreed within experimental error. In others, however, it appeared that as much as 25% more ammonium ion was lost than sulfate (based on the ratio of equivalents lost from the nebulizer). The apparent origin of the excess was the decomposition of a residue of ammonium sulfate that collected in the

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48. Halstead, W. D. Thermal Decomposition of Ammonium Sulphate. J. Appl. Chem., 20:129-132, 1970.

outer tube of the nebulizer at high injection rates. Presumably, the ammonium sulfate was converted to ammonium bisulfate, and ammonia gas was released.

Analytical Procedures

Before and after each experiment, the nebulizer solution was analyzed for ammonium sulfate. In addition, the flue gas was analyzed for the following possible degradation and recombination products: sulfur dioxide, sulfur trioxide, ammonia, nitric oxide, nitrogen dioxide, ammonium bisulfate, and ammonium sulfate. When LPA-40 was injected, the gas stream was also analyzed in some experiments for the traces of iron that were found in the analysis of the LPA-40 formulation.

Most of the analytical methods used were similar or identical to those described and referenced earlier in this report. Sulfur trioxide was determined by sampling the flue gas through a controlled condensation coil and by subsequently measuring the collected sulfate by the barium perchlorate-Thorin titration method[18] or by ion chromatography.[16] (In some instances, ammonia was present concurrently in the sampling stream, and the sulfur trioxide was actually collected as ammonium sulfate and not as condensed sulfuric acid.) Sulfur dioxide was collected in a bubbler containing 3% hydrogen peroxide solution, and the resulting sulfate was determined by ion chromatography. Ammonia gas was collected in bubblers containing 0.1 N sulfuric acid solution and determined by the phenol-hypochlorite colorimetric method.[17]

In the absence of added nitrogen oxides, nitrogen dioxide was determined by the Greiss-Saltzman procedure;[35] nitric oxide was first oxidized to nitrogen dioxide on firebrick impregnated with chromium trioxide and then analyzed by the Greiss-Saltzman method. In the presence of added nitrogen oxides, the phenol-disulfonic acid method[37] was used to determine the sum of nitric oxide and nitrogen dioxide concentrations, and the Greiss-Saltzman method was used to determine the nitrogen dioxide concentration. The concentration of nitric oxide was then determined by difference.

Heated Teflon filters and heated quartz wool plugs were employed for the collection of particulate material from the flue gas. Exposed filters and plugs were usually washed with distilled, deionized water; the wash was analyzed for ammonium ion by the phenol-hypochlorite colorimetric method and for sulfate, sulfite, nitrate, and nitrite by ion chromatography. The solid material that collected on the glass tubing used for connecting the various components of the sampling trains was also dissolved in water and analyzed for ammonium ion and the anions listed above. In some experiments, exposed filters were washed with tetrachloromercurate solution, and sulfite was determined by the West-Gaeke method.[45] In other experiments, iron was determined

by atomic absorption spectroscopy in the water washes of the quartz wool plugs. Frequently, the plugs were also washed with hot hydrochloric acid, and iron was determined in these washes.

Experimental Results

Injection of LPA-40 into Flue Gas Containing No Added Oxides of Sulfur or Nitrogen--

In the investigation of LPA-40 in the absence of added reactive oxides in the gas stream, the agent was always injected into the flue gas near the inlet of the 650 °C constant temperature zone, and the flue gas was always sampled near the outlet of the 650 °C zone. The types of experiments performed fell into two categories: (1) the determination of the degradation products at 650 °C and (2) the determination of the recombination products at 160 and 90 °C. In the thermal degradation experiments, the sampling train was maintained at a high temperature, while in the recombination studies the sampled flue gas was allowed to cool rapidly to 160 or 90 °C in the sampling train. The purpose of this sampling procedure was to minimize the wall losses that would have occurred in the flue gas train if the gas stream had been sampled at the outlets of the 160 and 90 °C constant temperature zones.

Thermal decomposition studies--In the thermal decomposition studies, a sampling train was employed that kept the sampled gas hot enough to avoid the formation of salts prior to the determination of the expected gases. The sampling train included a plug of quartz wool enclosed in a glass tube at approximately 500 °C followed by a sampling manifold at about 400 °C with three sampling ports. One port was for the determination of ammonia, a second for the determination of sulfur oxides, and a third for the determination of nitrogen oxides. In some experiments the manifold was omitted, and either ammonia or sulfur oxides were determined.

The results of these experiments are given in Table 18. The primary thermal degradation products were sulfur trioxide, sulfur dioxide, and ammonia. The sulfur oxides recovered were approximately 90% sulfur trioxide and 10% sulfur dioxide. Microgram quantities of a solid iron compound were also found but are not listed in Table 18. Nitrogen or nitrogen oxides should also have been produced along with sulfur dioxide by oxidation of ammonia by sulfur trioxide. Because of the large background levels of nitrogen in the flue gas, however, measurement of the trace amounts of nitrogen produced by this reaction was not possible. Nitrogen oxides were found at levels no higher than the background concentrations of approximately 10 ppb.

All of the ammonium sulfate injected into the gas stream as LPA-40 could not be accounted for in these experiments. Since no other decomposition product than those discussed above was found,

TABLE 18. DETERMINATION OF THERMAL DECOMPOSITION PRODUCTS OF LPA-40 AT 650 °C IN FLUE GAS CONTAINING NO ADDED SULFUR OR NITROGEN OXIDES

Sample No.	Concentration, meq/L x 10 000*					
	Observed				Injected	
	SO_3	SO_2	Total SO_x	NH_3	SO_4^{-2}	NH_4^+
1	7.62	0.71	8.33	5.65	6.78	-†
2	4.31	0.46	4.77	5.32	6.78	-
3	3.75	0.48	4.23	3.62	6.40	-
4	4.40	0.73	5.13	4.64	6.40	-
5	4.78	0.41	5.19	2.96	4.21	-
6A‡	-	-	-	8.14	9.39	10.39
6B‡	6.51	0.44	6.95	-		
7A‡	-	-	-	14.16	10.39	12.71
7B‡	7.91	0.56	8.47	-		

* Expressed for 25 °C; converted to the parts-per-million basis (gas by volume) by multiplying the SO_3 and SO_2 concentrations by 1.22 and the NH_3 concentration by 2.44.

† A dash indicates that the concentration was not determined.

‡ A filter was added near the end of the sampling train for ammonia.

the lack of mass balance must be chiefly attributed to peculiarities in the injection procedure, losses of species on the walls of the flue gas train, or artifacts in the sampling procedure. As discussed earlier, in some experiments more ammonia than sulfate (expressed in equivalents) was apparently injected into the gas stream. In addition, sulfur oxides may have been irreversibly sorbed on quartz or glass surfaces. The affinity of glass for sulfur trioxide was demonstrated; typically, over half of the sulfur trioxide recovered was collected by the quartz wool plug. Losses of ammonia (as ammonium sulfate) probably occurred during the collection of Samples Nos. 1 to 5 listed in Table 18. The passage of an ammonium salt through the bubblers employed for the collection of ammonia was evident during the collection of Samples Nos. 6A and 7A. It was found that 9 to 20% of the total amount of ammonia plus ammonium ion was collected on filters placed downstream from the bubblers.

Recombination studies--In the chemical recombination experiments, flue gas was sampled at 650 °C and cooled to 160 or 90 °C and passed through a Teflon filter heated to the same temperature.

The filter was followed by the sampling manifold; ammonia, sulfur dioxide, sulfur trioxide (or sulfuric acid vapor) and nitrogen oxides were determined at separate ports.

The results of these experiments are listed in Table 19. When the filter temperature was maintained at 160 °C, the primary product found was ammonium bisulfate, with lesser amounts of ammonium sulfate. The predominance of the bisulfate salt was indicated by the low ratios of ammonium ion concentration to the anion concentration. The average ratio expressed in terms of equivalents was 0.59, which corresponds to mole fractions of 0.83 for ammonium bisulfate and 0.17 for ammonium sulfate in the filter catch. An average of about 4% of the total sulfur species recovered was sulfur trioxide (or sulfuric acid vapor) and about 4% was recovered as sulfur dioxide. Ammonia was the only nitrogen compound found at significant concentrations. Nitrogen oxides were not above the background levels.

With a filter temperature of 90 °C, the primary recombination product was ammonium sulfate. The average ratio of ammonium ion concentration to anion concentration expressed in terms of equivalents was 0.89, which corresponds to mole fractions of 0.76 for ammonium sulfate and 0.24 for ammonium bisulfate in the filter catch. Sulfur trioxide (or sulfuric acid vapor) was found to be present at concentrations representing 0.5 to 0.8% of the sulfur compounds, while sulfur dioxide corresponded to 4 to 6%. Since no sulfuric acid should exist as vapor at 90 °C, the sulfuric acid found must have occurred as fine particles of condensed liquid that slipped through the filter. As above, ammonia was the only nitrogen compound found in significant concentrations.

The data in Table 19 do not reveal good mass balances. Since products other than those listed are not found, low recoveries must be attributed to peculiarities of the injection procedure, wall losses, and artifacts of the sampling as in the previously discussed results.

Injection of an Aqueous Solution of Ammonium Sulfate into Flue Gas Containing No Added Oxides of Sulfur or Nitrogen--

An aqueous solution of ordinary ammonium sulfate (rather than LPA-40) was injected into the flue gas near the inlet of the 650 °C constant temperature zone and was sampled near the outlet of the same reaction zone. The flue gas stream contained no added sulfur or nitrogen oxides. Determinations were made of the degradation products present at 650 °C and of the recombination products at 160 and 90 °C, as described in connection with the studies of LPA-40.

The primary thermal degradation products of ammonium sulfate found in these experiments were the same as those of LPA-40 at 650 °C—ammonia, sulfur trioxide (or sulfuric acid vapor), and small amounts of sulfur dioxide. The sulfur oxides recovered

TABLE 19. DETERMINATION OF RECOMBINATION PRODUCTS OF LPA-40 IN FLUE GAS CONTAINING NO ADDED SULFUR OR NITROGEN OXIDES
(Samples Taken from the 650 °C Reaction Zone)

Filter temp, °C	Sample No.	Concentration, meq/L x 10 000* Observed: HSO_4^- or SO_4^{-2}	SO_3	SO_2	Total sulfur species	SO_4^{-2} injected
160	1	7.62	0.31	0.37	8.30	14.76
	2	3.99	0.12	0.15	4.26	
	3	6.09	0.06	0.02	6.17	9.98
	4	5.58	0.18	0.26	6.02	
	5	6.93	0.96	0.66	8.55	
	6	13.63	0.12	0.42	14.17	19.08
90	7	13.70	0.08	0.53	14.31	
	8	15.89	0.14	0.94	16.97	
		NH_4^+	NH_3		Total nitrogen species	NH_4^+ injected
160	1	4.86	6.50		11.37	-†
	2	2.69	3.61		6.30	
	3	2.18	4.98		7.16	9.85
	4	3.77	3.51		7.29	
	5	4.15	7.22		11.37	
	6	8.02	9.50		17.52	19.30
90	7	12.46	5.27		17.73	
	8	13.67	5.77		19.44	

* Expressed for 25 °C; converted to the hypothetical parts-per-million basis (gas by volume) by multiplying the concentrations of the sulfur species by 1.22 and the concentration of NH_3 by 2.44.

† NH_4^+ not determined.

consisted of about 95% sulfur trioxide and 5% sulfur dioxide; there was no indication that the relative amount of sulfur dioxide changed as the result of the absence of the iron compound found in LPA-40.

At 160 °C the predominant recombination product found was ammonium bisulfate; at 90 °C the main product was ammonium sulfate, as during the injection of LPA-40. The predominance of one sulfate salt over the other was indicated by the ratios of ammonium ion concentrations to the sulfate and bisulfate concentrations. At 160 °C the average ratio expressed in terms of equivalents was 0.58, which corresponds to mole fractions of 0.84

for ammonium bisulfate and 0.16 for ammonium sulfate; at 90 °C the average was 0.85, which corresponds to mole fractions of 0.70 for ammonium sulfate and 0.30 for ammonium bisulfate.

Injection of LPA-40 into Flue Gas Containing Added Sulfur and Nitrogen Oxides--

Dilute, filtered solutions of LPA-40 were nebulized into the flue gas stream near the inlet of the 650 °C zone. Approximately 600 ppm sulfur dioxide, 1000 ppm nitric oxide, and 100 ppm nitrogen dioxide were present in the flue gas mixture. The gas stream was sampled near the outlet of the 650 °C zone to determine the thermal degradation products and, after rapid cooling from 650 °C to 160 or 90 °C in the sampling train, to determine the chemical recombination products. Sampling was also carried out from the outlet of the ESP (160 °C) and from the outlet of the 90 °C constant temperature zone.

Thermal decomposition studies--The results of the thermal decomposition experiments are presented in Table 20. The primary thermal decomposition products found were sulfur trioxide and ammonia, the same principal degradation products that were found in the absence of reactive gases in the flue gas stream. Because of the large background concentrations of sulfur dioxide (approximately 500 x 10^{-4} meq/L) that were added to the gas stream in these experiments, however, the small amounts of sulfur dioxide (0.48 x 10^{-4} meq/L) that occurred in the thermal degradation of LPA-40 in the absence of reactive gases could not be detected.

TABLE 20. DETERMINATION OF DECOMPOSITION PRODUCTS OF LPA-40 AT 650 °C IN FLUE GAS CONTAINING ADDED SULFUR AND NITROGEN OXIDES

Sample No.	Concentration, meq/L x 10 000*			
	Observed		Expected	
	SO_3	NH_3	SO_3‡	NH_3
1	12.11	10.38	11.53	8.19
2	4.18	2.51	11.19	7.85
3	2.67	3.91	11.19	7.85

* Expressed for 25 °C; converted to the parts-per-million basis (gas by volume) by multiplying the concentration of SO_3 by 1.22 and the concentration of NH_3 by 2.44.

† Based on SO_4^{-2} lost from the nebulizer.

‡ Includes the average background concentration of SO_3 (3.34 x 10^{-4} meq/L) and therefore exceeds the concentration of NH_3.

Recombination studies--The results of the chemical recombination experiments are listed in Tables 21 and 22. Table 21 shows the recombination products found in gas samples taken from the 650 °C constant temperature zone in external sampling trains at 160 and 90 °C. Table 22 shows the recombination products found in samples taken from the ESP and the 90 °C zone. The predominant recombination products found at 160 and 90 °C were ammonium sulfate salts in both types of sampling arrangements. The data obtained in the presence of reactive gases in the flue gas stream were, however, based on only a few determinations, had a large scatter, and gave poor mass balances. At 160 °C the ratio of ammonium ion concentration to anion concentration (each expressed in meq/L) was found to range from 0.85 in one experiment (which would indicate a predominance of ammonium sulfate) to 0.21 in another (which would indicate a predominance of ammonium bisulfate in an excess of sulfuric acid). At 90 °C the ratio ranged from 0.51 to 0.06. With the exception of the one value of 0.41, which corresponds to mole fractions of 0.98 for ammonium bisulfate and 0.02 for ammonium sulfate, these low ratios indicate an excess of sulfuric acid over any ammonium salt present. Any sulfate salt initially formed would have been converted to the bisulfate salt by the excess acid. Thus, the uncertainty in the data does not permit a definite conclusion to be drawn about the distribution of the recombination products between ammonium sulfate and ammonium bisulfate.

Additional experimental findings--The only chemical species found at significant levels in any of the experiments with added sulfur and nitrogen oxides in the gas stream were ammonium and sulfate ions, sulfur trioxide, and ammonia. Only negligible amounts of nitrite, nitrate, and sulfite ions could be detected in any of the filter washes analyzed by ion chromatography. And because of the high background levels of nitric oxide, nitrogen dioxide, and sulfur dioxide, the small quantities of these oxides that could possibly be formed in these experiments could not be determined. The lack of mass balances found in these experiments must be chiefly attributed to wall losses of the injected species and the thermal degradation products (or, in some cases, to desorption of previously adsorbed species back into the gas stream) and to artifacts in the injection and sampling procedures.

At the completion of the injections of LPA-40, the various reaction zones and heat exchangers of the flue gas train were washed, and the washings were analyzed by ion chromatography. The only anionic species found in other than negligible amounts was sulfate ion. Analysis of an acidic wash of the 650 °C reaction zone by atomic absorption spectrophotometry indicated that trace amounts of iron had been coated on the inside walls of the reaction zone.

TABLE 21. DETERMINATION OF RECOMBINATION PRODUCTS OF LPA-40 IN FLUE GAS CONTAINING ADDED SULFUR AND NITROGEN OXIDES
(Samples Taken from the 650 °C Reaction Zone)

		Concentration, meq/L x 10 000*				
		Observed			Injected†	
Filter temp, °C	Sample No.	HSO_4^- or SO_4^{-2}‡	NH_4^+	NH_3	SO_4^{-2}§	NH_4^+
160	1	43.21	36.86	0.16	24.54	21.20
	2	3.45	0.73	0.04	-#	-#
90	3	12.35	6.26	1.09	7.47	4.13
	4	8.89	0.50	0.00	19.38	16.04
	5	6.74	1.67	-#	9.68	6.34
	6	4.50	0.56	0.08	8.91	5.57

* Expressed for 25 °C; converted to the hypothetical parts-per-million basis (gas by volume) by multiplying the HSO_4^- or SO_4^{-2} concentrations by 1.22 and the NH_3 concentrations by 2.44.

† Based on SO_4^{-2} lost from nebulizer.

‡ Aerosol collected on the filter. Only small additional amounts of SO_4^{-2} were found as SO_3 when this substance was determined (0.47×10^{-4} meq/L in Sample No. 1 and 1.50×10^{-4} meq/L in Sample No. 3).

§ Includes the average background concentration of SO_3 (3.34×10^{-4} meq/L) and therefore exceeds the concentration of NH_3.

\# Not determined.

In most of the experiments with added nitrogen oxides present in the gas mixture, the concentrations of recovered ammonia and ammonium ion were significantly less than the injected concentrations of ammonium ion into the gas stream (see Tables 20, 21, and 22). This observation is consistent with the finding obtained in the studies with ammonia that extensive reaction occurs between nitrogen oxides and ammonia in the flue gas train at 650 °C.

Summary and Discussion of the Results

The decomposition and recombination products of LPA-40 injected at 650 °C into a simulated flue gas stream containing no added sulfur oxides or nitrogen oxides were essentially identical to those products found during the injection of an aqueous

TABLE 22. DETERMINATION OF RECOMBINATION PRODUCTS OF LPA-40 IN FLUE GAS CONTAINING ADDED NITROGEN AND SULFUR OXIDES (Samples Taken from the ESP [160 °C] and the 90 °C Reaction Zone)

		Concentration, meq/L x 10 000*			
		Observed			
Sampling temp, °C	Sample No.	HSO_4^- or SO_4^{-2}	SO_3	Total SO_4^{-2}	SO_4^{-2} injected†
160 (ESP)	1	15.06	3.29	18.35	7.47
	2	0.71	0.82	1.53	9.43
90	3	1.55	0.33	1.88	19.38
		NH_4^+	NH_3	Total $NH_4^+ + NH_3$	NH_4^+ injected
160 (ESP)	1	4.94	0.58	5.52	4.14
	2	0.40	0.04	0.44	6.10
90	3	0.64	0.00	0.64	16.04

* Expressed for 25 °C; converted to the hypothetical parts-per-million basis (gas by volume) by multiplying the HSO_4^- or SO_4^{-2} concentrations by 1.22 and the NH_4^+ or NH_3 concentrations by 2.44.

† Based on SO_4^{-2} lost from the nebulizer; includes the average background concentration of SO_3 (3.34×10^{-4} meq/L) and therefore exceeds the concentration of NH_3.

solution of pure ammonium sulfate. The primary degradation products at 650 °C were ammonia and sulfur trioxide. Small amounts of sulfur dioxide were also observed. Nitrogen oxides were not produced from LPA-40 in measurable quantities. Traces of an iron compound, however, were released into the gas stream from LPA-40. Nevertheless, comparison of the results with LPA-40 and the results with ordinary ammonium sulfate indicated that the presence of the iron compound in LPA-40 had no significant effect on the recovery of any of the species found in the flue gas.

The predominant species found when the decomposition products were cooled to 160 °C was identified as ammonium bisulfate, and the major species found at 90 °C was ammonium sulfate. Insofar as ammonium bisulfate is concerned, however, the equivalent

mixture of ammonium sulfate and sulfuric acid may have been present, as in the ammonium sulfate decomposition products studied by Scott and Cattell.[47]

The decomposition products of LPA-40 injected at 650 °C into a simulated flue gas stream containing added sulfur oxides and nitrogen oxides were essentially identical to those products found in the absence of reactive oxides in the flue gas: ammonia and sulfur trioxide. The predominant recombination products found at 160 and 90 °C with the reactive gases present were ammonium sulfate salts. But because of uncertainties in the data, the distribution of the recombination products between ammonium sulfate and ammonium bisulfate could not be determined.

DIAMMONIUM HYDROGEN PHOSPHATE

The final flue gas conditioning agent studied in this investigation was diammonium hydrogen phosphate. This agent was investigated solely as Apollo Chemical Corporation's proprietary formulation Coaltrol LPA-445, which, as discussed in Section 3 of this report, consists predominantly of an aqueous solution of diammonium hydrogen phosphate. Dilute, aqueous solutions of LPA-445 were introduced into the gas stream at 650 °C in both the absence and presence of added sulfur and nitrogen oxides, and the flue gas was sampled at 650, 370, 160, and 90 °C. As in the study of LPA-40, the main objectives in this study were to identify the thermal decomposition and chemical recombination products of diammonium hydrogen phosphate in the flue gas stream. The LPA-445 solutions were injected at 650 °C in all of these experiments because Apollo indicated that all of the LPA series of additives are intended for "high temperature" application, which implies injection of the LPA agents upstream from the economizer.

Background Information on Ammonium Phosphate Salts

Thermal Decomposition Pathways of Ammonium Phosphates--

All ammonium phosphates dissociate when heated, evolving gaseous ammonia and leaving phosphoric acid,[49] as illustrated by the following equation for diammonium hydrogen phosphate:

$$(NH_4)_2HPO_4 \xrightarrow{\Delta} 2NH_3 + H_3PO_4 \qquad (16)$$

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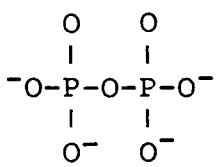
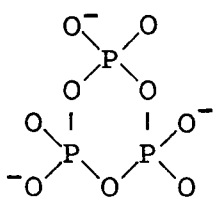
49. Van Wazer, J. R. Phosphoric Acids and Phosphates. In: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd ed., Vol. 15, H. F. Mark, J. J. McKetta, and D. F. Othmer, Eds. Interscience Publishers, New York, New York, 1968. pp 232-276.

This is the basis of the widespread use of ammonium phosphates as flame retardants. At the normal injection temperature of LPA-445 (650 °C), the phosphoric acid resulting from the decomposition of an ammonium phosphate could either decompose completely into phosphorus pentoxide (P_2O_5) and water or polymerize into species known as condensed phosphates.

Condensed phosphates are phosphate species containing several phosphorus atoms and having P-O-P linkages.[50] The three most important condensed phosphates are (1) the linear polyphosphates, whose anions have the general formula $[P_nO_{3n+1}]^{-(n+1)}$ (2) cyclic polyphosphates, or metaphosphates, whose anions have the general formula $[P_nO_{3n}]^{-n}$; and (3) "infinite chain" metaphosphates, whose anions also have the general formula $(P_nO_{3n}]^{-n}$. The most common linear polyphosphate is the pyrophosphate ion, whose structure is:



And the most common cyclic metaphosphate is the trimetaphosphate ion, whose structure is:



The thermal decomposition of diammonium hydrogen phosphate was studied by Erdey, Gal, and Liptay[51] by means of thermal gravimetry and differential thermal analysis. These researchers found that diammonium hydrogen phosphate thermally decomposes in a stepwise fashion with several decomposition processes proceeding sequentially as the temperature is raised. These processes are:

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50. Cotton, F. A., and G. Wilkinson. Advanced Inorganic Chemistry, 2nd ed. Interscience Publishers, New York, New York, 1967. 1136 pp.

51. Erdey, L., S. Gal., and G. Liptay. Thermoanalytical Properties of Analytical-Grade Reagents--Ammonium Salts. Talanta, 11:913-940, 1964.

$$(NH_4)_2HPO_4(s) \xrightarrow{\leq 150\ °C} NH_4H_2PO_4(s) + NH_3(g) \quad (17)$$

$$NH_4H_2PO_4(s) \xrightarrow{150\ °C} NH_4H_2PO_4(l) \quad (18)$$

$$2NH_4H_2PO_4(l) \xrightarrow{\geq 150\ °C} (NH_4)_2H_2P_2O_7(s) + H_2O(g) \quad (19)$$

$$n(NH_4)_2H_2P_2O_7(s) \xrightarrow{\leq 600\ °C} 2(NH_4PO_3)_n(s) + nH_2O(g) \quad (20)$$

$$2(NH_4PO_3)_n(s) \xrightarrow{600\text{-}800\ °C} 2nNH_3(g) + nP_2O_5(g) + nH_2O(g) \quad (21)$$

The thermal stability of ammonium orthophosphates has also been investigated by Margulis et al. (cited by Toy[52]) by thermogravimetric and differential thermal analyses. The minimum temperatures found for the onset of decomposition of triammonium phosphate, diammonium hydrogen phosphate, and ammonium dihydrogen phosphate were reported as 30, 140, and 170 °C, respectively. These data indicate that at the temperature of the 90 °C constant temperature zone, the only stable ammonium orthophosphate salts are ammonium dihydrogen phosphate and diammonium hydrogen phosphate. At the sampling temperature of the 160 °C zone and the ESP (160 °C), only ammonium dihydrogen phosphate would be stable. And at higher sampling temperatures (370 or 650 °C), no ammonium orthophosphate salt should be stable.

Data on Dissociation Pressures of Ammonium Orthophosphates--

The equilibrium dissociation pressures of the ammonium orthophosphates are also a measure of their thermodynamic stabilities. The dissociation pressure of an ammonium orthophosphate is the equilibrium partial pressure of gaseous ammonia over the solid salt. The dissociation pressures of ammonia over mono-, di-, and triammonium phosphate are listed below beneath the chemical equation corresponding to the particular decomposition (T is the absolute temperature):[53,54]

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52. Toy, A. D. F. Phosphorus. In: Comprehensive Inorganic Chemistry, Vol. 2, J. E. Bailar, H. J. Emeléus, R. Nyholm, A. F. Trotman-Dickenson, Eds. Pergamon Press, Elmsford, New York, 1973. pp 389-545.

53. Passillé, A. Dissociation of Ammonium Phosphates. Compt. rend., 199:356-358, 1934.

54. Warren, T. E. Dissociation Pressures of Ammonium Orthophosphates. J. Am. Chem. Soc., 49:1904-1908, 1927.

$$NH_4H_2PO_4(s) \rightleftharpoons NH_3(g) + H_3PO_4(\text{amorph.}) \quad (22)$$

$$p = 0.05 \text{ mmHg at } 125\ ^\circ C$$

$$(NH_4)_2HPO_4(s) \rightleftharpoons NH_3(g) + NH_4H_2PO_4(s) \quad (23)$$

$$\log p_{atm} = -\frac{3632}{T} + 1.75 \log T + 3.3$$

$$(NH_4)_3PO_4(s) \rightleftharpoons NH_3(g) + (NH_4)_2HPO_4(s) \quad (24)$$

$$\log p_{atm} = -\frac{2525}{T} + 1.75 \log T + 3.3$$

A tabulation of the dissociation pressures of the ammonium orthophosphate salts over the temperature range 50 to 160 °C is presented in Table 23.

TABLE 23. DISSOCIATION PRESSURES OF AMMONIUM ORTHOPHOSPHATE SALTS AS A FUNCTION OF TEMPERATURE

	Dissociation pressure, mmHg		
Temp, °C	$(NH_4)_3PO_4$*	$(NH_4)_2HPO_4$*	$NH_4H_2PO_4$†
50	574	0.22	-
60	1 040	0.49	-
70	1 820	1.08	-
80	3 090	2.27	-
90	5 110	4.57	-
100	8 220	8 88	-
110	12 900	16.7	-
125	24 500	40.6	0.05
130	30 000	53.9	-
140	44 400	93.0	-
150	64 600	156.0	-
160	92 400	257.0	-

* Calculated from the empirical formula given in Reference 53.

† From data in Reference 54, which gives a value of only the one temperature cited.

From this table, the order of increasing stability of the ammonium phosphates is seen to be $(NH_4)_3PO_4 < (NH_4)_2HPO_4 < NH_4H_2PO_4$ over the entire temperature range. The large magnitudes of the dissociation pressures of triammonium phosphate and diammonium hydrogen phosphate at 160 °C indicate that at this temperature

both salts are completely or nearly completely dissociated. At 90 °C triammonium phosphate is seen to be still completely dissociated and diammonium hydrogen phosphate significantly dissociated. Thus, like the thermogravimetric data, the dissociation pressure data indicate that at 90 °C ammonium dihydrogen phosphate is thermally stable and diammonium hydrogen phosphate partially stable, and at 160 °C (and higher) only the monoammonium salt is stable. These conclusions, however, assume that a sufficient amount of salt is present to give the indicated dissociation pressure and still leave a residue of the original salt in the system. The impact of this factor on conclusions about the salts present is discussed after the presentation of the experimental results.

Expected Decomposition and Recombination Products of LPA-445--

On the basis of the information discussed above, the injection of LPA-445 into the simulated flue gas stream at 650 °C was expected to result in the thermal decomposition of diammonium hydrogen phosphate into ammonia, water, phosphorus pentoxide (which would be analyzed as orthophosphate ion in aqueous solution), and possibly condensed phosphate species. As the temperature of the gas stream was lowered during passage through the gas train, various ammonium orthophosphates and condensed phosphates were expected to result from recombination reactions of the thermal decomposition products. Traces of nitrogen oxides might also occur as the result of the oxidation of ammonia in the gas stream. In addition, substantial amounts of the ammonia formed in the thermal decomposition of the injected LPA-445 might be destroyed in the 650 °C zone in the presence of added nitrogen oxides in the gas stream due to the reaction of ammonia with nitrogen oxides.

No unusual or highly toxic decomposition or reaction products of measurable concentration were expected to be formed in the flue gas stream when LPA-445 was injected. The only highly toxic compound that we could envision even possibly being formed in the gas stream was phosphine (PH_3). Phosphine is a colorless, highly toxic gas at room temperature and has an OSHA threshold limit value of 0.3 ppm. Phosphine could possibly be formed in the gas stream from the reduction of phosphorus pentoxide, orthophosphate ion, or some other phosphorous-containing species. Thus, plans were made for the gas stream to be sampled and analyzed specifically for phosphine.

Injection Procedure

Dilute, filtered aqueous solutions of LPA-445 were injected into the flue gas stream near the inlet of the 650 °C constant temperature zone at a nebulization rate of approximately 0.2 mL/min with a Retec X70/N nebulizer assembly.

Chemical analysis of the LPA-445 solutions in the nebulizer before and after a series of experiments indicated that ammonium and phosphate ions were not injected into the gas stream in the

mole ratio corresponding to diammonium hydrogen phosphate. Two ammonium ions would be expected for every phosphate ion (or hydrogen phosphate ion) injected if the salt were uniformly nebulized from solution according to its empirical formula, $(NH_4)_2HPO_4$. Instead, it was found that an excess of ammonium ion was nebulized into the gas stream. During the first half of the investigation, when no added sulfur oxides or nitrogen oxides were present in the gas mixture, the ratio of injected ammonium ions to injected phosphate ions was approximately 2.5:1.0. During the later experiments, when sulfur oxides and nitrogen oxides were added to the gas stream, the Retec nebulizer was not functioning properly. In these experiments the ratio of injected ammonium ions to injected phosphate ions was much higher than in the earlier experiments, averaging approximately 3.8:1.0. This phenomenon of excess ammonia injection can be partially explained by the appreciable vapor pressure of ammonia that is present over solutions of diammonium hydrogen phosphate, even at room temperature.[55] However, it cannot completely account for the excess ammonia injected, and no satisfactory explanation can be given.

During the experiments with reactive sulfur and nitrogen oxides present in the gas stream, the nebulizer outputs were significantly less than in the earlier experiments with no reactive gases present in the gas stream. The nebulizer outputs in the earlier experiments of this investigation averaged 2.15 μmol/L (expressed for 25 °C) for ammonium ion and 0.90 μmol/L for phosphate ion, whereas the average outputs determined during the later experiments were only 0.95 μmol/L for ammonium ion and 0.25 μmol/L for phosphate ion. The source of these injection discrepancies was traced to a malfunctioning of the aging Retec X70/N nebulizer assembly. The malfunctioning appeared to be related to stress deformation of the plastic components of the nebulizer.

The major significance of the low nebulizer outputs in the experiments with added sulfur and nitrogen oxides present in the gas stream is that the input concentration of phosphate ion into the gas stream was so low (equivalent to 6 ppm of a hypothetical gaseous species) that phosphate ion was hardly more than a trace species in the flue gas stream. This resulted in analytical difficulties in accurately determining the concentration of phosphate species that were sampled from the gas stream (especially at 160 and 90 °C, where polymerization and wall losses had drastically reduced the input phosphate concentration), and it complicated the observation and interpretation of the recombination processes that occurred at 160 and 90 °C.

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55. Waggarman, W. H. Phosphoric Acid, Phosphates, and Phosphatic Fertilizers. Reinhold Publishing Corporation, New York, New York, 1952. 683 pp.

Analytical Procedures

In the absence of added sulfur oxides and nitrogen oxides in the gas stream, the flue gas was sampled near the outlet of the 650 °C zone, the 370 °C zone, the ESP (160 °C), and the 90 °C zone. In most of the experiments, the gas stream was sampled through a particulate filter and then through a bubbler of 0.1 N sulfuric acid. In the gas samples collected at 650 or 370 °C, the filter was a heated plug of quartz wool. In the samples collected at 160 or 90 °C, the filter was a porous Teflon disc (2- to 5-μm porosity) mounted in a heated Pyrex holder. The material collected on a filter or in the bubbler was analyzed for ammonium ion, orthophosphate ion, and condensed phosphate species. In other experiments, the gas stream was sampled for nitrogen oxides. In a few experiments, the gas stream was sampled into a bubbler of a sodium bicarbonate-sodium carbonate buffer solution, and the solution was subsequently analyzed for anions by ion chromatography. (The bicarbonate-carbonate buffer solution was used as the collection medium because this buffer solution is the eluent commonly used in the determination of anions by ion chromatography.)

During the experiments with reactive sulfur and nitrogen oxides present in the gas stream, the flue gas was sampled at 650, 160, and 90 °C and was analyzed for background sulfur dioxide, sulfur trioxide, nitric oxide, and nitrogen dioxide when LPA-445 was not being injected into the gas stream. Then the flue gas was analyzed for ammonia, ammonium ion, orthophosphate ion, and condensed phosphate species during injection of LPA-445. The Teflon filters used in the sampling lines at 160 and 90 °C were washed with distilled water and the filter washes analyzed for anions by ion chromatography, specifically for orthophosphate and sulfate ions.

During the course of the investigation of LPA-445, two different colorimetric methods were used to analyze the phosphate species sampled from the gas stream. In the absence of reactive gases in the flue gas stream, orthophosphate and condensed phosphate ions were analyzed spectrophotometrically by the vanadomolybdophosphoric acid colorimetric method of Kitson and Mellon.[20] Orthophosphate ion was determined directly, whereas condensed phosphate ions were first hydrolyzed to orthophosphate ion by boiling in a dilute acid solution and were then determined colorimetrically. Due to the low concentrations of orthophosphate and condensed phosphate ions found in the presence of reactive gases in the flue gas stream, these species were analyzed by the

"stannous chloride" colorimetric method.[56] This method is much more sensitive and has minimum detection limits more than 60 times lower than the vanadomolybdophosphoric acid method.

The analytical methods for sulfur dioxide, sulfur trioxide, nitrogen oxides, and ammonia (or ammonium ion) have been described in detail and referenced earlier in this report, and a description of these methods will not be repeated here.

In one set of experiments the gas stream was sampled and analyzed for phosphine (PH_3) at 160 and 90 °C in the absence of added reactive gases and at 650 °C in the presence of added sulfur and nitrogen oxides to the gas stream. The method employed for the determination of phosphine was the colorimetric method of Dechant, Sanders, and Graul,[57] which is accurate in the range of 0.1 to 1 ppm of phosphine. The method consists of sampling the gas stream through a bubbler containing silver diethyldithiocarbamate reagent. Phosphine reacts quantitatively with this yellow reagent to form an orange-red complex, which is then analyzed spectrophotometrically.

Experimental Results

Injection of Diammonium Hydrogen Phosphate (as LPA-445) into Flue Gas Containing No Added Sulfur Oxides or Nitrogen Oxides--

LPA-445 was injected into the flue gas train at 650 °C. The flue gas was composed of only nitrogen, oxygen, carbon dioxide, and water vapor; it contained no added oxides of sulfur or nitrogen. The gas stream was sampled at 650 °C to determine the thermal decomposition products of diammonium hydrogen phosphate and was sampled near the outlets of the 370 °C zone, the ESP (160 °C), and the 90 °C zone to determine the recombination products of the decomposition fragments.

Thermal decomposition studies--The analytical results of the gas samples taken from the 650 °C zone are given in Tables 24 and 25. Table 24 compares the total amounts of ammonium and phosphate ions that were collected with the amounts injected. Table 25 gives the quantities of ammonium, orthophosphate, and condensed phosphate found on the filters and in the bubblers.

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56. Phosphate/Stannous Chloride Method. In: Standard Methods for the Examination of Water and Wastewater, 14th ed., M. C. Rand, A. E. Greenberg, and M. J. Taras, Eds. American Public Health Association, Washington, D. C., 1975. pp 479-480.

57. Dechant, R., G. Sanders, and R. Graul. Determination of Phosphine in Air. Am. Ind. Hyg. Assoc. J., 27:75-79, 1966.

TABLE 24. RECOVERY OF DECOMPOSITION PRODUCTS OF LPA-445 AT 650 °C IN FLUE GAS CONTAINING NO ADDED SULFUR OR NITROGEN OXIDES

Sample No.	Concentration, μmol/L* Injected† NH_4^+	Injected† Total PO_4^{-3}	Observed NH_4^+	Observed Total PO_4^{-3}	Recovery, % NH_4^+	Recovery, % Total PO_4^{-3}
1	0.748	0.325	0.607	0.211	81	65
2	0.415	0.456	1.199	0.208	85	46
3	2.809	1.493	2.273	0.891	81	60
4	2.809	1.493	1.987	0.632	71	42
5	1.511	0.494	1.587	0.387	105	78
6	1.511	0.494	1.141	0.097	76	20
7	1.397	0.394	1.522	0.206	109	52
8	1.397	0.394	1.410	0.210	101	53
9	1.397	0.394	1.431	0.258	103	65
Av	1.666	0.660	1.462	0.344	88	52

* Expressed for 25 °C. To convert to parts per million on the hypothetical volume basis, multiply by 24.4.

† Based on NH_4^+ and PO_4^{-3} lost from nebulizer.

TABLE 25. DISTRIBUTION OF DECOMPOSITION PRODUCTS OF LPA-445 AT 650 °C IN FLUE GAS CONTAINING NO ADDED SULFUR OR NITROGEN OXIDES

Sample No.	Concentration, μmol/L* Collected on filter NH_4^+	Collected on filter Ortho PO_4^{-3}	Collected on filter Condensed PO_4^{-3}	Collected in bubbler NH_4^+	Collected in bubbler Ortho PO_4^{-3}	Collected in bubbler Condensed PO_4^{-3}
1	0.034	0.060	0.025	0.573	0.079	0.048
2	0.073	0.115	0.009	1.126	0.084	0.000
3	0.347	0.389	0.098	1.926	0.380	0.024
4	0.101	0.240	0.050	1.886	0.342	0.000
5	0.053	0.079	0.082	1.534	0.179	0.047
6	0.058	0.037	0.010	1.083	0.032	0.019
7	0.162	0.051	0.071	1.360	0.076	0.008
8	0.164	0.058	0.024	1.246	0.111	0.016
9	0.121	0.075	0.000	1.310	0.121	0.062
Av	0.124	0.123	0.041	1.338	0.156	0.025

* Expressed for 25 °C. To convert to parts per million on the hypothetical volume basis, multiply by 24.4.

Table 24 shows a marked difference in the recoveries of ammonium and phosphate ions. For ammonium ion, the average value was 88%; but for phosphate ion, the average value was only 52%. This difference in recoveries strongly suggests that when LPA-445 was injected into the gas stream at 650 °C diammonium hydrogen phosphate decomposed extensively into gaseous ammonia and particulate phosphate species. The low recovery of the phosphate species can be attributed chiefly to wall losses of phosphate particles due to either impingement and adsorption or to settling out of the particles. The probability that wall losses occurred is enhanced by the extensive polymerization of orthophosphate ions to larger, heavier polyphosphate species that was observed at 650 °C (see below). In addition, condensed phosphate ions are quite reactive toward quartz[49] at the high temperature of the 650 °C reaction zone, and additional losses of phosphate could be attributed to such reactions of these species with the quartz walls of the reaction zone and sampling port.

Table 25 shows that, on the average, about 90% of the ammonium ions was collected in the bubbler, a result also indicating that extensive decomposition of the diammonium phosphate to ammonia gas occurred. For phosphate ions, roughly 50% was found either on the filter or in the bubbler. This result suggests that extensive volatilization of phosphate, perhaps to phosphorus pentoxide, also occurred. On the other hand, the presence of a significant fraction of the phosphate on the filter suggests that part of the phosphate remained as particulate. The mole ratio of ammonium ion to total phosphate on the filter was approximately 0.9. This ratio suggests that the filter may have collected an ammonium phosphate solid with a mole ratio of ammonium ion to phosphate of 1:1. The stabilities of ammonium orthophosphates discussed, however, make the existence of an ammonium phosphate solid appear improbable at 650 °C. Perhaps gaseous compounds were merely adsorbed on the quartz wool in a ratio suggesting a stoichiometric compound.

The decomposition studies at 650 °C also led to the following observations:

- Approximately 25% of the original orthophosphate was converted to condensed phosphate (see Table 26).

- Negligible quantities of ammonia were oxidized to nitrogen oxides. The total concentration of nitrogen oxides was about 1% of the concentration of ammonium ion collected on the filter and in the bubbler.

Recombination studies--The same species were found at 370, 160, and 90 °C as were found at 650 °C; that is, ammonium ion, orthophosphate ion, condensed phosphate ion, and traces of nitrogen oxides. The results of the gas sampling measurements at 370,

160, and 90 °C are given in Tables 26 and 27. Table 26 is a comparison of the total amounts of ammonium and phosphate ions that were collected with the amounts injected. Table 27 shows the distribution of the collected ammonium, orthophosphate, and condensed phosphate ions between the particle filter and the sulfuric acid bubbler.

TABLE 26. RECOVERY OF RECOMBINATION PRODUCTS OF LPA-445 AT 370, 160, AND 90 °C IN FLUE GAS CONTAINING NO ADDED SULFUR OR NITROGEN OXIDES

Sampling temp, °C	Concentration, μmol/L* Injected† NH_4^+	Injected† Total PO_4^{-3}	Observed NH_4^+	Observed Total PO_4^{-3}	Recovery, % NH_4^+	Recovery, % Total PO_4^{-3}
370	2.221	0.912	1.443	0.400	65	44
	2.221	0.912	1.608	0.458	72	50
	3.040	1.534	2.310	0.853	76	56
	3.040	1.534	1.727	0.644	57	42
	3.040	1.534	2.243	1.035	74	68
	3.154	1.559	2.861	0.881	91	73
	3.154	1.559	3.022	1.130	96	73
Av	2.838	1.363	2.173	0.772	77	57
160 (ESP)	3.615	1.564	1.870	0.213	52	14
	1.707	0.544	0.946	0.057	55	11
	1.622	0.545	0.858	0.113	53	21
	1.622	0.545	0.914	0.079	56	15
	1.179	0.334	1.065	0.089	90	27
Av	1.949	0.706	1.131	0.111	58	16
90	2.560	1.032	1.155	0.170	45	16
	2.685	1.207	0.603	0.073	22	6
	1.511	0.320	1.044	0.098	69	31
	2.328	0.957	0.882	0.136	38	14
Av	2.271	0.879	0.921	0.119	41	14

* Expressed for 25 °C. To convert to parts per million on the hypothetical volume basis, multiply by 24.4.

† Based on NH_4^+ and PO_4^{-3} lost from nebulizer.

The data in Table 26 show that the recovery of ammonium ion was greater than the recovery of total phosphate ion at each of the three collection temperatures. The recovery of ammonium ion averaged 77, 58, and 41%, respectively, at 370, 160, and 90 °C; the recovery of total phosphate species averaged 57, 16, and 14% at the same temperatures. The greater recovery of ammonium ion

TABLE 27. DISTRIBUTION OF RECOMBINATION PRODUCTS OF LPA-445 AT 370, 160, AND 90 °C IN FLUE GAS CONTAINING NO ADDED SULFUR OR NITROGEN OXIDES

	Concentration, μmol/L*					
	Collected on filter			Collected in bubbler		
Sampling temp, °C	NH_4^+	Ortho PO_4^{-3}	Condensed PO_4^{-3}	NH_4^+	Ortho PO_4^{-3}	Condensed PO_4^{-3}
370	0.225	0.256	0.100	1.218	0.031	0.012
	0.223	0.284	0.082	1.385	0.076	0.016
	0.241	0.386	0.187	2.069	0.225	0.055
	0.121	0.229	0.075	1.606	0.282	0.058
	0.169	0.474	0.099	2.074	0.454	0.008
	0.454	0.545	0.170	2.407	0.074	0.093
	0.438	0.580	0.326	2.584	0.172	0.052
Av	0.267	0.393	0.148	1.906	0.188	0.042
160 (ESP)	0.190	0.140	0.049	1.680	0.008	0.016
	0.075	0.034	0.010	0.871	0.000	0.013
	0.082	0.068	0.036	0.776	0.002	0.008
	0.069	0.042	0.028	0.845	0.000	0.009
	0.095	0.058	0.020	0.970	0.000	0.011
Av	0.102	0.068	0.029	1.028	0.002	0.011
90	0.251	0.122	0.018	0.904	0.004	0.026
	0.003	0.053	0.000	0.600	0.000	0.020
	0.111	0.072	0.011	0.933	0.007	0.008
	0.142	0.100	0.023	0.740	0.003	0.010
Av	0.127	0.087	0.013	0.794	0.004	0.016

* Expressed for 25 °C. To convert to parts per million on the hypothetical volume basis, multiply by 24.4.

relative to phosphate ion at all collection temperatures (including 650 °C) seems to indicate, as discussed previously, that the collected ammonium ion originated from a gaseous species (ammonia) in the flue gas stream and that the collected phosphate ions originated from particulate phosphate species. However, the data also show a general decrease in the recoveries of both ammonium ion and phosphate ion as the physical location of the sampling point was farther removed from the conditioning agent injection point. The decreasing recoveries of phosphate ions can be attributed to wall losses of particulate phosphate species, but wall losses alone would be inadequate to explain decreasing recoveries of gaseous ammonia. Rather, the trend of decreasing recoveries of ammonium ion indicates that recombination of ammonia with particulate phosphate species occurred in the gas stream at the lower

temperatures. The decreasing recoveries of ammonium ion at the lower temperatures can thus be partially attributed to wall losses of particulate ammonium phosphate salts.

The data in Table 27 show that on the average nearly 90% of the ammonium ion collected at each temperature was found in the bubbler solution. This indicates that the source of the ammonium ion collected in the bubbler was gaseous ammonia. This ammonia gas presumably originated from two separate sources: (1) the original decomposition of diammonium hydrogen phosphate, or (2) the injection of excess ammonia from the nebulizer.

At 370 °C, approximately 70% of the total collected phosphate was found on the particle filter. This percentage increased to approximately 85% at 160 and 90 °C. These results indicate that as the temperature was lowered the extent of recombination of the original decomposition products into solid ammonium phosphate salts increased significantly. At all of the sampling temperatures, approximately 75% of the phosphate ions collected on the particle filters were orthophosphate ions.

The mole ratios of ammonium ion to orthophosphate ion and ammonium ion to total phosphate ion collected on the Teflon filters were approximately the same at both 90 and 160 °C, 1.0:1.0 and 1.0:1.5, respectively. This indicated that the same recombination product was present at both temperatures. Thermodynamically, ammonium dihydrogen phosphate appeared to be the most probable recombination product at both 90 and 160 °C.

The amounts of phosphate ion found at 90 and 160 °C and the equilibrium dissociation pressures of monoammonium and diammonium phosphate at these temperatures indicated that the only species that would be expected to be found on the particulate filter at either of these temperatures was monoammonium phosphate at 90 °C. These data will be used first to argue against the existence of the diammonium salt at either temperature and then to confirm the possible existence of the monoammonium salt at 90 °C.

The weight of phosphate ion collected on the particulate filter at 90 °C corresponded to an average gas stream concentration of 3.0 ppm of phosphate as a hypothetical vapor. At 160 °C the weight collected corresponded to an average of 4.0 ppm of phosphate. The dissociation pressures of diammonium hydrogen phosphate at 90 and 160 °C as discussed earlier are 4.57 and 257 mmHg, respectively. These dissociation pressures correspond to 6 000 and 340 000 ppm of NH_3 at 90 and 160 °C, respectively. Thus, the amounts of phosphate collected at 90 and 160 °C were totally insufficient to produce the indicated dissociation pressures of diammonium hydrogen phosphate.

The dissociation pressure of monoammonium dihydrogen phosphate is 0.05 mmHg (66 ppm) at 125 °C.[54] The value is not known at 90 °C, but it is probably low enough to be consistent with the occurrence of the monoammonium salt at 90 °C. The dissociation pressure at 160 °C is also unknown, but it is certainly too high to be consistent with the occurrence of the monoammonium salt at 160 °C. Perhaps the salt is stabilized at this temperature by some process such as adsorption on the particulate filter.

Even at 370 °C, the analyses indicated that orthophosphate ion was the predominant phosphate species found on the particulate filter. This observation cannot be explained on a purely thermodynamic basis, and some other mechanism such as adsorption may have stabilized the orthophosphate at this temperature. There were insufficient experimental data to resolve the ammonium phosphate recombination products found at 370 °C into specific salts.

Phosphine determination--The results showed no indication of the presence of phosphine in the flue gas samples taken from the outlet of the electrostatic precipitator and the outlet of the 90 °C zone.

Injection of Diammonium Hydrogen Phosphate (as LPA-445) into Flue Gas Containing Added Sulfur Dioxide and Nitrogen Oxides--

LPA-445 was injected into the flue gas near the inlet of the 650 °C zone. In about half of the experiments, the gas stream was composed of nitrogen, oxygen, carbon dioxide, and water vapor plus approximately 600 ppm of sulfur dioxide and a background level of approximately 2 ppm of sulfur trioxide. In the remainder of the experiments, approximately 100 ppm of nitrogen dioxide and 1000 ppm of nitric oxide were additionally present in the flue gas stream. The gas stream was sampled at 650 °C to determine the thermal degradation products of diammonium hydrogen phosphate and was sampled near the outlets of the 370 °C zone, the ESP (160 °C), and the 90 °C zone to determine the recombination products of the decomposition fragments.

Thermal decomposition studies--The results of the sampling measurements at 650 °C are listed in Tables 28 and 29. Table 28 compares the total amounts of ammonium and phosphate ions that were collected with the amounts injected. Table 29 shows the quantities of ammonium, orthophosphate, and condensed phosphate ions found on the filters and in the bubblers.

On the average, approximately two-thirds of the injected ammonium ion and a little more than one-half of the injected phosphate ion were recovered at 650 °C, the remainder of the injected ions presumably being lost on the walls of the 650 °C reaction zone and sampling port. About 86% of the ammonium ions were collected in the bubbler, whereas 75% of the total phosphate ions was found on the filter and 25% in the bubbler. These results indicate that at 650 °C the diammonium hydrogen phosphate in

TABLE 28. RECOVERY OF DECOMPOSITION PRODUCTS OF LPA-445 AT 650 °C IN FLUE GAS CONTAINING ADDED SULFUR DIOXIDE BUT NO ADDED NITROGEN OXIDES

Sample No.	Concentration, μmol/L* Injected† NH_4^+	Injected† Total PO_4^{-3}	Observed NH_4^+	Observed Total PO_4^{-3}	Recovery, % NH_4^+	Recovery, % Total PO_4^{-3}
1	0.625	0.231	0.412	0.117	66	51
2	0.625	0.231	0.371	0.136	59	59
3	0.625	0.231	0.408	0.128	65	55
Av	0.625	0.231	0.397	0.127	63	55

* Expressed for 25 °C. To convert to parts per million on the hypothetical volume basis, multiply by 24.4.

† Based on analyses of NH_4^+ and PO_4^{-3} lost from nebulizer.

TABLE 29. DISTRIBUTION OF DECOMPOSITION PRODUCTS OF LPA-445 AT 650 °C IN FLUE GAS CONTAINING ADDED SULFUR DIOXIDE BUT NO ADDED NITROGEN OXIDES

Sample No.	Concentration, μmol/L* Collected on filter NH_4^+	Collected on filter Ortho PO_4^{-3}	Collected on filter Condensed PO_4^{-3}	Collected in bubbler NH_4^+	Collected in bubbler Ortho PO_4^{-3}	Collected in bubbler Condensed PO_4^{-3}
1	0.051	0.058	0.030	0.362	0.029	-†
2	0.056	0.061	0.039	0.315	0.032	0.004
3	0.063	0.075	0.022	0.344	0.024	0.007
Av	0.057	0.065	0.030	0.340	0.028	0.004

* Expressed for 25 °C. To convert to parts per million on the hypothetical volume basis, multiply by 24.4.

† An anomalous analytical result, indicating less total phosphate than orthophosphate, is not reported.

LPA-445 decomposed primarily into gaseous ammonia and particulate phosphate species, with some volatilization of phosphate, probably to phosphorus pentoxide, also occurring.

These results were obtained with sulfur dioxide as the only reactive gas added to the gas stream. They are qualitatively very similar to the results obtained in the absence of added reactive gases. Quantitatively, however, much larger recoveries of ammonium ion were found in the absence of added reactive gases (approximately 88%) than in the presence of added sulfur dioxide, and a larger fraction of the phosphate species was found in the bubblers (approximately 50%). These results indicate that more extensive thermal decomposition of diammonium hydrogen phosphate and more extensive volatilization of phosphate ion occurred in the absence of reactive gases than with sulfur dioxide added to the gas stream. No satisfactory explanation for this observation, however, can be offered.

Recombination studies--The results of the gas sampling measurements at 160 and 90 °C are given in Tables 30, 31, and 32. Table 30 is a comparison of the amounts of ammonium and phosphate ions that were injected with the amounts that were collected. Table 31 shows the distribution of the collected ammonium, orthophosphate, and condensed phosphate ions between the particle filter and the sulfuric acid bubbler. Table 32 gives the results of the ion chromatography analyses of the filter washes of the flue gas sampled from the 160 and 90 °C reaction zones with all reactive gases present in the flue gas stream.

With both sulfur oxides and nitrogen oxides added to the flue gas stream, the same general trends in the recovery and distribution of ammonium ion and phosphate species at 160 and 90 °C were observed as those trends observed in the absence of added reactive gases to the flue gas stream. These results indicate that gaseous ammonia and particulate phosphate species in the flue gas stream recombined into ammonium phosphate salts at 160 and 90 °C, with the extent of recombination increasing as the temperature was lowered. From the thermodynamic considerations discussed earlier in this section, the most probable recombination product at 160 and 90 °C is monoammonium dihydrogen phosphate ($NH_4H_2PO_4$).

From the ion chromatographic analyses of the filter washes, sulfate ion and nitrate ion were found to be present at concentrations comparable to or greater than the concentrations of orthophosphate. Thus, in the presence of added oxides of sulfur and nitrogen, there appears to be a competition for the available ammonia in the gas stream during recombination reactions at 160 and 90 °C among orthophosphate, sulfate, and nitrate ions. The background level of sulfur trioxide in the gas stream was the source of the sulfate species in these experiments. The background concentration of sulfur trioxide was measured and found to

TABLE 30. RECOVERY OF RECOMBINATION PRODUCTS OF LPA-445 AT 160 AND 90 °C IN FLUE GAS CONTAINING SULFUR DIOXIDE AND SOMETIMES NITROGEN OXIDES

Sampling temp, °C		Concentration, μmol/L* Injected† NH_4^+	Injected† Total PO_4^{-3}	Observed NH_4^+	Observed Total PO_4^{-3}	Recovery, % NH_4^+	Recovery, % Total PO_4^{-3}
160 (ESP)		0.707	0.141	0.278	0.020	39	14
(without NO_x)		1.006	0.100	0.217	0.016	22	16
		0.965	0.158	0.395	0.023	41	14
	Av	0.893	0.133	0.297	0.020	34	15
160 (ESP)		1.284	0.264	0.194	0.018	15	7
(with NO_x)		0.907	0.196	0.085	0.016	9	8
	Av	1.096	0.230	0.140	0.017	13	8
90		1.729	0.614	0.099	0.020	6	3
(with NO_x)		0.907	0.196	0.090	0.027	10	14
		1.057	0.365	0.046	0.028	4	8
	Av	1.231	0.392	0.078	0.025	7	6

* Expressed for 25 °C. To convert to parts per million on the hypothetical volume basis, multiply by 24.4.

† Based on NH_4^+ and PO_4^{-3} lost from nebulizer.

average approximately 2 ppm (0.1 μmol/L, expressed for 25 °C) with an average concentration of 600 ppm sulfur dioxide in the gas stream. The concentration of nitrate ion in the gas stream, on the other hand, was expected to be on the trace level. The source of the nitrate ion is assumed to be the oxidation of ammonia by the nitrogen oxides added to the gas stream, as was discussed earlier in this report in the section on the investigation of ammonia. However, as was pointed out earlier in this section, the average input concentration of phosphate ion into the gas stream at 650 °C in these experiments was so small (0.25 μmol/L, only two-and-a-half times greater than the average sulfur trioxide background level) and the apparent wall losses were so great that there is little significance to the observed competition between the phosphate ion and the sulfate and nitrate ions for the available ammonia in the gas stream in these experiments. In the presence of a large excess of phosphate ion relative to sulfate and nitrate ions, the competition might be negligible.

Reaction of ammonia with nitrogen oxides--When nitrogen oxides were present in the gas stream during the injection of LPA-445, the ammonia recoveries at 160 and 90 °C were

TABLE 31. DISTRIBUTION OF RECOMBINATION PRODUCTS OF LPA-445 AT 160 AND 90 °C IN FLUE GAS CONTAINING SULFUR DIOXIDE AND SOMETIMES NITROGEN OXIDES

Sampling temp, °C		Concentration, μmol/L*					
		Collected on filter			Collected in bubbler		
		NH_4^+	Ortho PO_4^{-3}	Condensed PO_4^{-3}	NH_4^+	Ortho PO_4^{-3}	Condensed PO_4^{-3}
160 (ESP)		0.201	0.011	0.001	0.077	0.005	0.003
(without NO_x)		0.062	0.007	0.005	0.155	0.001	0.003
		0.197	0.014	0.003	0.197	0.000	0.006
	Av	0.153	0.011	0.003	0.143	0.002	0.004
160 (ESP)		0.038	0.009	-	0.156	0.005	0.004
(with NO_x)		0.026	0.010	-	0.059	0.003	0.003
	Av	0.032	0.010	-	0.108	0.004	0.004
90		0.037	0.016	0.002	0.062	0.003	0.000
(with NO_x)		0.034	0.020	-	0.056	0.004	0.004
		0.009	0.017	0.002	0.036	0.006	0.004
	Av	0.027	0.018	0.001	0.051	0.004	0.002

* Expressed for 25 °C. To convert to parts per million on the hypothetical volume basis, multiply by 24.4.

TABLE 32. ION CHROMATOGRAPHIC ANALYSIS OF ANIONIC SPECIES IN FILTER WASHES OF SAMPLES OF FLUE GAS CONTAINING SULFUR DIOXIDE AND NITROGEN OXIDES

Sampling temp, °C	Gas stream concentration, μmol/L*			
	SO_4^{-2}	NO_3^-	Ortho PO_4^{-3}	Ortho PO_4^{-3}†
160	0.051	0.009	0.010	0.009
(ESP)	0.012	0.013	0.010	0.010
90	0.025	0.005	0.017	0.016
	0.017	0.007	0.019	0.020

* Expressed for 25 °C. To convert to parts per million on the hypothetical volume basis, multiply by 24.4.

† Results obtained by the stannous chloride colorimetric method for comparison with the ion chromatography results.

significantly less than those in the absence of added nitrogen oxides. Table 30 shows that the average recovery of ammonium ion was 34% at 160 °C with sulfur dioxide as the only reactive oxide added to the gas stream. This table shows further that with both nitrogen oxides and sulfur oxides added to the gas stream the recovery of ammonium ion averaged only 13%, less than one-half the recovery found at 160 °C with no nitrogen oxides present. This observation is consistent with the gas stream reaction of nitrogen oxides with ammonia at 650 °C observed during the investigations of ammonia and ammonium sulfate.

Phosphine determination--No measurable concentrations of phosphine could be found in the flue gas sampled from the 650 °C reaction zone during the injection of LPA-445 into flue gas containing added oxides of sulfur and nitrogen.

Summary and Discussion of the Results

In the absence and in the presence of added sulfur oxides to the flue gas stream, the primary thermal decomposition products of the LPA-445 formulation were ammonia, ammonium ion, orthophosphate ion, and condensed phosphate ion. The condensed phosphate species were not further characterized. Diammonium hydrogen phosphate, the major component of LPA-445, appeared to decompose thermally into gaseous ammonia and particulate phosphate species, with some volatilization of phosphate also occurring. The extent of both thermal decomposition and phosphate volatilization was found to be less with sulfur dioxide added to the gas stream than in the absence of sulfur dioxide; but no logical explanation for this observation is apparent.

The major recombination products found at 160 and 90 °C in the absence of added reactive oxides in the gas stream were ammonium phosphate salts. While the experimental data obtained are not subject to a definitive interpretation, the most probable recombination product at 160 and 90 °C appeared to be monoammonium dihydrogen phosphate ($NH_4H_2PO_4$). With added oxides of nitrogen and sulfur present in the gas stream, the major recombination products found at 160 and 90 °C were ammonium phosphate, ammonium sulfate, and ammonium nitrate salts. The apparent competition between phosphate ion and sulfate and nitrate ions for the available ammonia in the gas stream was probably exaggerated in these experiments, however, due to the low input concentrations of phosphate ion injected into the gas stream.

Large decreases in ammonia concentrations and the appearance of ammonium nitrate at 160 and 90 °C when nitrogen oxides were added to the flue gas stream strongly indicate that gas stream reactions occurred between ammonia and one or both of the added nitrogen oxides.

No phosphine could be detected, either in the presence or absence of added reactive gases, when LPA-445 was injected and the gas stream was specifically sampled and analyzed for phosphine.

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16. ABSTRACT The report gives results of a study of reactions of several flue gas conditioning agents in a laboratory-scale facility simulating conditions in the flue gas train of a coal-burning power plant. Primary purposes of the study were to characterize the chemical species resulting from adding conditioning agents to flue gas and to identify potentially hazardous chemical species originating from the agents that may be emitted into the environment. The compounds investigated were sulfur trioxide, ammonia, triethylamine, sodium carbonate, ammonium sulfate, and diammonium hydrogen phosphate. The predominant types of reactions observed in these experiments were thermal decomposition at high temperatures, recombination of decomposition fragments at lower temperatures, and reactions with normal components of the flue gas. The only significant environmental threat of any product identified during this study was the formation of N-nitrosodiethylamine as the result of injecting triethylamine into the flue gas. This potent carcinogen was found in trace amounts when triethylamine was injected at 160 C.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Sulfur Trioxide	Pollution Control	13B	07B
Treatment	Ammonia	Stationary Sources	14B	
Flue Gases	Tertiary Amines	Conditioning Agents	21B	07C
Coal	Sodium Carbonates	N-Nitrosodiethylamine	21D	
Pyrolysis	Ammonium Sulfate	Diammonium Hydrogen Phosphate	07D	
Analyzing				

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