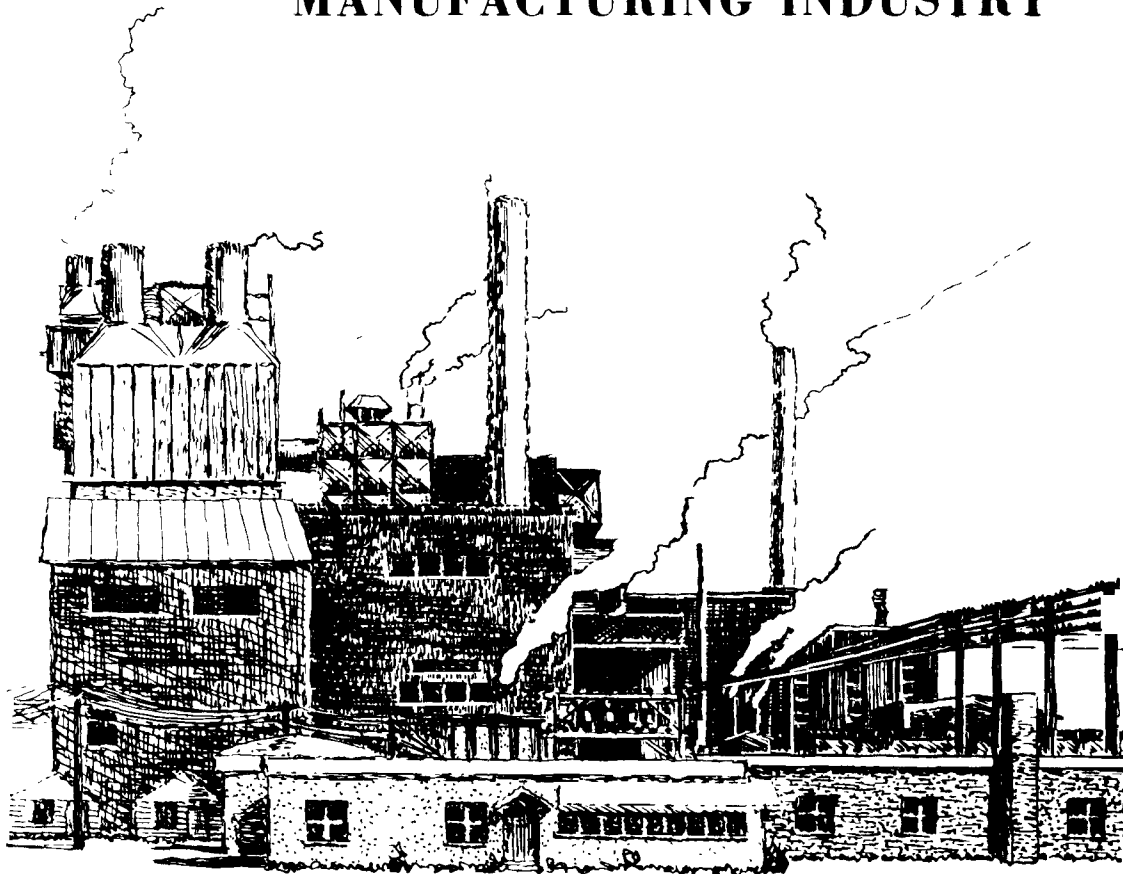# ATMOSPHERIC EMISSIONS FROM THE PULP AND PAPER MANUFACTURING INDUSTRY

U.S. ENVIRONMENTAL PROTECTION AGENCY

ATMOSPHERIC EMISSIONS
FROM THE PULP AND PAPER
MANUFACTURING INDUSTRY

ENVIRONMENTAL PROTECTION AGENCY

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PREFACE

To provide reliable information on the air pollution aspects of the pulp and paper industry, the National Council of the Paper Industry for Air and Stream Improvement, Incorporated (NCASI), and the Office of Air Quality Planning and Standards of the U.S. Environmental Protection Agency (EPA) entered into an agreement in April 1967. A cooperative program was established to study atmospheric emissions from the various industry processes and publish information about them in a form helpful to air pollution control and planning agencies and to the pulp and paper industry management. Direction of this study was vested in a NCASI-EPA Steering Committee composed at the time of completion of the following representatives:

EPA	NCASI
*Stanley T. Cuffe	*Isaiah Gellman
John L. McGinnity	Peter Wrist
Joseph J. Sableski	Malcolm L. Taylor

Mr. Edwin J. Vincent of EPA and Mr. Rusell O. Blosser of NCASI were the principal investigators during much of this project and authored much of this report. Before joining the steering committee, Mr. Joseph J. Sableski of EPA and Dr. Isaiah Gellman of NCASI also served as principal investigators.

Information in the report describes the nature and range of atmospheric emissions during normal operating conditions and the performance of established devices and methods employed to limit and control these emissions.

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*Principal representative.

ACKNOWLEDGMENTS

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ABSTRACT

This report contains information on the nature and quantities of the atmospheric emissions from chemical pulping operations, principally the kraft process. The information was gathered in a cooperative study by the National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI), and the Environmental Protection Agency (EPA). Principal sources of information were a comprehensive questionnaire sent to all the pulp mills, special NCASI studies reported in Technical Bulletins, other literature sources, and a field sampling program conducted by EPA. Control techniques are described and emission ranges reported for each of the operations involved in the chemical pulping processes.

GLOSSARY

ABBREVIATIONS

acfm	actual cubic feet per minute
ADP	air dried pulp (assumed to contain 10 percent moisture)
Btu	British thermal units
°C	degrees Celsius (centigrade)
cfm	cubic feet per minute
cm^3	cubic centimeters
dscfm	dry standard cubic feet per minute
EPA	U. S. Environmental Protection Agency
°F	degrees Fahrenheit
ft^3	cubic feet
g	grams
gal.	gallons
gpm	gallons per minute
gr	grains
hr	hours
i.d.	inside diameter
lb	pounds
max.	maximum
min.	minimum
min	minute
ml	milliliter
NCASI	National Council of Paper Industry for Air and Stream Improvement
NSSC	neutral sulfite semichemical
ppb	parts per billion by volume
ppm	parts per million by volume
psig	pounds per square inch gauge
scf	standard cubic feet
sec	seconds
T	tons
TRS	total reduced sulfur (expressed as an equivalent amount of hydrogen sulfide)

CHEMICAL SYMBOLS

$CaCO_3$	Calcium carbonate
CaO	calcium oxide
$Ca(OH)_2$	calcium hydroxide
CH_3SH	methyl mercaptan
$(CH_3)_2S$	dimethyl sulfide
$(CH_3)_2S_2$	dimethyl disulfide
CO_2	carbon dioxide
H_2	hydrogen
H_2O	water
H_2S	hydrogen sulfide
H_2SO_3	sulfurous acid
N_2	nitrogen
Na	sodium
Na_2CO_3	sodium carbonate
$NaOH$	sodium hydroxide
Na_2S	sodium sulfide
Na_2SO_3	sodium sulfate
$Na_2S_2O_3$	sodium thiosulfate
O_2	oxygen
SO_2	sulfur dioxide

DEFINITIONS

Black liquor	Liquor recovered from the digesters.
Green liquor	Liquor made by disolving smelt in weak wash liquor.
Heavy (strong) liquor	Black liquor that has been concentrated in preparation for recovery.
Oxidation efficiency	Percentage of sodium sulfide in the black liquor that is oxidized by air introduced into the liquor.
Recovery furnace	Combustion unit used to recovery the spent chemicals from the digestion liquor and to produce steam.
Smelt	Molten chemicals from the recovery furnace, consisting mostly of sodium carbonate and sodium sulfide.

Sulfiditity	Percentage of sodium sulfide to total alkali in white liquor, obtained by the formula

$$\frac{Na_2S}{Na_2S + NaOH} \times 100$$

where the sodium compounds are expressed as sodium oxide.

Weak wash liquor	Liquid stream resulting from washing of the lime mud.
White (cooking) liquor	Liquor made by causticizing the green liquor with lime. White liquor is ready for use in the digesters.
Weak liquor	Black liquor as recovered from the digesters prior to concentration (see "heavy liquor").

CONVERSION FACTORS,
BRITISH TO METRIC UNITS

Multiply	By	To obtain
British thermal units	1.06×10^3	newton-meters
cubic feet	2.83×10^{-2}	cubic meters
degrees Fahrenheit[a]	5/9	degrees Celsius (centigrade)
feet	3.05×10^{-1}	meters
gallons	3.79×10^{-3}	cubic meters
grains	6.48×10^{-5}	kilograms
inches	2.54×10^{-2}	meters
inches of water	2.49×10^2	newtons per square meter
pounds (mass)	4.54×10^{-1}	kilograms
pounds per square inch	6.89×10^3	newtons per square meter
tons	9.07×10^2	kilograms

[a]To obtain Celsius (centigrade) temperature (t_c) from Fahrenheit temperature (t_f), use the formula $t_c = (t_f - 32)/1.8$.

SUMMARY

The pulp and paper manufacturing industry consists of two well defined segments, pulping and paper making. Pulping is the conversion of fibrous raw materials such as wood, cotton, or used paper into a material suitable for use in paper, paperboard, and building materials. The principal source of the fibers is wood. The fiberous material ready to be made into paper is called pulp.

Wood pulp is prepared either mechanically or chemically. Mechanical pulp is produced by grinding or shredding wood to free the fibers. In chemical pulping processes, the wood fibers are freed by dissolving the binding material (lignin) in chemical solutions. Mechanical pulping and the paper making process itself produce negligible air pollution, except for the boilers that produce steam and electric power to run the mills. Therefore, this report is concerned only with the chemical pulping processes, power boilers, bark-burning boilers, and combination boilers. Further, emphasis is on the kraft process, which accounts for 81.5 percent of annual chemical pulp production.

PRODUCTION OF CHEMICAL PULP

In 1970, the production of pulp by chemical pulping processes and the number of mills involved were as follows:

Process	Number of mills	Production, million tons
Kraft	116	29.6
Sulfite	38	3.0
Semichemical	50	3.6
Soda	5	0.2
Total	209	36.4

CHEMICAL PULPING PROCESSES

Kraft (Sulfate) Process

In the kraft process, the digesting liquor is a solution of sodium hydroxide and sodium sulfide. The spent liquor (black liquor) is concentrated, sodium sulfate is added to make up for chemical losses, and the liquor is burned in a recovery furnace, producing a smelt of sodium carbonate and sodium sulfide. The smelt is dissolved in water to form green liquor, to which is added quicklime to convert the sodium carbonate back to sodium hydroxide, thus reconstituting the cooking liquor. The spent lime cake (calcium carbonate) is recalcined in a rotary lime kiln to produce quicklime (calcium oxide) for recausticizing the green liquor.

Sulfite Processes

Sulfite cooking liquors contain sulfurous acid and the bisulfite of calcium, sodium magnesium, or ammonia. Calcium based liquor is prepared by absorbing sulfur dioxide in water in a tower filled with crushed limestone. Sodium based liquor is formed by absorbing sulfur dioxide in a solution of sodium carbonate. Magnesium based liquor is made by absorbing sulfur dioxide in a slurry of magnesium hydroxide. Ammonium based liquor is made by absorbing sulfur dioxide and ammonia in water.

Semichemical Processes

Semichemical pulps are produced by digesting with reduced amounts of chemicals, followed by mechanical treatment to complete the fiber separation. The most extensively used process is the neutral sulfite semichemical (NSSC) process. The cooking solution is a nearly neutral sulfite solution containing an alkaline agent such as sodium carbonate, bicarbonate, or hydroxide.

Soda Process

The cooking liquor is a solution of sodium hydroxide. The spent liquor can be recovered by concentration and incineration. The make-up chemical is sodium carbonate. This process has declined to relative insignificance.

KRAFT PROCESS, SPECIFIC EMISSION SOURCES AND CONTROLS

Types of Emissions

The emissions from the kraft process include both gaseous and particulate matter. The gaseous emissions are principally hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide, and sulfur dioxide.

The particulate emissions are largely sodium sulfate from the recovery furnace, smelt tanks, and lime kiln, as well as calcium compounds from the lime kiln.

Hydrogen sulfide and the organic sulfides are extremely odorous, being detectable at a concentration of a few parts per billion. Thus odor control is one of the principal air pollution problems of a kraft pulp mill.

Digester Relief and Blow

The gases formed during batch digestion are vented to maintain proper cooking conditions. At the end of the cooking cycle, the contents of the vessel are blown to a tank at atmospheric pressure, flashing off large amounts of steam, as well as noncondensable gases. Gases formed in the digester include hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide.

The steam in relief and blow gases is usually condensed to recover heat. Noncondensables are either vented to atmosphere or treated. Treatment methods include burning, scrubbing with alkaline solutions, and chemical oxidation. Burning is usually accomplished in a lime kiln, and is the most effective method. Scrubbing with sodium hydroxide (white liquor) is effective only for hydrogen sulfide and methyl mercaptan. Scrubbing with chlorine solutions is of limited effectiveness.

Six respondents to the questionnaire presented data on relief and blow gases. No treatment facilities were indicated. Median value for relief gas emissions was 1.2 pounds per ton of air dried pulp (lb/T ADP) as total reduced sulfur (TRS). Median emission rate for blow gases was 0.08 lb/T ADP as sulfur. Eleven respondents discussed treatment facilities. Of these, six respondents indicated they burned these gases in lime kilns, and five used chlorination stage bleachery effluent for treatment. EPA field test results at two mills indicated that virtually complete destruction of reduced sulfur gases was obtained by burning in lime kilns.

Multiple Effect Evaporators

Emissions from evaporation arise from noncondensable vent gases and liquid condensate. Liquid condensate is usually sewered, and noncondensables are often vented to the atmosphere. These gases contain high concentrations of hydrogen sulfide and organic sulfides.

Noncondensable vent gases may be combined and controlled with digester blow and relief gases, using incineration or alkaline scrubbing.

Six mills reported emission data from evaporator vents. The median rate was 0.37 lb/T ADP as hydrogen sulfide.

Gaseous sulfur compounds can be stripped from evaporator condensate with steam or air and the off-gases incinerated in a lime kiln or separate incinerator.

Recovery Furnace Systems

Concentrated black liquor is burned in a furnace to produce a smelt of sodium carbonate and sodium sulfide that is used to reconstitute cooking liquor. Steam is produced as a by-product.

In a conventional system, the final stage in concentrating the black liquor utilizes the furnace flue gas in a direct contact evaporator. Emissions from the system are those originating in the furnace plus those released in the direct contact evaporator.

Gaseous emissions from the recovery furnace include hydrogen sulfide and much smaller amounts of organic sulfides. These emissions are very low from a well regulated furnace but can be considerable if operation is not optimum.

Considerable amounts of hydrogen sulfide can be released in the direct contact evaporator by the reaction of the acidic gases in the flue gas with the sodium sulfide in the liquor. Such emissions can be reduced by black liquor oxidation, which converts the sodium sulfide to sodium thiosulfate, a more stable form. The amount of emission reduction is dependent on the degree of oxidation. Very low levels, 0 to 3 parts per million (ppm) TRS, can be reached as the degree of oxidation approaches completeness.

Several alternate systems that do not use a direct contact evaporator have been developed, thus eliminating this source of emissions. One system utilizes additional stages of indirect evaporation of the black liquor plus additional heat exchange surface in the furnace. The other system utilizes a flue gas-to-air heat exchanger plus an air contact evaporator. The flue gas imparts heat to a stream of air. The air then concentrates the black liquor in a contact evaporator. This air is then used as combustion air in the furnace. A modification of this system eliminates the contact evaporator but retains the heat exchanger to preheat the combustion air. Additional indirect evaporation of the black liquor is also used in this system.

Total reduced sulfur emission data were reported for 42 conventional recovery furnace systems where black liquor oxidation was not used. Median TRS emission rate was 5.9 lb/T ADP. The EPA test team measured TRS emission rates from two mills with well designed and operated black liquor oxidation systems. Emission rates were 0.19 and 0.075 lb/T ADP, respectively.

Particulate emissions from the recovery furnace consist primarily of sodium sulfate and sodium carbonate caused by small particle carry-over and sublimation-condensation.

The electrostatic precipitator is the most widely used particulate control device. Secondary scrubbers are sometimes used after electrostatic precipitators. Where used, direct contact evaporators function as precleaners. Two-stage venturi systems function as both direct contact evaporator and final particulate collector.

Particulate emission data from 87 kraft recovery furnace systems with direct contact evaporators and electrostatic precipitators were reported in the questionnaire survey. The range of emission rates was 1.3 to 95 lb/T ADP. The median rate was 14 lb/T ADP, with 10 percent less than 2.5 and 44 percent less than 10 lb/T ADP. Data for 10 venturi recovery units show a range of 15 to 115 lb/T ADP, with a median value of 45 lb/T ADP. Emissions from seven systems with scrubbers following electrostatic precipitators had a range of 1.8 to 13 lb/T ADP, with a median value of 2.8 lb/T ADP.

Black Liquor Oxidation Systems

Black liquor oxidation is the practice of oxidizing the sodium sulfide in the liquor at least to the sodium thiosulfate stage, using air or oxygen, as represented in the following equation:

$$2Na_2S + O_2 + H_2O \quad Na_2S_2O_3 + 2NaOH$$

Sodium thiosulfate will not react with carbon dioxide and sulfur dioxide in the flue gas to produce hydrogen sulfide as does sodium sulfide.

Oxidation can be performed on either weak or heavy (strong) black liquor. Packed towers or bubble tray towers are used for weak liquor oxidation. Air sparged reactors, some with mechanical mixers, are used to oxidize heavy liquor. Oxidation of weak liquor may reduce emissions in the evaporation process, but reversion to sulfide in subsequent evaporation stages or in storage may cancel this benefit. Heavy liquor oxidation is advantageous in oxidizing liquors high in resin soap, which foam excessively when oxidized weak.

During the oxidation of black liquor, the air passing through the liquor strips out some reduced sulfur gases. Data from the questionnaires, EPA tests, and special studies give median values of reduced sulfur emissions of 0.14 lb/T ADP for weak black liquor oxidation systems and 0.10 lb/T ADP for strong liquor systems.

Smelt Dissolving Tanks

The molten smelt from the recovery furnaces is discharged into a tank of water to form green liquor. Particulate emissions are entrained in the vent gases. Some reduced sulfur gases are formed by reactions in the tank.

Wire mesh mist eliminators are the most widely used particulate control device. Scrubbers and cyclones are also used. Questionnaire data give a median emission rate to the atmosphere of 1.0 lb/T ADP. An EPA test gave a rate of 0.8 lb/T ADP from a smelt tank controlled by a wire mesh mist eliminator.

Gaseous emission test data from questionnaire data gave a median emission rate of TRS of 0.1 lb/T ADP as hydrogen sulfide. Two EPA tests gave an average rate of 0.03 lb/T ADP.

Lime Kilns

Lime kilns supply quicklime, which is slaked and used to causticize the green liquor to produce white liquor. The spent lime mud, $CaCO_3$, is recycled back to the lime kilns.

Particulate emissions consist of sodium salts from sublimation-condensation of salts retained in the sludge and calcium carbonate and calcium oxide resulting from entrainment. Hydrogen sulfide can be formed from the reaction of carbon dioxide in the flue gas with sodium sulfide remaining in the lime mud after washing. Other organic sulfides can originate in the scrubbing liquor used in the particulate control device.

Impingement scrubbers and medium efficiency venturi scrubbers are used in controlling particulate emissions. Questionnaire data yielded a median emission rate of 2.7 lb/T ADP at a concentration of 0.4 grain per dry standard cubic foot. Two EPA tests gave an average emission rate of 1.6 lb/T ADP from a venturi scrubber. Gaseous emission data from the questionnaires gave a median emission rate for TRS gases of 0.43 lb/T ADP. Two EPA test gave an average emission rate of 0.23 lb/T ADP.

Brown Stock Washers

Gaseous emissions from brown stock washers occur from two points, the roof vents of the hood over the filter and vents of vacuum pumps, called under vents. The emissions are predominantly dimethyl sulfide and dimethyl disulfide.

The level of the emissions changes when condensate is used instead of fresh water. A special study of 17 washing systems gave median results as follows: roof vents using fresh water — 0.04 lb/T ADP as hydrogen sulfide; roof vents using condensate — 0.35 lb/T ADP; undervents using fresh water — 0.08 lb/T ADP; undervents using condensate — 0.11 lb/T ADP.

Emission Ranges

From all the data acquired in the conduct of the study, typical values were selected to illustrate the range of emissions from kraft mill operations.

These data are tabulated below. In most cases, the average emission rate is approximately in the middle of the range. The emissions are to the atmosphere, following control devices where used.

Process	Emission rate, lb/T ADP	
	Particulates	TRS
Recovery furnaces	1 to 25	0.05 to 12
Smelt tanks	0.05 to 2	0.01 to 0.6
Lime kilns	0.5 to 7	0.02 to 1
Digesters	—	0* to 2
Multiple effect evaporators	—	0* to 1.5
Black liquor oxidation	—	0.05 to 0.2
Brown stock washers	—	0.01 to 0.9

SEMICHEMICAL SULFITE PROCESS

Semichemical pulps are produced by digesting with reduced amounts of chemicals followed by mechanical treatment to complete the fiber separation. The most extensively used process is the neutral sulfite semichemical (NSSC) process. The cooking solution is a nearly neutral sulfite solution containing an alkaline agent such as sodium carbonate, bicarbonate, or hydroxide.

Spent cooking liquor may be discharged as a liquid effluent or concentrated and burned with or without chemical recovery. In some cases, a fluid bed furnace recovers the chemical as sodium sulfate and sodium carbonate, which can be used as make-up chemicals in a kraft process. In others using the cross-recovery method, the spent liquor is combined with kraft black liquor for recovery and reuse in the kraft process.

Gaseous emissions in the NSSC process are essentially limited to sulfur dioxide, except that in those cases where kraft-type green liquor is sulfited hydrogen sulfide may be emitted. Emissions sources are blow tanks, spent liquor evaporators, and the liquor burning or chemical recovery furnace. Absorbers may be controlled by extra absorption stages. Blow gases can be controlled by venting to the absorber. Recovery furnace processes control sulfur dioxide absorption. Nonrecovery burning processes vent sulfur dioxide to the atmosphere. No significant emission data were obtained from the questionnaires.

SULFITE PROCESS

Sulfite cooking liquors contain sulfurous acid and the bisulfite of a base such as calcium, sodium, magnesium, or ammonium. Recovery processes can be used with all bases except calcium, for which scaling is excessive.

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*Noncondensables incinerated in a lime kiln.

Sources of sulfur dioxide emissions are blow pits, digester relief vents, absorbers, and recovery furnaces. Relief and blow gases can be controlled by extra stages or scrubbers. Recovery furnaces are controlled by an absorption or scrubbing system. Nonrecovery burning processes vent sulfur dioxide to the atmosphere.

Twenty sulfite mills returned questionnaires. Fifteen of the 20 used some control on absorbers, 15 of 16 controlled digester relief gases, and 4 of 18 controlled blow gases. No significant emission data were give.

STEAM AND POWER GENERATION

Pulp and paper mills generate steam in industrial type boilers. Questionnaire information was provided by 288 mills, representing 66 percent of the total pulp and/or paper produced. Fuels consumed by these mills were: coal — 26,000 tons/day, oil — 3,450,000 gallons/day, gas — 498 million cubic feet/day, and bark/wood waste — 24,300 tons/day.

Coal and oil used had mean sulfur contents of 1.9 and 1.8 percent, giving a total sulfur dioxide emission rate of 1470 tons per day.

Particulate emission data were reported for 17 boilers fired with coal, all controlled by cyclone type collectors. Average emission rate was 0.39 grain per standard cubic foot, or 18 pounds per ton of coal.

Particulate emission data were reported for 26 boilers fired with bark/wood waste plus other fuels. All these boilers were controlled by cyclone collectors. Average emission rate was 0.45 grain per standard cubic foot. This is equivalent to 23 pounds per ton of bark/wood burned.

Data are also presented for the single electrostatic precipitator that has been installed on a combination coal/bark fired boiler. Emissions from this boiler were reported as 0.0052 grain per standard cubic foot.

ATMOSPHERIC EMISSIONS FROM THE PULP AND PAPER MANUFACTURING INDUSTRY

INTRODUCTION

BACKGROUND

Information in this report describes the nature and range of atmospheric emissions from pulp and paper manufacturing operations during normal operating conditions as determined from survey questionnaires completed in the early phases of the study. In the interim, the Enviromental Protection Agency (EPA), in cooperation with three mills, conducted a program of stack sampling and analysis specifically for this study. Data from this study are also included. The period from initiation of this study until preparation of the report also represents a period during which strides were made by the industry in a series of special studies to define the reduced sulfur emission control capabilities of the kraft recovery furnace system, which includes the kraft recovery furnace and the contact evaporator. This technology is included as a portion of the report since it represents a significant element in the performance of process operations and control devices and the methods employed to limit and control the emissions from these sources. Also included is information on emissions from miscellaneous sources such as black liquor oxidation vents, brown stock washer systems, and lime kilns. This information was generated in special studies reported in the literature, the above referenced field sampling programs conducted by EPA, and a special study conducted by the National Council of the Paper Industry for Air and Stream Improvement (NCASI). [1]

SOURCES OF INFORMATION

Various sources of information about pulping operations and atmospheric emissions were utilized in compiling this report. The principal sources were:

1. Questionnaire surveys conducted in 1968.
2. Field investigations, including source sampling conducted in 1969, 1970, and 1971.
3. The literature.

1

The emission data presented in this report were developed using different sampling and analytical procedures. Those gaseous emission data gathered in special studies and field investigations were collected using analytical procedures considered to be much more sensitive and precise than those used earlier, when these procedures had not been developed, to collect data for the questionnaire surveys. Current definitions of particulate matter and the procedures used for sampling may also be more sensitive than those used for collection of the particulate data for the questionnaire surveys. A summary of the sampling and analytical procedures used during collection of the data is presented in Appendix B.

Questionnaire Surveys

Three questionnaire surveys were conducted:

1. Kraft pulp industry survey.
2. Acid sulfite and nonintegrated neutral sulfite semichemical (NSSC) pulp industry survey.
3. Steam and power boiler survey.

The comprehensive kraft questionnaire form was sent to 116 mills. Returned forms with usable information were received from 80 of these mills. Very few of the mills were able to answer all of the questions on the form. The data on each process or operation were tabulated and summarized. These tables are found in the sections where the operations are discussed and in Appendix A.

The sulfite questionnaire form was sent to 60 mills. Forms were received from 34 of these mills. The amount of information obtained from this survey was rather limited. The information is summarized and discussed in the section on sulfite processes.

The power boiler survey was sent to 450 mills, and replies were received from 288 of these mills. The information is summarized and discussed in the section on power boilers.

Field Sampling Program

The objectives of the field sampling program were to obtain data to verify the reasonableness of the emission data reported on the questionnaires and to obtain emission data from well controlled mills.

A mobile source sampling laboratory was developed by the Emission Measurement Branch of the Office of Air Quality Planning and Standards. A continuous heated gas sampling line transfers a filtered sample to a dynamic dilution system. This system provides dilution levels

up to six orders of magnitude. The diluted samples are delivered to various instruments. The instruments installed included two gas chromatographs, employing a flame photometric detector; a total sulfur analyzer, also employing a flame photometric detector; coulometric titrator; an oxygen analyzer; a carbon dioxide analyzer; a carbon monoxide analyzer; and particulate sampling equipment. Details of the equipment are given in Appendix B.

Field sampling was conducted at three mills. Only limited data were obtained at Mill A, as this was the initial operation of the equipment. More extensive information was obtained at Mills B and C. These mills were selected because they had good air pollution control programs and the results were expected to typify the emission levels from well controlled plants. The results are reported under the description of process emissions and their control in the appropriate sections of the report. Limited odor surveys were conducted at Mills B and C. Results were rather inconsistent and are reported in Appendix C.

Literature

Several literature sources provided information for this report. Published literature in text books[2,3] and the final report, "Control of Atmospheric Emissions in the Wood Pulping Industry,"[4] of a study conducted for EPA served as the basis for materials on process descriptions. Information on emissions, particularly that referring to definitions of control technology capabilities and miscellaneous source emissions, was derived from several sources. These included technical journals and papers presented at technical meetings but as yet unpublished. NCASI Technical Bulletins, as well as data collected as part of ongoing special study programs but not yet published in Technical Bulletin form, also served as sources of information.

PULP AND PAPER MANUFACTURING INDUSTRY

The pulp and paper manufacturing industry is reported to be the ninth largest manufacturing industry in the United States, accounting for nearly 4 percent of the value of all manufacturing. It consists of two well defined segments, pulping and paper making. Pulping is the conversion of fibrous raw materials such as wood, cotton, or used paper into a material suitable for use in paper, paperboard, and building material. Wood is the dominant source of fibers for paper production. Pulp is produced by two general methods: mechanical pulp is produced by grinding or shredding the wood to free the fibers; chemical pulp is produced by cooking wood chips in chemical solutions that dissolve the lignin binding material. Since the air pollution aspects of the chemical pulping processes are much more significant than those of the mechanical processes, this report will only be concerned with the chemical processes.

Introduction   **3**

The kraft process is the leading chemical pulping process. A solution of sodium hydroxide and sodium sulfide is used as cooking liquor. The spent liquor is concentrated and burned in a furnace to recover the chemicals. The sulfide process utilizes a cooking liquor made by absorbing sulfur dioxide gas in a solution or slurry of one of the following base chemicals: sodium carbonate, magnesium hydroxide, ammonia, or calcium carbonate. Chemical recovery may or may not be practiced. Semichemical pulps are produced by digesting with reduced amounts of chemicals, followed by mechanical treatment to complete the fiber separation. The soda process utilizes a solution of sodium hydroxide for digestion.

Practically all of the wood pulp produced in the United States is consumed in this country, with only approximately 7 percent exported.[5] Imported wood pulp is equivalent to approximately 10 percent of the pulp manufactured in this country. Wood pulp accounts for approximately 80 percent of the raw fiberous material for paper and board manufacturing in the United States, the remaining 20 percent consisting generally of recycled paper. In addition, significant quantities of filler and coating materials are employed to achieve desired product properties. About 90 percent of the wood pulp produced is used on site for the manufacture of paper, paperboard, and building paper products.

The nature of air quality protection measures in the pulp and paper manufacturing industry closely parallels the nature and growth of its chemical pulping industry. The air quality protection problems of paper and paperboard manufacturing, and mechanical pulping as well, are minor, consisting almost entirely of those from the combustion of fuel used to generate steam and power.

Current Production

The production of wood pulp in the United States in 1969 was 41 million tons (air dry). Of this, 27.6 million tons of paper grade pulp and a small amount (less than 1 million tons) of dissolving and alpha cellulose pulp were made by the kraft process Paper grade pulp produced by the sulfite process amounted to 2.3 million tons, with less than 1 million tons of alpha and dissolving pulp made by this process. Semichemical pulp production was 3.4 million tons. Other grades of pulp produced (mechanical, defibrated, exploded) amounted to 5.3 million tons. The capacity for wood pulp production in 1969 was 45.6 million tons.[6]

There were reported to be 209 chemical pulp mills at the end of 1970. One hundred and sixteen were kraft mills, 38 sulfite mills, 50 semichemical pulp mills, and 5 soda mills. These data are summarized in Table 1.

Industry Growth Trends

The per capita consumption of paper and paperboard in the United States is a relative indication of growth in the U. S. wood pulping industry since the amount of imported wood pulp used in these products through the

**Table 1. SUMMARY OF U.S. CHEMICAL
PULP MILL PRODUCTION, 1969**

Process	Number of mills	Annual production, million tons
Kraft	116	29.6
Sulfite	38	3.0
Semichemical	50	3.6
Soda	5	0.2
Total	209	36.4

years has been small. The consumption of paper and paperboard has shown an annual growth rate of about 3 percent. In 1970, the pulp and paperboard consumption was 56.8 million tons, or 556 pounds per person.

It has been estimated that chemical pulp production will double between 1970 and 1985, rising by about 35 million to 70 million tons annually.[4] As shown earlier, over 80 percent of the current annual chemical pulp production is produced by the kraft process. This or a more dominant position for the kraft chemical pulping process is projected through 1975.[4] While forecasts are subject to the hazards of a changing economy, there is no reason to suspect that chemical pulping will not experience a continuing favorable growth rate. Neither is there reason to suspect a major rearrangement in the position of processes used for the manufacture of chemical pulp during the previously referenced 15-year projection. Radical changes in technology, however, although not now expected, could result in such a shift by the end of the 15-year period.

Introduction   **5**

KRAFT (SULFATE) PULPING PROCESS

INTRODUCTION

Process Description

The kraft pulping process (Figure 1), which came into being in 1879, was a modification of the caustic soda system in that sodium sulfide was added to the cooking liquor. The introduction of the spray type recovery furnace in the period 1928 to 1934 brought about a tremendous increase in the use of kraft pulp; recovery of cooking chemicals from kraft spent liquor is essential for the kraft process to be competitive in cost with other processes. The recovery of chemicals is accomplished by spraying concentrated spent liquor (black liquor) into the recovery furnace, where the organic compounds are burned and an inorganic smelt of sodium sulfide and sodium carbonate is formed. To make up for chemicals lost in the operating cycle, salt cake (sodium sulfate) is usually added to the concentrated spent liquor before it is sprayed into the furnace.

The smelt of sodium sulfide and sodium carbonate flows from the furnace and is dissolved in water to form green liquor. This solution is reacted with quicklime to convert the green liquor to cooking liquor (white liquor), which is a solution of sodium hydroxide and sodium sulfide. The calcium carbonate created by this reaction is settled out, dewatered, and burned in a lime kiln. The resultant calcium oxide is returned for reaction with the green liquor to close the chemical recovery cycle.

Raw Materials and Process Characteristics

The presence of caustic soda in the cooking liquor permits the pulping of practically all wood species. The other active chemical, sodium sulfide, has a buffering action that allows digestion to take place at a lower $(OH)^-$ ion concentration, thus reducing damage to the fibers and producing pulps that are stronger than those made from NSSC or sulfite processes. Small amounts of sodium sulfide react with lignin and carbohydrates in the wood to form odorous compounds that may cause a reduction of air quality.

Cooking chemicals (caustic soda and sodium sulfide) are expensive relative to chemicals used in some other pulping processes. Thus their recovery is an economic necessity. During the recovery process, steam is produced from the combustion of the organic materials, adding to the economic benefits of the recovery system.

7

Figure 1. Kraft pulping process.

The kraft process produces a dark-colored pulp that normally represents from 45 to 50 percent of the initial weight of the wood used. Because of its dark color, the unbleached pulp is usually used only in board, wrapping, and bag papers. For use in the manufacture of white papers, the pulp must be treated further in a bleach plant.

Emission Sources

Gaseous Emissions

The kraft mill odor problem arises from the use of sodium sulfide as one component of the disgesting liquor. In the digesters, the sulfide ion from the sodium sulfide combines with various organic side-chain radicals from the cellulose and the lignin of wood chips to form such organic sulfides as methyl mercaptan, CH_3SH; dimethyl sulfide, $(CH_3)_2S$; dimethyl disulfide, $(CH_3)_2S_2$; and small amounts of similar ethyl sulfide compounds.[7] In addition, hydrogen sulfide is formed in considerable amounts. These gases are released with the digestor relief and blow gases, as well as other sources.

These sulfides are extremely odorous, being detectable at concentrations as low as 1 part per billion (ppb). Table 2 shows odor thresholds for some of the compounds mentioned above.[8,9]

Table 2. ODOR THRESHOLDS OF SOME MALODOROUS SULFUR COMPOUNDS

Compound	Odor threshold, ppm
H_2S	0.0047^a
CH_3SH	0.0021^a
$(CH_3)_2S$	0.0010^a
$(CH_3)_2S_2$	0.0056^b
SO_2	0.47^a

[a] Odor threshold defined as the concentration at which all panel members detect odor.

[b] Odor threshold defined as the median concentration detected by the individual panel members.

The residual sodium sulfide and other sulfur compounds in the spent cooking liquor (black liquor) can be the source of additional emissions. In the multiple effect evaporators, the sodium sulfide reacts with dissolved lignin to produce additional amounts of the gases mentioned above. These gases are released from the noncondensables vents of the evaporator condenser. Other unit processes that handle black liquor in a manner permitting its contact with ventilation air, such as brown stock washing systems and black liquor oxidation systems, are also sources of reduced sulfur emissions. Scrubbers designed to control particulate emissions sometimes use process water containing residual sulfur compounds and are

a source of gaseous sulfur compounds. The kraft recovery furnace system, which in most cases includes a direct contact evaporator, is the largest potential source of reduced sulfur emissions. Sulfur dioxide is also a potential emission. Smelt tanks can also be a source of reduced sulfur compounds. In the direct contact evaporator, carbon dioxide in the flue gas from the recovery furnace reacts with sodium sulfide in the black liquor to produce hydrogen sulfide. In the lime kiln, carbon dioxide in the combustion gases can react with sodium sulfide remaining in the wet lime mud after incomplete washing to produce hydrogen sulfide.

Particulate Emissions

Particulate emissions occur primarily from the recovery furnace, the lime kiln, and the smelt dissolving tank. They are caused mainly by the carry-over of solids plus the sublimation and condensation of inorganic chemicals. The sublimation and condensation produce a fume that initially is probably submicron in size but has a tendency to agglomerate. In addition, particulate emissions occur from power boilers and boilers fired with bark in combination with other fuels.

Particulate emissions from the recovery furnace consist primarily of sodium sulfate and sodium carbonate. These emissions may be carried up by the furnace draft or formed by the vaporization-condensation step. The high flue gas velocity may cause the carry-up of small droplets of black liquor that have been sprayed into the furnace. These droplets should burn in the oxidizing zone, but the resulting fine particles may be carried out of the furnace.

Particulate emissions from the lime kiln consist principally of sodium salts, calcium carbonate, and calcium oxide. The sodium salts result primarily from the sublimation-condensation of salts that are retained in the sludge because of incomplete washing. Calcium carbonate and calcium oxide emissions result from entrainment.

Particulate emissions from the smelt dissolving tank are primarily caused by the entrainment of particles in the vent gases. Because of the violent reactions taking place in each of these tanks, it is reasonable to expect that the turbulence of the dissolving water will splash droplets containing both dissolved and undissolved inorganic salts above the surface. These droplets may be carried out by the vent gases if they are not of sufficient weight to drop back into the liquid.

Emissions Control Systems - General

Gaseous Emissions

Three general principles are utilized in controlling gaseous emissions from kraft mill operations: effluent treatment, process control, and process change. Combustion, absorption, and liquid phase oxidation are examples of effluent treatment. Process control involves the manipulation of process

variables to minimize emissions. Process change includes the alternation, elimination, or addition of unit process equipment or operations.

Combustion involves the thermal oxidation of reduced sulfur compounds in pulp mill noncondensable gases to sulfur dioxide. For example, noncondensable gases from the multiple effect evaporators and digestors can be vented to the inlet of the combustion air fan of the lime kiln. In some cases, a separate incinerator is used if the distance from the source to the lime kiln makes installation costs prohibitive. Sulfur dioxide is considered less objectionable than the compounds from which it was formed. In the lime kiln, most of the sulfur dioxide reacts with lime in the kiln or is absorbed in the scrubber that controls particulate emissions from the kiln. The volume of the lime kiln combustion air limits the volume of emissions that can be handled in this manner. There is also a limited practice of combustion of gases from digestion and evaporation as well as those from brown stock washer system vents in the recovery furnace.

Absorption usually involves scrubbing the gas stream with an alkaline process liquor, such as sodium hydroxide, lime mud weak wash, or white liquor. Absorption is limited to gases containing little or no carbon dioxide, such as evaporator or digester noncondensable gases and those from smelt tanks. Effectiveness is limited largely to hydrogen sulfide and methyl mercaptan removal. Packed towers and sprayed mist pads are the types of scrubbers usually used for absorption.[4]

Liquid phase oxidation is used to convert reduced sulfur compounds to less odorous or more stable substances. Oxidizing agents used are chlorine, atmospheric oxygen, and molecular oxygen.

Chlorination can be used on streams containing sulfur gases such as those from digester relief and blow condensers and multiple effect evaporator vents. A portion of the required chlorine is frequently available in the chlorination stage washer effluent from the bleach plant, if present. The dimethyl sulfide is absorbed and oxidized to sulfone. The dimethyl disulfide is absorbed and oxidized to methyl sulfonyl chloride. This technique is of limited effectiveness.

Black liquor oxidation is accomplished by the use of atmospheric oxygen, or occasionally tonnage oxygen. This operation oxidizes the sodium sulfide in the liquor to sodium thiosulfate. The purpose is to prevent the formation of hydrogen sulfide by carbon dioxide and sulfur dioxide in the recovery furnace flue gases.

Process control as a means of minimizing reduced sulfur emissions is applicable to both the recovery furnace and lime kiln. Proper manipulation of process feed rate and air supply both result in minimizing emissions from these sources. The thoroughness of lime mud washing, which is reflected in the amount of residual sulfide, also affects emissions from the lime kiln.

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Process and equipment change — An example of a process and equipment change is black liquor oxidation. This process, described earlier, is designed to minimize emissions from the flue gas direct contact evaporator by stabilizing sulfur to prevent its loss from black liquor brought in contact with flue gas.

Another example of an equipment and process change designed to minimize reduced sulfur emissions is the elimination of the flue gas direct contact evaporator. This is accomplished in one of two systems. Both extend the heat recovery systems commonly employed on recovery furnaces. One uses heated air from an indirect heat recovery unit for direct contact concentration of black liquor. This air is used as combustion air in the furnace. The second utilizes additional steam produced from an added economizer section to carry evaporation in a forced circulation concentration stage beyond that point normally accomplished in multiple effect evaporation.

Particulate Emissions

In the kraft pulping process, particulate emissions are controlled by electrostatic precipitators, scrubbers, cyclone collectors, and wire mesh demister pads.[4]

The high-voltage electrostatic precipitator is the dominant type of collector used to control recovery furnace particulate emissions. Most precipitators are designed for collection efficiencies of 90 to 99+ percent. In some instances, a low- or medium-energy scrubber is installed after the precipitator. Such scrubbers can be effective because of their agglomerating effect.

Scrubbers may be used for particulate emission control from several sources. A venturi recovery system using black liquor as a scrubbing medium serves as a primary particulate collection device as well as a flue gas direct contact evaporator. Lime kiln particulate emissions are exclusively controlled by scrubbers. Some smelt tank vent particulates are controlled with scrubbers. Secondary scrubbers are installed behind the primary collection devices, electrostatic precipitators, or venturi recovery units on kraft recovery furnaces.

Cyclone collectors, and wire mesh demister pads and scrubbers are used to control particulate emissions from smelt tanks. A liquid spray, usually lime mud weak wash, is used, in most cases, with these devices.

SPECIFIC EMISSION SOURCES AND CONTROLS

Digester Relief and Blow

The batch digestion of wood chips takes place in large cylindrical mild-steel vessels averaging about 4000 cubic feet (ft^3) in volume. The chips are cooked at temperatures ranging from 170 to 175 degrees Celsius ($^\circ$C) and

pressures ranging from 100 to 135 pounds per square inch gauge (psig). At the end of the cooking cycle, the contents of the digester vessels are blown to a tank at atmospheric pressure, flashing off large amounts of steam as well as noncondensable gases. Digesters are also equipped with a noncondensable relief-vent system for use during the cook. Most kraft pulping is done in batch digesters; although increasing numbers of continuous digesters are being employed in the industry.

Emissions

The objectionable odors from the digester are a result of the chemistry of the digestion process. The active ingredients in the cooking liquor normally consist of about three-fourths sodium hydroxide and one-fourth sodium sulfide in water solution. Sodium sulfide provides sulfide ions that combine with organic components of the wood to produce organic sulfides.

The organic sulfides formed in the digester include methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. Other sulfides in smaller amounts, as well as terpenes, may also be present.

Control Techniques

As previously stated, the flashed material from the blow tank, as well as the relief stream, consists of both steam and malodorous noncondensable and condensable organic materials, including turpentine. The steam is usually condensed to recover heat. Some of the odorous materials are also condensed in this process. The noncondensable fraction containing hydrogen sulfide and organic sulfides can then be vented to a control device.

In most cases, relief gas is piped to a vapor-liquid separator such as a cyclone, to recover entrained cooking liquor, before going to the condenser. If turpentine recovery is economical, as it is in many southern mills that cook softwood (pine) chips, the vapor from the cyclone is condensed and sent to a decanter, which separates the liquid turpentine for storage, the water being sewered. Noncondensables from the condenser are either vented to atmosphere or treated.

The blow gases are condensed in a direct-contact condenser or in a surface condenser. Noncondensable gases are vented from this condenser. The condenser cooling water recovers the heat in the blow steam and may be used in some other process such as the cooking liquor make-up system.

Methods used to dispose of noncondensable malodorous sulfur compounds include burning, scrubbing with an absorbent, and chemical oxidation. The methods most prevalent in the industry are burning and scrubbing.

Burning of the gases is accomplished in the lime kiln or in a special separate incinerator.[10] In burning, care must be taken to avoid the occurrence of explosive mixtures. In a batch digestion system, the problem of preventing large surges of gas to the burning device arises. Gas surge

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capacity is provided by using either large spherical tanks equipped with a movable nonporous diaphram[11] or conventional gas holders. Burning can be a very effective technique for disposal of these gases. Data in the section on lime kilns illustrate this point.

Scrubbing the gas stream with a sodium hydroxide solution offers a partial control method for digester emissions. Effectiveness is limited to hydrogen sulfide and methyl mercaptan. Some mills use such scrubbers for preliminary treatment of gases before burning them. Three objectives are achieved: (1) some sulfur is recovered, (2) steam is condensed, and (3) turpentine vapors and mists are removed, mitigating an explosion hazard.

Scrubbing with chlorine solutions is practiced in some mills. In the case of bleached kraft mills, chlorine-containing effluent from the bleach plant may be used to scrub the gases. It is necessary that residual chlorine be present at all times in these effluents to maintain the effectiveness of this technique, which is of limited effectiveness at best.

Emission Data

Questionnaire Data—Of 80 respondents to the questionnaires, 6 presented data on the composition and amount of sulfur compounds in the relief and blow gas streams from batch digesters. No treatment facilities were indicated.

The data are presented in Table 3. The emission rates on a weight basis were computed on the assumption that the average flow rate multiplied by the duration and the number of cooks per day was a measure of the total daily gaseous effluent volume. The validity of this assumption is not known. For units 3 and 5, the average flow rate of blow gases is the rate ahead of the condenser. The gas concentrations appear to be taken after the condenser. Hence, the weight rates of sulfur gases computed for these mills is probably incorrect. Disregarding these two values, the median value of total reduced sulfur (TRS) from blow gases was derived as 0.40 pound per ton of air-dried pulp (lb/T ADP). The median value for TRS from relief gases is 1.03 lb/T ADP as hydrogen sulfide.

Two plants submitted sample data on the combined relief and blow gas noncondensable streams from continuous digester systems prior to any treatment. These data are summarized in Table 4.

Of 80 respondents to the questionnaires, 16 indicated they treated their relief or blow gas noncondensables in some way, and eight indicated they did not. The remaining respondents did not indicate whether or not they employed control techniques for these sources. Of those providing description of their treatment method, six burned the gases in lime kilns, five used chlorination stage bleachery effluent for treatment. one used a catalytic afterburner, one scrubbed with black liquor, and one vented the gases into the black liquor oxidation tank. Data adequate to evaluate the operation were not given in any of these questionnaires.

Table 3. GASEOUS EMISSIONS FROM DIGESTER RELIEF AND BLOW, QUESTIONNAIRE DATA

Source	Unit	Production rate, T ADP/day	Average gas flow rate, acfm	Gas temperature, °F	Duration, min.	Cooks per day	SO_2, ppm	Reduced sulfur gases, ppm				TRS as H_2S		
								H_2S	CH_3SH	$(CH_3)_2S_2$	$(CH_3)_2S_2$	ppm	lb/day	lb/T ADP
Relief gases	1	225	50	75	160	21	0	0	10	0	93	196	2.7	0.012
	2	260	60	130[a]	150	54	—	—	1150	—	—	1,150	42.8	0.16
	3	875	272	83	150	59	0	0	2742	1,892	—	4,634	902	1.03
	4	520	46	90	160	45	18	142	2060	19,800	2000	26,000	690	1.33
	5	740	1,574	100[a]	150	58	—	29	126	570	206	1,137	1220	1.65
Blow gases	6	695	3,700	212[a]	10	72	—	2	35	—	—	37	—	0.009
	2	260	5,000	205[a]	12	54	—	—	375	—	—	375	80.3	0.31
	4	520	1,630	170	13	45	660	223	2000	452	1350	5,375	357	0.69
	1	225	5,600	205[a]	20	21	0	69	461	220	415	1,570	224	1.03
	5	740	115,000	205[a]	14	58	—	169	127	210	292	1,090	6700	9.1
	7	875	52,000	212[a]	12	59	0	20	3110	393	143	3,809	9200	10.5

[a] Assumed temperature.

Table 4. SULFUR COMPOUND EMISSIONS FROM CONTINUOUS DIGESTERS, SUMMARY OF QUESTIONNAIRE DATA

Compound	Emission rate, lb/T ADP	Number of mills
H_2S	0.0021 and 4.17	2
SO_2	—	—
CH_3SH	0.13	1
$(CH_3)_2S$	0.303	1
$(CH_3)_2S_2$	1.04	1

EPA Test Results—Two systems for treatment of noncondensable gaseous emissions from digester relief and blow and from multiple effect evaporator vents were sampled by the EPA test team.

Mill B operated both batch digesters and a continuous digester, with a combined capacity of about 1150 T/day. Relief and blow gases are collected in a vaporsphere similar to that described by Morrison.[1] The gases from the vaporsphere are scrubbed in a rock-filled packed tower utilizing weak wash liquor. The scrubber removes some of the sulfur gases and most of the turpentine vapors. The multiple effect evaporator gases are scrubbed in a packed tower with white liquor. Tests by mill personnel indicate that the scrubber removes essentially all the hydrogen sulfide and methyl mercaptan, which represent about 96 percent of the sulfur compounds from this stream. The outlet gases from the two scrubbers are combined and vented into the combustion air fan of the lime kiln. This stream was sampled by the EPA test team. The plant flow meter indicated an average flow rate of 20 cubic feet per minute (cfm). Results are given in Table 5.

Mill C operated only a continuous digester. The condensate from the blow heat recovery system is stripped of sulfur gases by aeration. This off-gas, together with the noncondensable gases from the digester relief and the multiple effect evaporator vents, is piped directly to the lime kiln for burning. The total volume of this gas stream had been measured by plant personnel at 380 standard cubic feet per minute (scfm) at a mill production rate of 500 T ADP/day. The composition of the stream was sampled by the EPA test team. Results are given in Table 5.

Tests run on the emissions from this lime kiln revealed only traces of organic sulfur compounds, as noted in the section on results of EPA tests of lime kilns later in the report. This indicates that burning these gases is a very effective treatment method.

Table 5. COMPOSITION OF GAS STREAMS VENTED TO LIME KILN, EPA TEST RESULTS

| Mill | Reduced sulfur gases, ppm | | | | | TRS as H_2S | | |
	H_2S	SO_2	CH_3SH	$(CH_3)_2S$	$(CH_3)_2S_2$	ppm	lb/hr	lb/T ADP
B	—	2500	21,100	11,500	6,100	44,400	4.8	0.19
C	291	—	6,000	6,500	500	13,790	28.1	1.36

Multiple Effect Evaporators

The kraft process utilizes multiple effect evaporation to concentrate weak black liquor (spent cooking liquor) washed from the pulp. Removal of large amounts of water from the liquor is necessary to facilitate combustion of the dissolved organic material in the recovery furnace. The liquor is concentrated in the multiple effect evaporators from a solids content between 12 and 18 percent to one between 40 and 55 percent.[12]

Most kraft mills utilize long-tube vertical shell-and-tube type evaporators. The weak black liquor is fed to the tube side of the latter evaporation effects and steam is supplied to the shell side of the first effect. As shown in Figure 2, the liquor proceeds through the tube side of each effect from last to first, being heated in each by condensation of the vapor driven off the boiling liquor in the tube side of each preceding effect.

Evaporated water vapor from the last effect of the set is condensed in one of two types of condensers: direct contact barometric condensers or a surface condenser with steam ejectors. The condenser must remove vapor fast enough to create a vacuum in the vapor space of the last effect. Each type of condenser is equipped with a small steam ejector to remove noncondensables.

Emissions

Emissions from the multiple effect evaporator system occur from the condenser and the various steam ejectors. The shell side of each effect is vented through a relief valve for noncondensables. Common practice is to vent all noncondensables to the condenser. It is possible, however, to vent noncondensables from those effects that are above atmospheric pressure directly to the atmosphere.

Emission Data

Information in questionnaires and the number of units reporting the composition of effluent gases from the evaporator hot well vent stack are presented in Table 6.

The questionnaire data on which the above table is based may be found in Table 7. No data were reported on the composition of condensate

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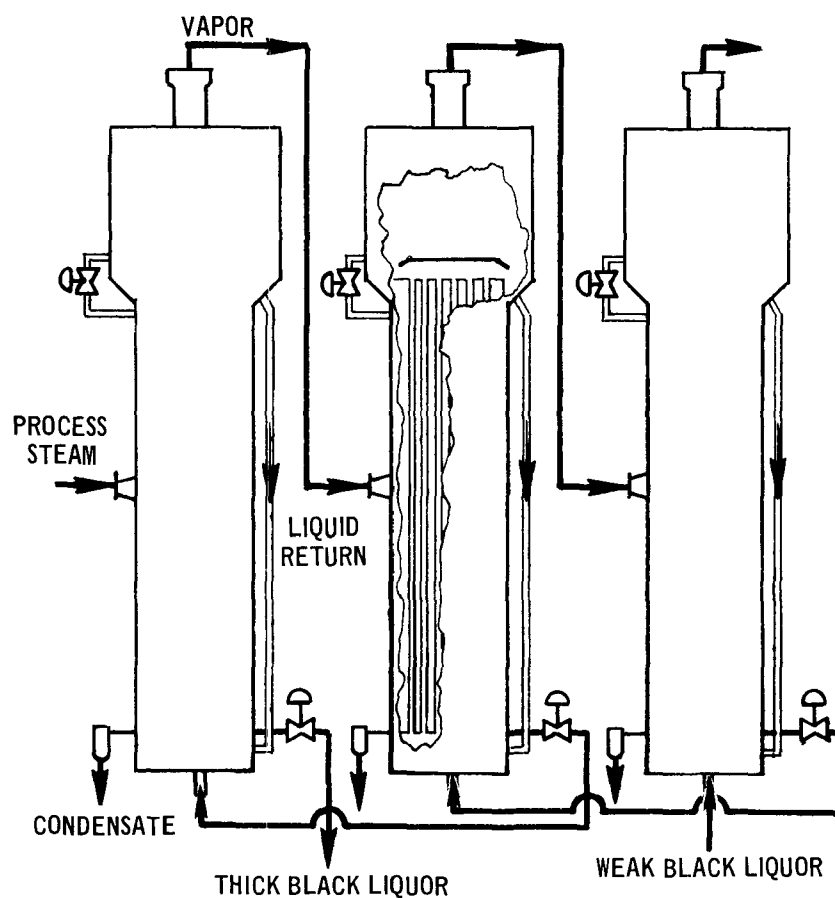
Figure 2. Multiple effect long-tube vertical evaporators (backward feed).

streams. The large variations in the data result because it is difficult to measure the volume of this stream and because analytical techniques were not standarized. While this stream is referred to as "noncondensables," it contains a high and variable percentage of water vapor. Accurate measurement of the volume flow rate is very difficult.

Control Techniques

Emissions from evaporation arise from noncondensable vent gases and liquid condensate. Liquid condensate is usually sewered, and noncondensables are often vented to the atmosphere.

Table 6. EMISSIONS FROM MULTIPLE EFFECT EVAPORATORS, SUMMARY OF QUESTIONNAIRE DATA

	Emissions				Number of mills
	Concentration, ppm		Rate, lb/T ADP as H_2S		
Compound	Range	Median	Range	Median	
H_2S	0 to 44,000	1055	0 to 5.9	0.29	10
CH_3SH	5 to 211	59	0.002 to 0.116	0.011	6
$(CH_3)_2S$	10 to 196	22	0.0002 to 0.095	0.012	6
$(CH_3)_2S_2$	10 to 1200	50	0.0003 to 1.23	0.033	6

Noncondensable vent gases may be combined and controlled with digester blow and relief gases, using such methods as incineration or alkaline scrubbing. (See digester control techniques section earlier in report.) Two mills reported utilization of control techniques for vent gas emissions other than burning. Both of these mills used packed scrubbers. Table 8 summarizes data from these mills. High removal efficiency on sulfur dioxide and hydrogen sulfide are shown, but effectiveness on removal of organic sulfur gases is not reported.

Pilot plant investigation of the feasibility of stripping malodorous gases from kraft mill condensate streams (including evaporator condensate) was conducted in 1958 by a major pulp and paper company.[13] Steam stripping in an eight-stage bubble-cap type fractionating column accomplished significant separation of these gases from condensate effluent streams. Preheated condensate feed was passed downward through the column countercurrent. to steam injected at the bottom. The resulting overhead streams consisted of noncondensable gases (which could be disposed of by the previously mentioned methods) along with relatively pure water. Removal of 95 percent or more of the hydrogen sulfide, mercaptans, and dimethyl disulfide was accomplished.

Malodorous gases may also be removed from condensate streams by air stripping. The condensate is aerated in a closed, agitated tank, and off-gases are piped to a lime kiln. Tests on an installation of this type treating condensates from digestion and evaporation showed 75 percent removal of dimethyl sulfide and 85 percent removal of methyl mercaptan. [14]

Kraft Recovery Furnace Systems

Introduction

The first two kraft recovery furnace systems shown in Figure 3 consist ot two to four separate processes, depending upon whether primary and/or

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Table 7. GASEOUS EMISSIONS FROM MULTIPLE EFFECT EVAPORATORS, QUESTIONNAIRE DATA

Unit	Production rate, T ADP/day	Average gas flow, acfm	Gas temperature, °F	SO_2, ppm	Reduced sulfur gases, ppm				TRS as H_2S		
					H_2S	CH_3SH	$(CH_3)_2S$	$(CH_3)_2S_2$	ppm	lb/day	lb/T ADP
1	174	42	188	—	1,200	—	10	10	1,230	5.3	0.03
2	348	52	188	—	2,100	—	10	10	2,130	11.5	0.03
3	131	472	162	—	908	211	162	91	1,463	75.0	0.57
4	376	455	152	0	2,181	103	196	1200	4,880	240	0.65
5	630	400	212	—	18	54	10	5	92	3.7	0.005
6[a]	1030	1430	195	—	44,000	—	—	—	44,000	6500	6.3
6[b]	1030	945	180	—	2,000	—	—	—	2,000	198	0.19
7	145	4000	160	—	8	5	34	219	485	210	1.5
8[a]	700	778	180	—	126	73	—	—	199	16.2	0.23
8[b]	700	768	170	—	0	17	—	—	17	1.4	0.02

[a]Before control.
[b]After control.

**Table 8. CONTROL TECHNIQUES FOR
MULTIPLE EFFECT EVAPORATOR EMISSIONS,
SUMMARY OF QUESTIONNAIRE DATA**

Mill	Equipment	Gas flow rate, dscfm	Concentration, ppm	
			Inlet	Outlet
34	Packed scrubber (fluid, weak white liquor at 36 gpm)	110	$H_2S = 44,000$ $SO_2 = 24$	$H_2S = 2000$ $SO_2 = 0$
60	Packed scrubber (fluid, weak black liquor at 35 gpm)	496	$H_2S = 126$ $CH_3SH = 73$	$H_2S = 0$ $CH_3SH = 17$

secondary control devices are employed. These are (1) the kraft recovery furnace, (2) the flue gas direct contact evaporator, (3) the primary particulate emission control device, and (4) the secondary particulate emission control device. In some situations, the flue gas direct contact evaporator has served the dual purpose of a black liquor evaporator and particulate emission control device. In recent years, it has also been eliminated or modified in its manner of use in a limited number of new installations, as illustrated in the last three diagrams in Figure 3, being replaced with extended multiple effect evaporation or operated with hot air rather than flue gas as a source of energy for evaporation. The emissions from the *kraft recovery furnace system* therefore always consist of those from the kraft recovery furnace, as well as those from the flue gas direct contact evaporator, when one is used, since gas flows from the furnace through the evaporator prior to its discharge. Under certain conditions, some constituents of the recovery furnace gases are absorbed in the alkaline black liquor in the direct contact evaporator.[15]

Kraft Recovery Furnace — The primary function of the kraft recovery furnace is recovery of chemicals from black liquor, although steam is produced from the heat of combustion of organic residue in the liquor. Concentrated black liquor is sprayed into the lower part of the furnace, which is designed for operation in a reducing atmosphere near the bottom and an oxidizing atmosphere in the remainder. Essentially all of the recovered chemicals are removed from the bottom of the furnace as a molten smelt consisting principally of sodium sulfide and sodium carbonate. Particulate matter, normally consisting principally of sodium sulfate with some sodium carbonate present, is carried from the reducing zone, as are gaseous sulfur compounds.

Flue Gas Direct Contact Evaporators—Until recently, concentrated black liquor from the multiple effect evaporators in the kraft recovery process was almost always further concentrated in a contact evaporator prior to its combustion by bringing recovery furnace flue gas in contact with black

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A. CONVENTIONAL FLUE GAS DIRECT CONTACT SYSTEM
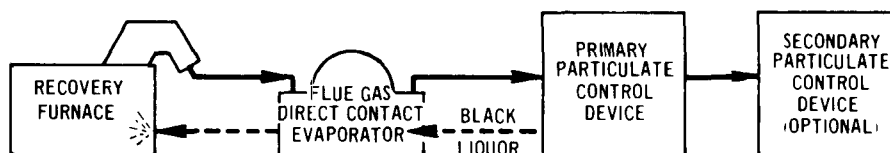
B VENTURI RECOVERY UNIT SYSTEM
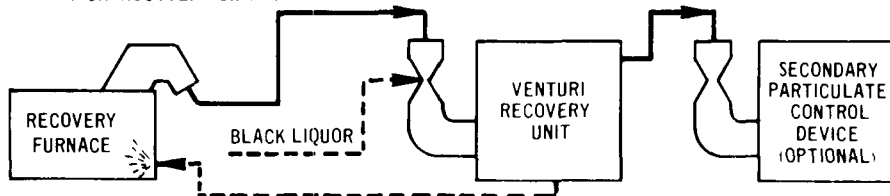
C. B & W HIGH SOLIDS SYSTEM WITH NO DIRECT CONTACT EVAPORATOR ADDED
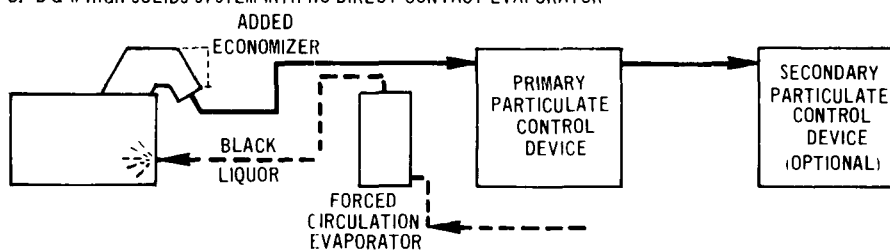
D. CE SYSTEM WITH NO FLUE GAS DIRECT CONTACT EVAPORATOR
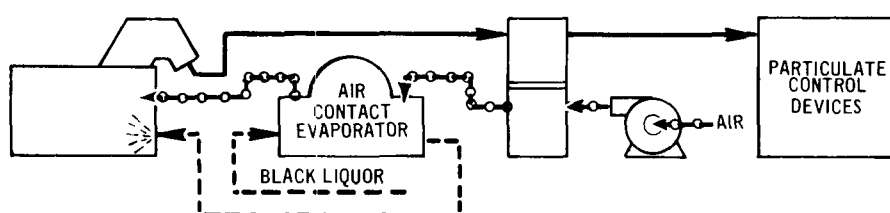
E. CE SYSTEM WITH NO DIRECT CONTACT EVAPORATOR
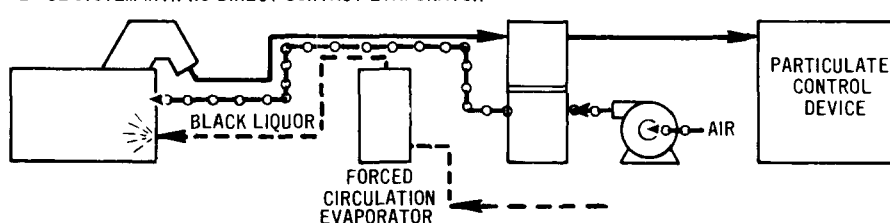
Figure 3. Typical kraft recovery furnace system options.

liquor. These evaporators are of three forms. Cascade evaporators provide for the contact of black liquor with recovery furnace flue gas through the use of rotating wheels, the bottom portions of which move through a vat of black liquor that is carried into a moving stream of hot combustion gas from the recovery furnace. In cyclone evaporators, black liquor is sprayed into the hot gas stream and then separated from the gas stream by the use of a cyclone. The third type of contact evaporator used is commonly called the venturi recovery unit. In these units, black liquor is introduced into a stream of recovery furnace flue gas at a venturi throat and then separated in a centrifugal separator. Venturi recovery units differ from other types of contact evaporators so far as emissions are concerned principally in that particulate removal efficiencies are higher. Cascade and cyclone evaporators are commonly believed to remove from 40 to 50 percent of the particulate matter leaving the recovery furnace, while venturi recovery units have been designed for greater than 90 percent capture of particulate matter. While capturing particulate matter and sulfur dioxide present in recovery furnace exhaust gas, the contact evaporator is a potential source of reduced sulfur compounds, the amount depending on the residual sulfide in the black liquor fed to the evaporator.

Recovery Systems without Flue Gas Direct Contact Evaporators — Both manufacturers of kraft recovery furnaces in the United States have participated in recent years in the development of innovated designs for kraft recovery furnace systems that eliminate the use of a flue gas direct contact evaporator. Both recover the bulk of the heat formerly used for evaporation of black liquor in the flue gas direct contact evaporator. The Babcock and Wilcox (B&W)* system shown in Figure 3C uses an extended economizer section for this heat recovery. The Combustion Engineering Company (CE) design shown in Figure 3D uses a flue gas-to-air heat exchanger to heat ambient air, which is subsequently used to evaporate black liquor in a conventional contact evaporator. In the CE design, the exhaust from the contact evaporator serves as a portion of the combustion air for the recovery furnace. A modification of this system (Figure 3E) eliminates the contact evaporator but retains the heat exchanger to preheat the combustion air. Additional indirect evaporation of the black liquor is also used in this system.

While both these designs eliminate the flue gas direct contact evaporator as a potential source of reduced sulfur emissions, the particulate load on subsequent particulate emission control devices is almost doubled. Sulfur dioxide formed in the recovery furnace by the burning of black liquor is maintained at reasonable levels by the contact evaporator. Its control in those systems with no flue gas direct contact evaporator is dependent on currently ill-defined furnace and other process operating variables.

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*Mention of commercial products or company names does not imply endorsement by EPA or NCASI.

Both gaseous sulfur compounds and particulate matter are generated in and emitted from kraft recovery furnaces. In essentially all cases, the gaseous sulfur compounds leaving the kraft recovery furnace contain sulfur dioxide and varying amounts of hydrogen sulfide. Organic sulfur compounds consisting of methyl mercaptan, dimethyl sulfide, and dimethyl disulfide may be present, although their presence is usually contingent on the manner in which the recovery furnace is operated and is not common. When present, these gases seldom represent more than a small percentage, less than 10 percent, of the hydrogen sulfide present. The particulate matter emitted from the recovery furnace consists of sodium sulfate and sodium carbonate and may contain small amounts of sodium chloride. The presence of the latter depends on whether the wood used for pulping has been stored in saline water and on the chloride levels in make-up chemicals used in process.

Particulate Emissions — The particulate matter levels in kraft recovery furnace flue gas before it reaches a control device normally range from 8 to 12 grains per standard cubic foot (gr/scf) or 200 to 450 lb/T ADP. The actual emission level is a function of control device efficiency, which is a function of the system design. In conventional recovery furnace systems, those with flue gas direct contact evaporators, recovery furnace particulate emission control consists of (1) the contact evaporator, (2) a primary control device, which is either a precipitator or a venturi recovery unit, and (3) possibly a secondary scrubber. Where no flue gas direct contact evaporator is used, particulate emission control in current designs is by precipitators alone, although nothing precludes the use of secondary scrubbers. Emission ranges for existing conventional draft recovery furnace systems are described in a following section. Currently, high-efficiency electrostatic precipitators with design collection efficiencies of greater than 99 percent are commonplace in new and replacement installations.

Gaseous Emissions — The kraft recovery furnace is one of the two largest potential emission sources of reduced sulfur compounds in the kraft recovery furnace system, the second being the contact evaporator. Control of reduced sulfur emissions from the kraft recovery furnace depends on operational control of the furnace. Depending on the mode of furnace operation, reduced sulfur concentration in the furnace exhaust gas may be as low as 1 ppm or as high as several hundred ppm. This range of possible reduced sulfur emission levels is independent of the presence or absence of a flue gas direct contact evaporator. Therefore, new recovery furnace system designs that eliminate the flue gas direct contact evaporator only eliminate one potential source of reduced sulfur emission. Those operational factors that account for control of reduced sulfur emissions from the recovery furnace apply regardless of furnace age.

Historically, there has been little concern for the sulfur dioxide generated in a kraft recovery furnace. In conventional kraft recovery

furnace system designs, concentrations are substantially reduced when furnace exhaust gas passes through the contact evaporator. After the contact evaporator, they are characteristically between 50 and 150 ppm, well below those resulting from the combustion of fossil fuels containing 0.5 percent sulfur, i.e. less than 300 ppm. Concentrations of sulfur dioxide in recovery furnace exhaust gas range from less than 50 to as high as 700 or 800 ppm. The factors responsible for this range of concentration are not well identified. Blue and Llewellyn,[16] and results of currently unpublished studies as well, indicate that sulfur dioxide generation in kraft recovery furnaces is a function of several variables. One is cooking liquor sulfidity, an indirect measure of the soda and sulfur ratio in black liquor fed to the furnace. Others include smelt bed depth, manner in which liquor is sprayed into the furnace, ratio of primary to secondary combustion air, and possibly temperature within the furnace itself. Blue and Llewellyn show sulfur dioxide emission levels of about 50 to 100 ppm from a kraft recovery furnace during performance tests. Actual operating experience with several other furnaces has failed to define the reasons for sulfur dioxide emissions of 5 to 10 times this level. As stated previously, the higher concentrations are of limited practical concern except in those recovery furnace system designs that eliminate the contact evaporator.

Several operating and design variables that have some effect on, or relationship to, the control of reduced sulfur compounds emitted from the kraft recovery furnace have been identified. Among these have been the quantity and manner of introduction of combustion air, rate of solids (concentrated black liquor) feed, turbulence in the oxidation zone, oxygen content of the flue gas, spray pattern and droplet size of the liquor fed the furnace, and smelt bed disturbance.[15,17] The impact of these variables is independent of the absence or presence of a contact evaporator.

The presence of adequate oxygen throughout the oxidation zone of the recovery furnace and its thorough mixing with the products of combustion are major factors in assuring that reduced sulfur compounds lost from the smelting (reducing zone) in the bottom of the furnace are oxidized to less odorous forms of sulfur such as sulfur dioxide. The amount of combustion air and its distribution between the various points for its admission, i.e. primary, secondary, and tertiary combustion zones of the furnace, have been found to be factors in assuring that satisfactory conditions of combustion exist for a minimum emission of reduced sulfur. Combustion conditions may also be enhanced by adjusting engineering variables, such as inlet air velocity, to improve the turbulence and mixing in the oxidation zone. Some designs also provide for introduction of combustion air tangential to the walls of the furnace to enhance mixing and promote complete combustion.[15,17]

A partial measure of an adequate supply of air to support combustion in the recovery furnace and hence contribute to the factors accounting for a minimum reduced sulfur emission is residual oxygen content of the flue gas. Special studies on 26 recovery furnaces showed that some residual

oxygen content was necessary to achieve minimum reduced sulfur emission levels. However, a residual oxygen content in the flue gas was not a guarantee of minimum reduced sulfur emission rate. The point of introduction of combustion air, degree of mixing, and leaks are all probably responsible for a range of residual oxygen contents, all of which were associated with minimum reduced sulfur emissions in different furnaces.[15] These and other studies have demonstrated that minimum reduced sulfur emissions are not commonly observed, however, unless residual oxygen content of the flue gas is in the range of 2.5 to 4.5 percent.

Physical disturbance in the smelting zone, created either by excessive impingement of combustion air on the surface of a high smelt bed or smelt sloughing from the walls, has been identified as a factor that may increase emission levels of reduced sulfur compounds![7] The size of liquor droplets sprayed into the furnace is also considered to be of some significance, reduced sulfur emissions increasing as droplet size decreases. Some control of smelt bed height is possible in operation of the furnace. Smelt sloughing from the walls, however, is not controllable with current design. Spray droplet size is partially controlled by altering viscosity through temperature control of the black liquor feed.

One of the most significant, but not the sole, factor in control of reduced sulfur emissions from the kraft recovery furnace is the rate of concentrated black liquor feed. Detailed investigations of recovery furnaces indicate that an optimum liquor firing rate can be defined for each furnace. The optimum rate, coupled with proper control of previously described operating variables, will result in a minimum reduced sulfur emission rate. The investigations that lead to this conclusion involved tests, lasting from a few to several hundred hours, of more than 20 recovery furnaces.[15,17]

An example of the interrelation of liquor feed rate, TRS emission level, and steam generation efficiency for one furnace is shown in Figure 4.[15] The geometric increase in reduced sulfur emissions once a certain liquor feed rate (34,000 lb/hr in this case) is exceeded is typical of furnaces fired above the critical level for minimum TRS emission. This minimum emission rate for individual furnaces was also observed to bear a relationship to the ratio of air to solids fired (lb/lb). This is illustrated in Table 9,[15] where reduced sulfur emissions are shown to increase substantially when the air-to-solids ratio fell below 4.25. Like oxygen content, this ratio covered a range for different furnaces, usually falling between 3.5 and 4.5.

No well defined relationship between solids firing rate at minimal reduced sulfur emissions rate and rated furnace capacity was found in these studies. In only one case did maximum firing rate for a minimum reduced sulfur emission level and manufacturer's rated solids firing capacity coincide. Commonly, minimal emissions rate occurred at 1.15 times rated capacity, on one occasion, at 1.4 times rated capacity, and never below rated capacity.[15] Several factors can account for these differentials, including divergence in heat value of that liquor actually burned from

liquor characteristics used for design purposes. Probably most important, however, has been a changing definition of rated capacity throughout the years and the fact that it was not originally conceived with the idea that it was related to emissions.[15]

The above referenced studies showed that there are a series of primary operating variables for recovery furnaces whose control is required for a minimum emission of TRS. Among these factors are: (1) liquor firing rate, (2) available oxygen for combustion, (3) air-to-solids ratio, and (4) probably the ratio of primary to secondary and tertiary air.

Under the most favorable control of primary operating variables, there have also been observed a series of secondary operating variables, such as (1) smelt falling from the walls, (2) a smelt bed of sufficient height to prohibit good mixing of the products of pyrolysis with air, and (3) plugged ash hoppers and bridged liquor feed guns, which can superimpose a condition resulting in a temporary increase of emissions that are variable, of limited magnitude, and usually of short duration. There has been no evidence that sulfide content of the liquor being burned bears any relationship to the reduced sulfur emissions from a recovery furnace. This is not to be confused with sulfur compounds generated or stripped in the flue gas contact evaporator.
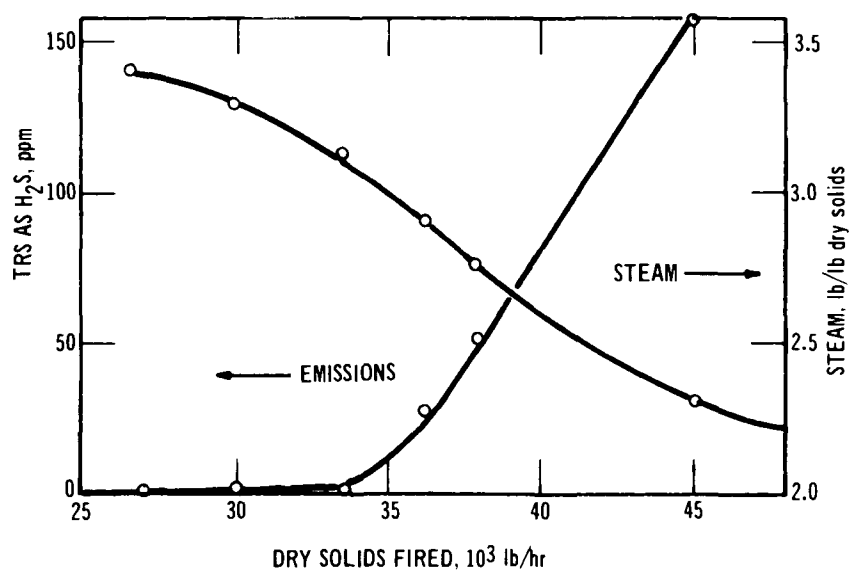
Figure 4. Effect of solids firing rate on reduced sulfur emissions and steam generation efficiency.

**Table 9. EFFECT OF FURNACE FIRING RATE
AND AIR SUPPLY ON TRS EMISSION
FOR KRAFT RECOVERY FURNACE**

Dry solid firing rate, lb/hr	Air, lb/lb dry solids	Oxygen, percent	Average TRS as H_2S, ppm
20,000	5.40	6.2	1.4
20,000	5.40	6.4	1.0
19,300	5.25	5.8	1.7
24,200	4.50	5.0	1.5
24,000	4.50	4.8	1.4
24,400	4.42	5.3	1.3
24,200	4.40	4.8	1.5
23,100	4.35	4.2	1.9
23,500	4.25	4.7	2.6
25,200	4.16	2.8	52.0
30,000	3.33	1.6	560.0

Ability to maintain maximum control of the above operating variables is somewhat dependent on age and furnace appurtenances. Application of best available operation control technology for new recovery furnaces may therefore result in different emission levels than those from older furnaces. Emission levels observed during extended study periods characterize the reduced sulfur emissions control possible on recovery furnaces built during the period 1955 to 1968, which usually have more refined combustion and firing controls. As illustrated in Figure 5, these furnaces showed total reduced sulfur emissions below 1 ppm 65 percent of the time, below 2 ppm 80 percent of the time, below 4 ppm 90 percent of the time, and below 16 ppm 99 percent of the time.[15] Llewellyn reports similar reduced sulfur emissions from a new recovery furnace using a Babcock and Wilcox high solids system; daily average TRS emissions ranged from 0.5 to 8.8 ppm with a median of 2 ppm, which represented 0.064 lb/T ADP. The mean of monthly mean TRS emission rates for this furnace over a 1-year period was 0.022 lb/T ADP, and monthly averages ranged from 0.011 to 0.098 lb/T ADP. These values are contrasted with those from performance tests, which are usually of short duration, on the same furnace; performance tests indicated an average of 0.4 ppm, or about 0.01 lb/T ADP, and a maximum of 1.1 ppm, or approximately 0.03 lb/T ADP.

Only limited data are available on the degree of reduced sulfur emission control possible with older recovery furnaces, which are characterized within the structure of existing knowledge as those constructed without (1) the refined metholds of combustion air measurement, air distribution to
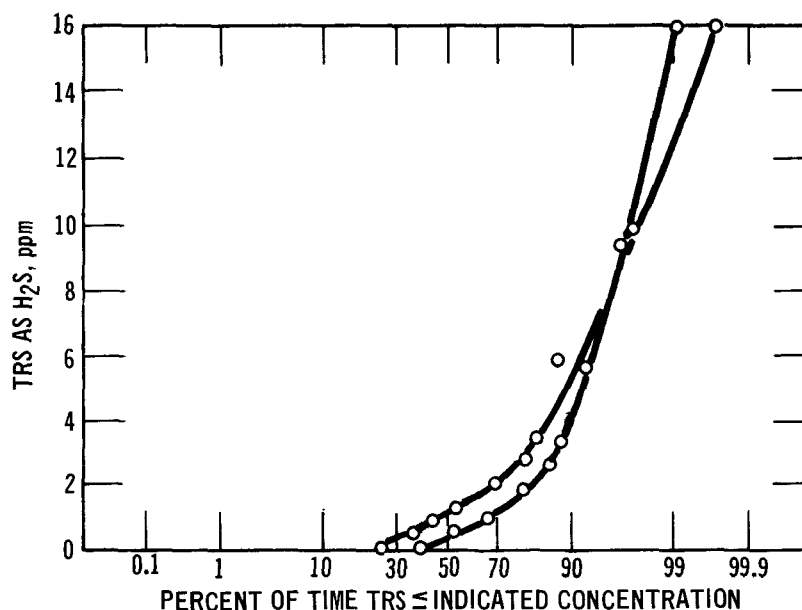
Figure 5. Observed frequency of total reduced sulfur concentrations in exit gases from two recovery furnaces with good combustion controls.

various zones of the furnaces, and what is currently believed to be its proper method of introduction, (2) refined control of the liquor feed apparatus, and (3) indicators of adequate combustion conditions such as flue gas oxygen analyzers, combustible meters, and reduced sulfur monitors.

An 84-hour study on one furnace built in 1947, which is routinely fired for minimum emission level by controlling liquor feed rate and maintaining residual oxygen content of 5 percent in the flue gas, is illustrative of the possibility for controlling emissions from furnaces not equipped with the more up-to-date firing control devices. As shown in Figure 6,[15] sulfur emission, which was essentially all hydrogen sulfide, was below 5 ppm 50 percent of the time, below 15 ppm 90 percent of the time, and below 30 ppm 98 percent of the time. Other data, gathered in studies of shorter duration on furnaces of a similar vintage, revealed emission levels of less than 15 ppm of TRS.[15] This indicates that the emission control possible with furnaces of this era is neither fully explored nor adequately understood.

When recovery furnaces are operated in conjunction with flue gas direct contact evaporators that are fed highly oxidized black liquor, their reduced sulfur emissions are absorbed. A combination of best furnace operation and very high degree black liquor oxidation may therefore represent the control necessary for a nonobjectionable operation except in extreme situations.

Kraft (Sulfate) Pulping   **29**
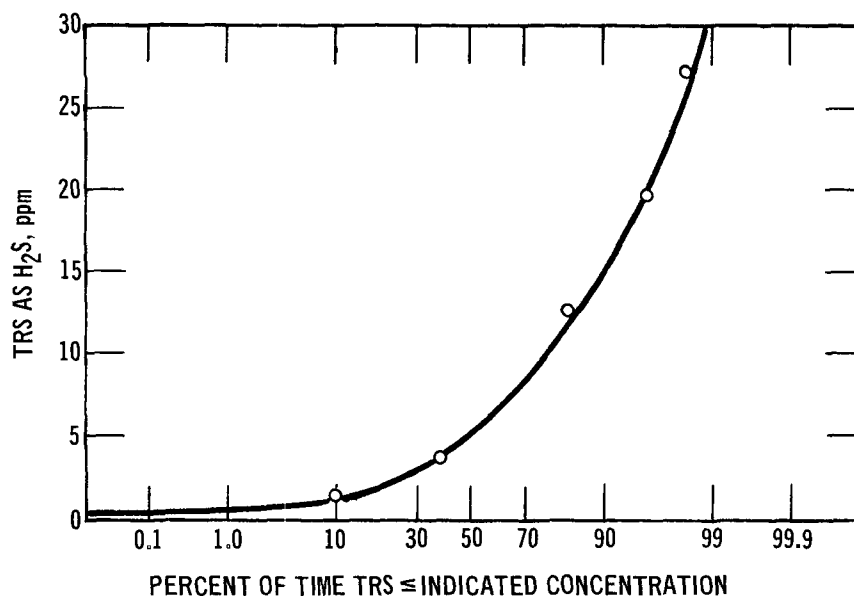
Figure 6. Observed frequency of total reduced sulfur concentrations in exit gases from a recovery furnace with limited combustion controls.

Composition and Control of Emissions from Flue Gas Direct Contact Evaporators

The flue gas direct contact evaporator is recognized as a potentially large source of TRS emissions in the kraft process. The corrective action that can be taken to reduce and virtually eliminate the TRS contributions of this process is black liquor oxidation, described elsewhere in this report. Essentially, the process consists of oxidizing the sulfide present in black liquor to thiosulfate, which does not participate in the reactions with acidic gases, such as carbon dioxide and sulfur dioxide, in recovery furnace flue gas. Hence the stripping of hydrogen sulfide is prevented. Control of black liquor pH, creating a favorable equilibrium for the maintenance of sulfide in solution, is another mechanism for controlling emissions from this source.[18,19]

A failure to recognize (1) the high degree of black liquor oxidation required and (2) the occurrence of sulfur compound reversion to sulfide during multiple effect operation, as well as during extended storage of both oxidized weak and strong liquor, has resulted in confusion over the reduced sulfur emission control possible at the flue gas direct contact evaporator. In the past, black liquor oxidation system performance efficiency has been

defined on the basis of the percentage of the total sulfur that is oxidized by the process, and the reversion of sulfur compounds to sulfide prior to the time the liquor enters the direct contact evaporator has been neglected. Residual sodium sulfide levels of the black liquor entering the evaporator must be no higher than 0.1 gram per liter (currently the minimum measurable amount) if emissions are to be near zero (i.e., less than 0.2 ppm). However, since initial sodium sulfide concentration can range from 8 to 35 g/liter and percent conversion can cover a correspondingly wide range, percent conversion is not an adequate measure of the performance of a black liquor oxidation unit. Improved engineering designs that permit continuous high-level-performance black liquor oxidation have led to the realization of full reduced sulfur emission control capabilities at the flue gas direct contact evaporator; and recently developed techniques to isolate the contact evaporator for studies of factors controlling emissions on a continuous, real-time basis have demonstrated their efficiency.

Data obtained in a series of special studies, as well as observations of currently existing installations, illustrate the potential for controlling the reduced sulfur emissions from the contact evaporator through control of residual sulfide content by black liquor oxidation and pH adjustment of the liquor entering the contact evaporator.[15] These studies showed that reduced sulfur emission control was not of maximum benefit until the residual sodium sulfide content of the black liquor entering the contact evaporator approached zero. Illustrative of the relationship of residual sulfide in black liquor and reduced sulfur contributions of the contact evaporator are the data in Figure 7.[15] These data, which are from two contact evaporators, illustrate a general increase in contact evaporator contribution of reduced sulfur from almost zero to about 275 ppm as sodium sulfide concentration in the liquor increases from less than 0.05 to 24 g/liter.[15]

A similar relationship is shown in Figure 8[15] for sodium sulfide concentrations of less than 1 liter in the liquor fed to one of these evaporators. TRS contributions fell from 22 ppm, at sodium sulfide levels of 0.8 g/liter to zero or less as a result of absorption of reduced sulfur from the recovery furnace flue gas at sodium sulfide concentrations of zero. Once the sodium sulfide levels fell below 1.0 g/liter, the flue gas direct contact evaporator contribution of dimethyl sulfide fell to zero from 3 ppm. Methyl mercaptan contributions did not reach zero until the sodium sulfide levels in the feed liquor were essentially zero. [15]

At a third installation where high-degree black liquor oxidation is practiced, the reduced sulfur contribution of the contact evaporator over a 30-hour period ranged from 0.1 to 3.1 ppm while residual sodium sulfide levels in the black liquor ranged from 0.06 to 0.2 g/liter.[15] As a result of more effective and continuous high-performance black liquor oxidation at this mill, resulting in only trace amounts of residual sulfide in the black liquor entering the flue gas direct contact evaporator, emissions from this source were shown to range from zero to less than 1 ppm. [15]

Kraft (Sulfate) Pulping
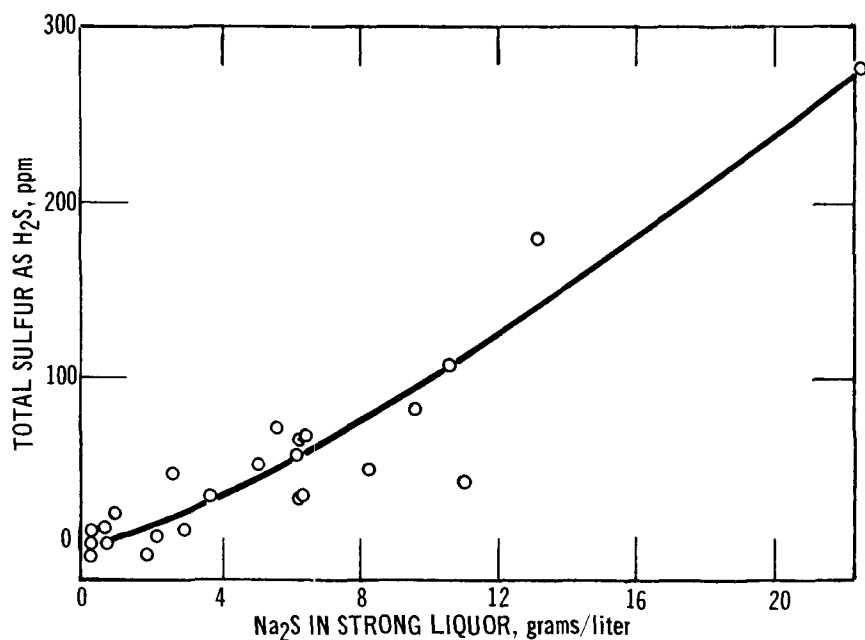
Figure 7. Total sulfur increase across the direct contact evaporator, sodium sulfide concentrations from 0 to 20 g/liter.
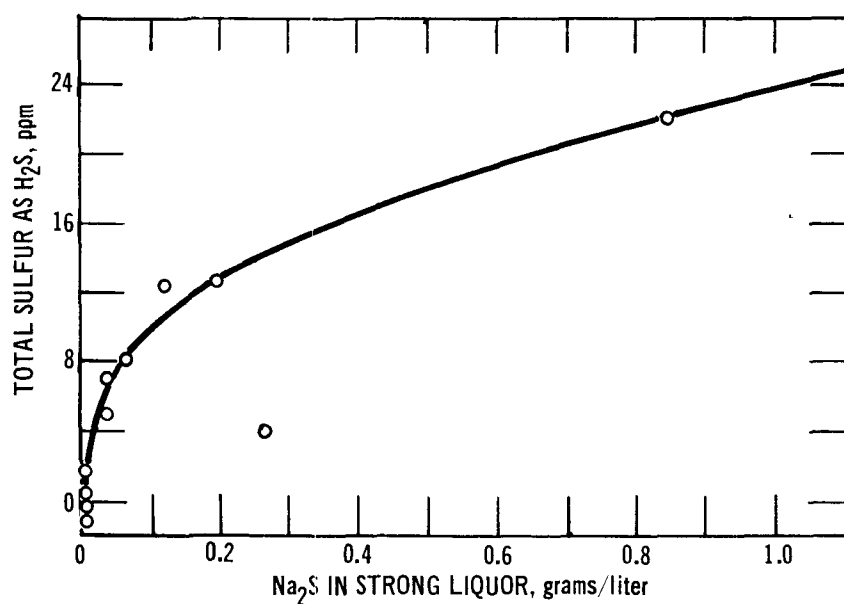
Figure 8. Total sulfur increase across the direct contact evaporator, sodium sulfide concentrations from 0 to 1 g/liter.

Walther and Amberg recently reported contribution from a flue gas direct contact evaporator of 0 to 1 ppm TRS when liquor entering the contact evaporator was at pH 12 and contained 0.2 to 0.4 g/liter of sodium sulfide. This study served to verify the work of other investigators who had found that significant reductions in reduced sulfur emissions from the flue gas direct contact evaporator can be made by adjusting the normal liquor pH upward. At similar residual sulfide levels with no pH adjustment, emissions from the contact evaporator ranged from 0 to 12 ppm. [18]

Other benefits of highly oxidized black liquor feed to a contact evaporator in controlling reduced sulfur emissions have also been demonstrated. In one case, a cascade evaporator followed an older recovery furnace that was fired for nominal emission but had an unstable TRS emission level. The liquor, subjected to high degree oxidation, usually showed zero to trace quantities of sodium sulfide. During a 71-hour study, residual sodium sulfide concentration normally ran at 0.05 g/liter or less and never exceeded 3.5 g/liter, the high value being due to a brief mechanical failure in the oxidation system. Data collected at this installation illustrate the potential of the contact evaporator to act as an equalizer when furnace emission levels are erratic. The evaporator acted as an absorber 21 percent of the time, it produced no change 7 percent of the time, and there was some contribution of reduced sulfur from it 72 percent of the time. The TRS changes, their magnitude, and their frequency are shown in Table 10.[15]

Table 10. ANALYSIS OF DIRECT CONTACT EVAPORATOR FUNCTION IN ALTERING FURNACE GAS TRS CONTENT

Condition	Difference in TRS as H_2S, ppm	Duration of condition hours	percent	Total duration, percent
Absorption (-)	> 21.0	2	2.8	
	11 to 20	8	11.2	
	6 to 10	3	4.2	
	1 to 5	2	2.8	21.0
No change	0	5	7.0	7.0
Release (+)	0 to 5	13	18.3	
	6 to 10	9	12.7	
	11 to 20	18	25.5	
	> 21.0	11	15.5	72.0
Total		71	100.0	100.0

Kraft (Sulfate) Pulping 33

In summary, information at hand indicates that proper black liquor oxidation can control the reduced sulfur emissions from contact evaporators to the level of 0 to 3 ppm, a level almost identical to that from well operated recovery furnaces. Additional reduced sulfur absorption from erratic recovery furnace discharge and sulfur dioxide absorption from recovery furnace flue gas are other results of feeding the direct contact evaporator a highly oxidized black liquor.

Emission Data

Questionnaire Data — Particulate emission data from 87 kraft recovery furnace systems equipped with flue gas direct contact evaporators and electrostatic precipitators. 10 with venturi recovery units, and 7 with electrostatic precipitators ahead of secondary scrubbers were received in the questionnaire survey. Reduced sulfur emission data were received from 42 recovery furnace systems that did not employ black liquor oxidation and from 20 that did. These data are covered in the following sections.

Particulate emissions — Particulate emission data from 87 kraft recovery furnace systems equipped with flue gas direct contact evaporators and electrostatic precipitators were reported in the questionnaire survey. The particulate emission levels reported are arranged by decile in Table 11. The mean emission level in the lowest decile was 2.1 lb/T ADP, while that in the highest decile was 75.2 lb/T ADP. The range of particulate emission levels

Table 11. PARTICULATE EMISSIONS FROM RECOVERY FURNACES CONTROLLED BY ELECTROSTATIC PRECIPITATORS, AVERAGED BY DECILE GROUPS

Emission decile	Average emission rate, lb/T ADP
First (lowest)	2.1
Second	3.3
Third	4.8
Fourth	6.8
Fifth	12.4
Sixth	17.0
Seventh	18.4
Eighth	28.4
Ninth	46.3
Tenth (highest)	75.2

reported was from 1.3 to 95 lb/T ADP, the median was 14 lb/T ADP, and 44 percent of those reporting had particulate emissions less than 10 lb/T ADP. The concentration and particulate emission rates generally reflected both the age of the precipitators and their design efficiencies, which ranged from 75 to 99.5 percent. The complete emission data from furnaces equipped with electrostatic precipitators are presented in Table A-1 in Appendix A. These data are plotted in Figure 9.
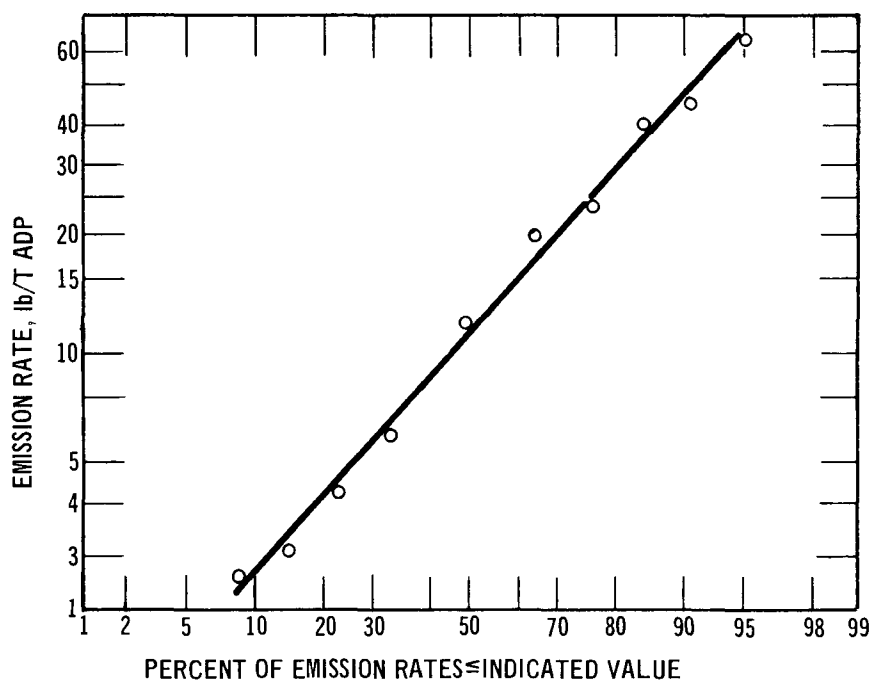
Figure 9. Particulate emissions from recovery furnaces with electrostatic precipitators, questionnaire data.

Data on particulate emissions from 10 recovery furnace systems equipped with venturi recovery units show a range of 15 to 115 lb/T ADP. The median was 45 lb/T ADP compared with a median of 14 lb/T ADP from those systems equipped with precipitators. These data are shown in Table 12.

The particulate emissions from seven kraft recovery furnace systems equipped with electrostatic precipitators ahead of secondary scrubbers ranged from 1.8 to 13.1 lb/T ADP. These data are shown in Table 13.

Kraft (Sulfate) Pulping   **35**

Table 12. PARTICULATE EMISSIONS FROM RECOVERY FURNACES WITH VENTURI SCRUBBER SYSTEMS, QUESTIONNAIRE DATA

Unit	Pulp production rate, T ADP/day	Gas flow rate, dscfm	Ratio of flow rate to production, dscfm T ADP/day	Particulate concentration, gr/dscf		Collection efficiency, percent	Emission rate, lb/T ADP
				Inlet	Outlet		
1	807	110,000	136	6.5	0.5	92.4	14
2	308	32,700	106	7.26	0.86	88.2	19
3	493	104,000	211	6.51	0.477	92.7	21
4	320	45,000	141	6.25	1.25	80.0	36
5	290	66,500	229	2.61	0.78	70.2	43
6	290	66,200	228	2.89	0.73	74.9	47
7	277	63,000	227	7.12	1.17	83.6	55
8	352	87,500	249	7.65	1.16	84.1	59
9	362	76,800	212	3.86	1.53	60.4	66.9
10	352	95,500	271	6.12	2.06	66.7	115

Table 13. PARTICULATE EMISSIONS FROM RECOVERY FURNACES WITH SECONDARY SCRUBBERS AFTER ELECTROSTATIC PRECIPITATORS, QUESTIONNAIRE DATA

Unit	Pulp production rate, T ADP/day	Gas flow rate, dscfm	Ratio of flow rate to production, dscfm/T ADP/day	Particulate concentration, gr/dscf			Collection efficiency, percent			Emission rate, lb/T ADP
				Electrostatic precipitator		Scrubber outlet	Electrostatic precipitator	Scrubber	Overall	
				Inlet	Outlet					
1	254	58,000	228	—	1.86	0.038	—	98	—	1.8
2	284	78,500	276	7.0	0.18	0.055	97.5	70	99.2	2.3
3	294	45,400	154	2.62	0.21	0.077	92.0	63	97.1	2.5
4	400	69,700	174	—	0.5	0.078	—	84.5	—	2.8
5	500	116,000	232	2.5	0.125	0.06	95.0	52	97.6	2.9
6	291	59,400	204	2.28	0.22	0.10	90.6	55	95.6	4.2
7	291	50,100	172	—	0.735	0.368	—	50	—	13.1

Gaseous emissions—Reduced sulfur emission data were received for 42 recovery furnace systems where black liquor oxidation was not used. The reduced sulfur emission rates from these systems ranged from 35 to 1300 ppm, representing 1.5 to 62 lb/T ADP, with a median of 5.9 lb/T ADP. Sulfur dioxide emission data were reported for 33 of these systems. These ranged from 0 to 575 ppm, representing from 0 to 55 pounds of sulfur dioxide or 27.5 lb/T ADP as sulfur. The median sulfur dioxide emission rate was 20 ppm or 2.4 lb/T ADP. These data are presented in Table 14.

Reduced sulfur emission data were received for 20 recovery furnace systems operated with black liquor oxidation systems. The range of reduced sulfur emissions from these furnace systems was from 0.2 to 25.9 lb/T ADP, with a median of 3.7. This median compared with 5.9 lb/T ADP for those systems without black liquor oxidation. The lowest emission rate reported was associated with the black liquor of lowest sodium sulfide content from the black liquor oxidizer, containing 0.2 g/liter. The low emission rate of 0.2 lb/T ADP indicates a combination of low recovery furnace emissions and low flue gas direct contact evaporator emissions for a low total system emission level. In two other situations reported, the emissions from recovery furnace systems receiving the same oxidized black liquor were 3 (units 13 and 17) and 20 (units 4 and 15) times as great in one recovery furnace system as in the other. This served to illustrate earlier discussions that pointed out the need for detailed knowledge of the recovery furnace contribution in evaluating the control capability of black liquor oxidation. The emission data for recovery furnace systems with black liquor oxidation are shown in Table 15.

EPA Test Results—As mentioned earlier, EPA conducted tests at three mills, designated Mills A, B, and C. Particulate measurements were made only at Mills B and C. Gaseous emissions were sampled at all three mills. The data obtained are discussed in the following sections.

Particulate emissions — The EPA test team made particulate measurements on two recovery furnace systems. The emissions from Mill B were controlled with an electrostatic precipitator having a manufacturer's rating of 97.5 percent. The average of three tests showed a precipitator operating efficiency of 95.5 percent and an emission rate of 4.5 lb/T ADP. At Mill C, the particulate control devices include a 96 percent efficiency rated precipitator followed by a wet scrubber guaranteed to collect 80 percent of all particles larger than 2 microns. The tests showed the precipitator to have a 97.4 percent collection efficiency, the scrubber a 51.3 percent efficiency, and the overall particulate collection system a 98.7 percent efficiency. The emission rate was 3.3 lb/T ADP. These data are summarized in Table 16.

Gaseous emissions—Gas analyses were made at one mill (Mill A) not practicing black liquor oxidation. Results in Table 17 show that reduced sulfur emissions from the furnace itself were only 2.2 ppm (0.06 lb/T ADP) but that there was a substantial increase of 500 ppm of TRS across the direct contact evaporator.

Table 14. GASEOUS EMISSIONS FROM RECOVERY FURNACES WITHOUT BLACK LIQUOR OXIDATION, QUESTIONNAIRE DATA

Unit	Pulp production, T ADP/day	Exit gas flow rate, actfm	Gas temperature, °F	Ratio of flow rate to production, actfm T ADP/day	SO_2, ppm	Reduced sulfur gases, ppm				TRS as H_2S		
						H_2S	CH_3SH	$(CH_3)_2S$	$(CH_3)_2S_2$	ppm	lb/hr	lb/T ADP
1	318	234,000	326	736	20	29	6	–	–	26	20	1.5
2	492	158,000	265	321	338	81	–	–	–	81	47	2.3
3	626	200,000	300	320	67	94	–	–	–	94	65	2.5
4	657	230,000	300	350	80	90	–	–	–	90	72	2.6
5	210	140,000	580	667	5	30	50	–	–	80	28	3.2
6	327	92,400	520	283	3	178	37	–	–	215	53	4
7	340	80,500	568	237	1	208	54	9	–	261	54	4
8	375	120,000	260	320	13	157	3	–	–	160	70	4.5
9	1120	432,000	300	386	20	–	8	10	–	18	27	4.6
10	525	210,000	300	400	–	150	0	0	0	150	110	5.0
11	316	150,000	260	474	–	121	–	0.8	–	122	67	5.1
12	380	121,000	240	318	405	230	–	–	–	230	105	6.6
13	225	80,500	250	380	–	200	–	–	4	208	66	7
14	225	96,000	280	427	–	191	–	13	0.1	204	70	7.5
15	494	199,000	60	405	138	148	16	1.6	1.3	168	170	8.3
16	328	120,000	300	366	170	340	–	–	–	340	142	10

Table 14. GASEOUS EMISSIONS FROM RECOVERY FURNACES WITHOUT BLACK LIQUOR OXIDATION, QUESTIONNAIRE DATA (Con't)

Unit	Pulp production, T ADP/day	Exit gas flow rate, acfm	Gas temperature, °F	Ratio of flow rate to production, acfm T ADP/day	SO_2, ppm	Reduced sulfur gases, ppm				TRS as H_2S		
						H_2S	CH_3SH	$(CH_3)_2S$	$(CH_3)_2S_2$	ppm	lb/hr	lb/T ADP
17	163	75,500	532	463	1	331	45	7	—	383	77	11
18	318	152,000	224	478	0	70	48	6	66	256	151	11
19	200	62,000	270	310	5	390	69	—	—	459	106	12
20	400	120,000	150	300	3	350	30	6	5	391	204	12
21	437	262,000	270	600	—	266	6	2	16	306	290	16
22	437	262,000	270	600	—	266	6	2	16	306	290	16
23	370	227,000	60	613	119	222	18	0	12	242	278	18
24	621	162,000	270	261	253	203	114	—	6	329	194	19
25	358	132,000	240	369	69	360	212	0	3	578	288	19
26	807	200,000	170	248	—	750	—	—	—	750	628	19
27	239	160,000	300	670	—	200	210	20	5	440	244	26
28	271	169,000	295	623	—	515	19.9	0	—	535	316	28
29	315	232,000	200	736	4	490	—	—	—	490	454	35
30	225	90,000	260	400	0	1350	122	26	0	1498	485	52
31	235	115,000	150	489	12	600	480	37	—	1117	557	57
32	317	177,000	282	558	575	1000	235	38	15	1303	820	62

Table 15. GASEOUS EMISSIONS FROM RECOVERY FURNACES WITH BLACK LIQUOR OXIDATION, QUESTIONNAIRE DATA[a]

Unit	Black liquor oxidation unit					SO$_2$, ppm	Furnace emissions					
	Na$_2$S, g/liter		Oxidation temperature, °F	Liquid percent solids	Percent liquor oxidized		Reduced sulfur gases, ppm				TRS as H$_2$S	
	Inlet	Outlet					H$_2$S	CH$_3$SH	(CH$_3$)$_2$S	(CH$_3$)$_2$S$_2$	ppm	lb/T ADP
1	10	0.2	170 to 180	18	100	20	3	1	0	0	4	0.2
2	—	—	—	—	—	64	25	3.5	3.0	1.5	33	1.3
3	4.5	1.5	180	16	100	49	45	0	5	2	52	1.9
4	—	—	—	—	—	5	15	0.5 to 1	<0.5	<0.5	16	2.3
5	8.9	2.5	170	13.2	66	23	17	2	1	7	34	2.6
6	5.5 to 8	0 to 0.5	180	13	50	25	55	1.5	0	5.0	61.5	2.7
7	—	—	—	—	—	0	77	6.3	1.0	0.5	85	3.1
8	10	0.5	160	16	100	0	100	20	—	—	120	3.3
9	—	—	—	—	—	12.5	62	3.5	Ng	2.5	70	—
10	15	0.5	210	52	100	0	125	4.7	2.2	45.0	177	6.2
11	—	—	—	—	—	—	280	10	1	0	291	7.7
12	—	—	—	—	—	0	300	—	—	—	300	8.0
13	N/A	N/A	175	50	100	96.1	141.7	56.9	Tr	Tr	199	9.6
14	—	—	—	—	—	0 to 50	30 to 200	0 to 30	0 to 10	0 to 10	145	9.8
15	5.5	0.5	175	15	100	25	115	15	5	5	145	12.5
16	18 to 30	1 to 3	175 to 185	22 to 27	100	0	380	81	2	5	458	19.0
17	—	—	—	—	—	11.8	651	72.7	Tr	Tr	723	25.9

[a] Ng—negligible; Tr—trace; N/A—not available.

Table 16. RECOVERY FURNACE SYSTEM PARTICULATE EMISSIONS, SUMMARY OF EPA TEST RESULTS

Measurement or calculation	Mill B	Mill C
Equivalent production, T ADP/day	957	560
Stack flow rate, scfm	133,300	172,000
Ratio of volume to production, $\dfrac{\text{scfm}}{\text{T ADP/day}}$	139	307
Electrostatic precipitator inlet loading, gr/scf	3.71	4.18
Electrostatic precipitator inlet loading, lb/hr	4,330	6,160
Electrostatic precipitator outlet loading, gr/scf	0.162	0.107
Electrostatic precipitator outlet loading, lb/hr	185	158
Scrubber outlet loading, gr/scf	—	0.052
Scrubber outlet loading, lb/hr	—	77
Electrostatic precipitator collection efficiency, percent	95.7	97.4
Scrubber collection efficiency, percent	—	51.3
Overall collection efficiency, percent	95.5	98.7
Emission rate, lb/ T ADP	4.5	3.3

Gas analyses were made at two mills practicing black liquor oxidation. At Mill B, where strong black liquor oxidation is practiced, reduced sulfur emission rates were 0.005, 0.11 and 0.19 lb/T ADP, respectively, following the recovery furnace, flue gas direct contact evaporator, and electrostatic precipitator. At Mill C, where weak black liquor oxidation is practiced, the reduced sulfur emissions were 0.014, 0.023, 0.035, and 0.075 lb/T ADP, respectively, at the recovery furnace, contact evaporator, electrostatic precipitator, and wet scrubber. Each of these points was sampled on a different day; hence direct comparisons are not valid. The test data from these two studies are shown in Tables 18 and 19.

The sulfur dioxide concentrations in the furnace exit gases differed substantially, being 1 ppm at Mill B and 239 ppm at Mill C. The reduced sulfur concentrations in the furnace exit gases at both mills were low. The contribution of reduced sulfur from the contact evaporators differed substantially at the two mills, being about 0.1 lb/T ADP at Mill B and only 0.01 lb/T ADP at Mill C. No information was collected on the sulfide content of black liquor entering the flue gas direct contact evaporator at these mills. The data support earlier observations concerning the very low reduced sulfur emission levels of the recovery furnace and flue gas direct contact evaporator when high-degree black liquor oxidation is practiced.

Table 17. RECOVERY FURNACE SYSTEM GASEOUS EMISSIONS, MILL A WITHOUT BLACK LIQUOR OXIDATION, EPA TEST RESULTS

Sample location	SO_2 ppm	Reduced sulfur gases, ppm				TRS as H_2S		
		H_2S	CH_3SH	$(CH_3)_2S$	$(CH_3)_2S_2$	ppm	lb/hr	lb/T ADP
Direct contact evaporator inlet	1 4	1.2	1.0	—	—	2.2	2.3	0.06
Electrostatic precipitator inlet	—	500	—	—	3	503	525	14 8
Electrostatic precipitator outlet	—	300	—	—	—	300	313	8 8

Table 18. RECOVERY FURNACE SYSTEM GASEOUS EMISSIONS, MILL B WITH BLACK LIQUOR OXIDATION, EPA TEST RESULTS

Sample location	Number of samples	SO_2, ppm	Reduced sulfur gases, ppm				TRS as H_2S		
			H_2S	CH_3SH	$(CH_3)_2S$	$(CH_3)_2S_2$	ppm	lb/hr	lb/T ADP
Direct contact evaporator inlet	6	1 0	0 19	ND	ND	Tr	0 19	0 21	0 005
Direct contact evaporator outlet	7	Tr	1 7	1 4	0 37	0 27	4 0	4 4	0 12
Electrostatic precipirator outlet	9	0 12	4 5	1 4	0 83	0 40	7 5	7 7	0 20

[a]Tr — trace, ND — not detected

Table 19. RECOVERY FURNACE SYSTEM GASEOUS EMISSIONS, MILL C WITH BLACK LIQUOR OXIDATION, EPA TEST RESULTS

Sample location	Number of samples	SO_2, ppm	Reduced sulfur gases, ppm				TRS as H_2S		
			H_2S	CH_3SH	$(CH_3)_2S$	$(CH_3)_2S_2$	ppm	lb/hr	lb/T ADP
Direct contact evaporator inlet	6	239	Tr	ND	ND	0 12	0 24	0 34	0 015
Direct contact evaporator outlet	8	75 2	0 08	ND	ND	0 15	0 38	0 54	0 02
Electrostatic precipitator outlet	8	73 2	0 21	ND	ND	0 19	0 59	0 84	0 04
Scrubber outlet	—	40 8	1 0	Tr	ND	0 13	1 26	1 79	0 08

[a]Tr — trace, ND — not detected

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Black Liquor Oxidation Systems

Black liquor oxidation is the practice of oxidizing the sodium sulfide in either weak or strong black liquor, using either oxygen or air, to sodium thiosulfate or possibly higher oxidation stages, as represented in the following reaction

$$2Na_2S + 2O_2 + H_2O \rightarrow Na_2S_2O_3 + 2NaOH$$
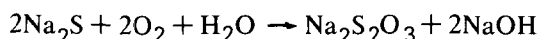
Sulfur present in the latter form is not displaced by the acid components of recovery flue gas, carbon dioxide and sulfur dioxide, as it passes through the direct contact evaporator. Increase in the proportion of hydrogen sulfide and methyl mercaptan present in undissociated form as a result of passage of acidic flue gases through the liquor is thereby prevented, and their stripping in the form of hydrogen sulfide and methyl mercaptan is avoided. The benefits of black liquor oxidation are outlined in the section on kraft recovery furnace systems. To be most effective, the black liquor oxidation must reduce sodium sulfide levels to 0.1 g/liter or less in the black liquor entering the flue gas direct contact evaporator. During the oxidation of black liquor, some reduced sulfur compounds are stripped by the air passing through it. This source of emissions is commonly classified as a miscellaneous emission source. The improvement in emission levels at the flue gas direct contact evaporator resulting from black liquor oxidation favors its use even though the emissions from the black liquor oxidation system may not be treated.

Designs, Application, and Performance

Black liquor oxidation systems that use air are of three types, (1) packed towers, (2) bubble tray towers, and (3) air-sparged reactors, which may be equipped with mechanical mixing devices to enhance oxygen transfer. One existing black liquor oxidation system uses tonnage oxygen. Except in rare instances, air is the more economical source of oxygen. A new oxidation system designed for use with air in series with existing units to reduce residual sodium sulfide levels of about 3 g/liter or less to almost zero represents a new concept in black liquor oxidation application.[20]

Packed towers and bubble trays have found application almost exclusively in the northern and northwestern United States where weak black liquor (direct from the brown stock washing system) of low foaming potential permits satisfactory use. Improvements in foam-breaking equipment have led to at least three recent installations of bubble trays for high-foaming-potential black liquor from the pulping of pine. Air-sparged reactors are also used for oxidation of low-foaming-potential weak black liquor.

When satisfactorily designed and maintained, all weak liquor oxidation systems have been demonstrated to be capable of producing a liquor with only trace amounts of residual sodium sulfide. One of the benefits once

assigned to weak liquor oxidation, namely reduction of sulfur losses at the multiple effect evaporators, may be overbalanced from an emissions standpoint by sulfur reversion to sulfides in the multiple effect evaporators and subsequent storage. Another benefit attributed to weak black liquor oxidation is a reduction in the amount of dissolved sulfur compounds in the evaporator condensate.

In general, some of the benefits once claimed for weak black liquor oxidation have been minimized if not negated by subsequent developments:

1. The development of methods for collecting low molecular weight sulfur compounds from the multiple effect evaporators and returning them to process.

2. The development of a control technique to adequately dispose of the high molecular weight sulfur compounds from the multiple effect evaporators.

3. Continued absence of demonstrated practical improvements in evaporator condensate quality where weak black liquor oxidation is practiced.

Strong black liquor oxidation has found most extensive and almost exclusive use in the oxidation of black liquor that is high in resin soap, such as that in the southern United States. To substantially reduce the foaming potential of the high resin soap content liquor, the liquor is partially evaporated, to about 25 percent solids content, and a high percentage of the soaps is removed. The liquor may be oxidized after soap removal and then further concentrated in multiple effect evaporators to about 50 percent solids content, and the 50 percent solids liquor may be oxidized. Heavy black liquor oxidation systems are currently exclusively air-sparged systems. The designs for most of these systems are similar, with (1) air introduced through a series of nozzles, (2) provisions for deaeration storage time after oxidation to permit satisfactory pumping of the liquor, and (3) usually provisions for foam collection and breaking in the exhaust air. Residence time of 3 or more hours is usually provided.[21] Like weak liquor oxidation systems, when properly designed and operated they produce a a liquor containing almost no sodium sulfide. Sulfide reversion has been observed to occur if the liquor is permitted to stand in storage for periods in excess of 4 to 6 hours.

The selection of black liquor oxidation systems should be made on the ability of the system to produce a very low sodium sulfide concentration in the liquor entering the direct contact evaporator.

Emission Data

Special Studies - The emissions from 11 weak and 4 heavy liquor oxidation systems measured in special studies[1] are shown in Table 20. Nine of the 11 weak liquor oxidation systems had reduced sulfur emissions ranging from

0.08 to 0.13 lb/T ADP, one 0.22 lb/T ADP, and the other 0.02 lb/T ADP. The median was 0.12 lb/T ADP. The reduced sulfurs present were essentially all the organic sulfur compounds of dimethyl sulfide and dimethyl disulfide. The heavy black liquor oxidation systems had TRS emission rates ranging from 0.01 to 0.18 lb/T ADP. The median emission rate for heavy liquor oxidation systems, 0.10 lb/T ADP, was about the same as the median for weak liquor oxidation units.

Questionnaire Survey — Emission data from six black liquor oxidation systems were received in the questionnaire survey. These data are summarized in Table 21. The emissions from four weak liquor oxidation systems ranged from 0.004 to 0.73 lb/T ADP, and those from the heavy liquor oxidation systems were 0.01 and 0.054 lb/T ADP. The median emission level was about 6 times greater from weak than from heavy liquor oxidation systems. The organic sulfur compounds, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide were the principal sulfur compounds present.

Table 20. REDUCED SULFUR EMISSIONS FROM BLACK LIQUOR OXIDATION SYSTEMS, SPECIAL STUDIES DATA

Type of system	Oxidation efficiency, percent	TRS		Emission rate, lb/T ADP
		Percent H_2S and CH_3SH	Percent $(CH_3)_2S$ and $(CH_3)_2S_2$	
Weak	83	0	100	0.1
	87	0	100	0.08
	90	0	100	0.13
	90	0	100	0.08
	50	—	—	0.12
	60	2	98	0.12
	60	2	98	0.09
	80	6	94	0.22
	80	2	80	0.11
	80	0	100	0.02
Heavy	85	0	100	0.06
	97	25	75	0.02
	97	0	100	0.01
	95	0	100	0.10
	99	—	—	0.03
	99	—	—	0.09
	98	—	—	0.18
	80	—	—	0.14

Table 21. GASEOUS EMISSIONS FROM BLACK LIQUOR OXIDATION, QUESTIONNAIRE DATA

Type of system	Pulp production rate, T ADP/day	Gas flow rate, acfm	Gas temperature, °F	Ratio of flow rate to production, acfm T ADP/day	SO_2, ppm	Reduced sulfur gases, ppm				TRS as H_2S		
						H_2S	CH_3SH	$(CH_3)_2S$	$(CH_3)_2S_2$	ppm	lb/day	lb/T ADP
Weak	740	15,830	163	21	6.5	0	20	177	69	335	538	0.73
	1100	6,500	140	6	—	20	0	40	3	66	45.3	0.004
	480	9,530	170	20	1	0	40	6	2	50	48	0.1
	500	5,600	155	11	—	5	30	20	80	215	124	0.25
Heavy	458	8,400	170	18	—	13	0	16	0	29	24.5	0.054
	536	25,140	155	47	0	0	3	0	0	3	7.8	0.01

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EPA Test Results — The EPA test team sampled the emissions from two mechanically agitated air-sparger black liquor oxidation systems. The reduced sulfur emissions of 0.13 lb/T ADP from the weak liquor oxidation system were about 3 times those of the heavy liquor oxidation system. As found previously, the bulk of the reduced sulfur compounds were organic sulfurs. The data from these tests are summarized in Table 22.

Control Techniques

There is no existing emission control system for black liquor oxidation exhaust emissions. A logical method is combustion since there is no known effective chemical absorption or oxidation process. If thermal oxidation were to be practiced, a separate incineration device, the recovery furnace, or a power boiler would represent logical approaches since the volume of exhaust gas exceeds that which can be handled in the lime kiln.

Table 22. EMISSIONS FROM BLACK LIQUOR OXIDATION TANKS, EPA TEST RESULTS

Measurement or calculation	Heavy liquor	Weak liquor
Production rate, T ADP/day	957	560
Effluent volume, cfm	18,500	17,000
Ratio of volume to production, $\dfrac{cfm}{T\ ADP/day}$	19	30
SO_2, ppm	Trace	1.4
H_2S, ppm	Trace	9.0
CH_3SH, ppm	1.2	21.3
$(CH_3)_2S$, ppm	0.79	7.1
$(CH_3)_2S_2$, ppm	10.8	1.9
TRS, ppm	23.6	41.2
TRS, lb/hr	1.76	3.0
TRS, lb/T ADP	0.047	0.15

Smelt Dissolving Tanks

The smelt dissolver is a large tank (3000 to 5000 ft³ or 22,400 to 37,400 gallons, measuring about 25 feet in diameter by 10 feet high) located below the recovery furnace hearth; in it, molten sodium carbonate and sodium sulfide smelt that accumulates on the floor of the furnace are dissolved in water to form green liquor. It is equipped with an agitator to assist dissolution, and a steam or liquid shatterjet system to break up the smelt stream before it enters the solution. The dissolved sodium carbonate in the

green liquor is later causticized, forming (with the dissolved sodium sulfide) white cooking liquor, and completing the recovery cycle. After clarification (settling out of suspended solids), the white liquor is ready for use as the cooking chemical in the digesters. Contact of the molten material with the water causes the evolution of large volumes of steam, which must be vented at about 200 degrees Fahrenheit ($^\circ$F) (dry bulb).

Emissions

Particulate matter (finely divided smelt, from submicron size to several hundred microns in diameter) is entrained in the vapor that leaves the tank. Because of the presence of a small percentage of reduced sulfur compounds in the smelt, some of these odorous materials escape the tank with the flashed steam.

Control Techniques

A widely used smelt tank control device is the mist eliminator. This usually is a wire mesh that is supported in the vent stack and intermittently backwashed with liquid to return the particulate matter to the smelt tank.

Wet scrubbers, pack towers, and cyclones are also used to remove entrained material. Some means is usually provided, regardless of the control device used, whereby large volumes of steam unexpectedly flashed in a short time can by-pass the control device to prevent rupture of the tank or ductwork.

On the questionnaires, nine mills reported sufficient data to compute the efficiency of their smelt tank control system. These data are given in Table 23.

Emission Data

Questionnaire Data—Smelt tank particulate emissions reported by 17 kraft mills ranged from 0.05 to 2.38 lb/T ADP as sodium oxide, with an approximate median value of 1.0 lb/T ADP. These data are tabulated in Table A-2 in Appendix A. Frequency distribution of the particulate emissions is shown in Figure 10. Concentrations ranged from 0.016 to 0.582 gr/dscf (60 $^\circ$F, 1 atmosphere), with a median value of 0.30 gr/dscf.

Gaseous emission data were reported by 18 mills. These data are tabulated in Table A-3 in Appendix A. Total reduced sulfur compounds range from 0.013 to 3.70 lb/T ADP as sulfur, with a median value of 0.09 lb/T ADP. Data on individual compounds are summarized in Table 24.

Special Study - A special study was conducted by NCASI personnel in 1970 and 1971.[1] The reduced sulfur contributions from 20 smelt tank vents are summarized and reported in Table 25. Some of these units were equipped with spray showers, demister pads, or packed towers for particulate control.

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Table 23. EFFECTIVENESS OF SMELT TANK PARTICULATE CONTROL DEVICES, QUESTIONNAIRE DATA

Control device	Gas flow rate, dscf	Particulate concentration, gr/dscf		Collection efficiency, percent	Emission rate, lb/T ADP
		Inlet	Outlet		
Pad entrainment separator	2,100	0.39	0.11	71.8	0.052
	2,700	0.412	0.094	77.2	0.15
	5,050	0.72	0.16	77.8	0.63
	5,600	5.94	0.581	90.2	2.3
	9,000	4.73	0.311	93.4	1.2
	9,090	1.65	0.482	70.8	1.58
Pad plus shower scrubber	9,800	1.58	0.06	96.2	0.41
Pad plus packed scrubber	37,000	1.6	0.13	91.9	1.20
Packed scrubber	6,350	1.0	0.016	98.4	0.05
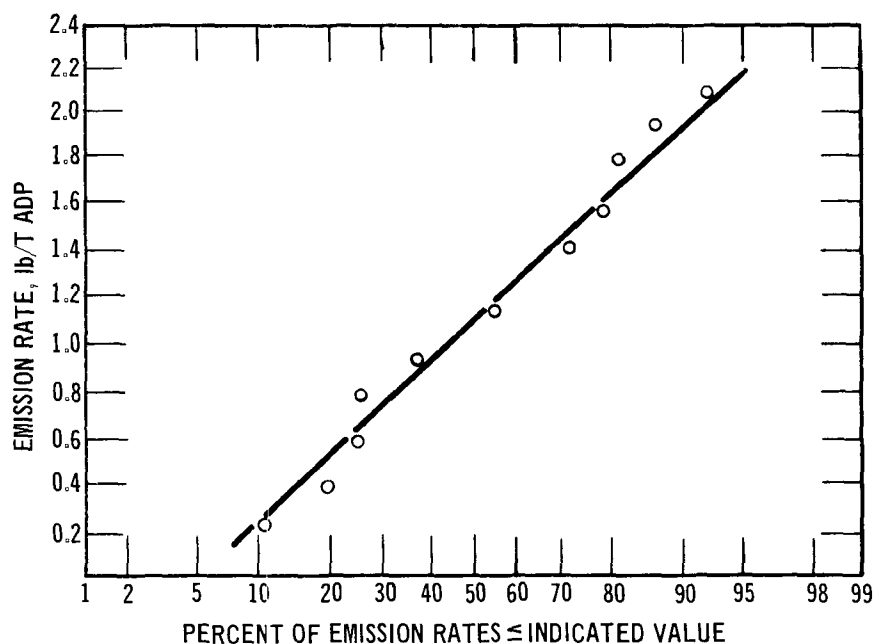
Figure 10. Smelt tank particulate emissions, questionnaire data.

PULP AND PAPER INDUSTRY EMISSIONS

**Table 24. SMELT TANK GASEOUS EMISSIONS,
SUMMARY OF QUESTIONNAIRE DATA**

| | Emissions | | | | Number of units |
| Compound | Concentration, ppm | | Rate, lb/T ADP as H_2S | | |
	Range	Median	Range	Median	
SO_2	2 to 385	92.2	0.005 to 2.1	0.08	8
H_2S	0 to 337	37.2	0 to 1.7	0.05	16
CH_3SH	0 to 400	47.2	0 to 2.0	0.05	12
$(CH_3)_2S$	0 to 150	27.2	0 to 1.7	0.16	11
$(CH_3)_2S_2$	0 to 25	7.5	0 to 0.37	0.17	10

These were operated on either lime mud washer filtrate water, fresh water, or contaminated condensate.

As shown in Table 25, the mass emission rate of TRS from those units operated without a particulate control device, with spray showers, or with demister pads varied from negligible to 0.03 lb/T ADP with the exception of one unit at Mill 4. The data reported for Mill 4 indicated the operation of demister pads with fresh water to be responsible for a slight absorption of reduced sulfur. The same conclusion was drawn from a similar study conducted at Mill 5. However, the use of lime mud washer filtrate water for demister pad shower water at Mill 5 resulted in a small contribution of TRS.

Only two vents equipped with packed towers for particulate control have been monitored to date. The values reported for Mill 2 indicated a potential for the evolution of soluble sulfides from either the scrubbing solution or the particulate matter collected. This was attributed to the practice of scrubbing solution recirulation and the absorption of carbon dioxide. This is substantiated to some degree by the results reported at Mill 5 upon the use of a shower water rich in soluble sulfides. Current particulate regulations specific to smelt tank vent emissions dictate the use of packed towers or possibly fine demister pads equipped with high-volume showers and recirculation. Consequently, the necessity of further studies on smelt tank vents equipped with high-efficiency particulate control devices is indicated, to determine the effects of shower water source, recirculation rate, and sulfide content of the particulate collected on reduced sulfur emission rate.

The study did indicate that the concentration of reduced sulfur in the emission could be maintained at 10 ppm or less. The compounds present were mainly hydrogen sulfide and methyl mercaptan. It appears treatment needs in the future would be predicated on emission appearance rather

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**Table 25. SMELT TANK TRS EMISSIONS,
SPECIAL STUDIES DATA**

Mill	Production rate, T ADP/day	Water source[b]	Control device or test point	TRS Concentration, ppm	TRS Rate, lb/T ADP as H_2S
1	130	—	No control device	1.0 to 2.5	0.01
2	250	1	Packed tower	10 to 40	0.12
3	145	2	Spray showers	ND to 0.6	Ng
	215	2	Spray showers	1.0 to 20.0	0.04
	215	2	Spray showers	3.0 to 26.0	0.04
4	435	2	After demister	10 to 35	0.08
	435	—	Before demister	20 to 66	0.11
	435	2	After demister	1.5 to 3.0	0.01
	435	—	Before demister	4 to 9	0.02
	420	2	After demister	ND	ND
	420	—	Before demister	ND	ND
5	520	1	After demister	2.0 to 4.0	Ng
	520	—	Before demister	0.8 to 1.8	Ng
	520	2	After demister	ND	ND
6	155	—	Showers	4 to 6	0.02
	310	2	Showers	5 to 8	0.03
7	400	3	After demister	2 to 5	0.01
8	—	—	No control device	ND	ND
9	240	2	After demister	4 to 6	0.02
	400	2	After demister	4 to 6	0.01
	375	2	After demister	2 to 6	0.01
10	600	1	Packed tower	ND	ND
11	350	1,3	After demister	1 to 1.5	Ng
	350	1,3	After demister	ND to 2.5	Ng

[a]Ng - negligible; ND - not detected.

[b]1 - lime mud washer filtrate, 2 - fresh water; 3 - contaminated condensate.

than possible ground level concentrations of reduced sulfur that might occur at most mill locations. Venting to the main stack for increased dilution and despersion appears to be an effective control technique.

EPA Test Results — Two smelt tanks serving one recovery furnace were tested for particulates by the EPA test team. Total effluent volume averaged 28,000 scfm. Emissions were controlled by wire mesh mist eliminators. Measurements were made only after the mist eliminator. Average emissions for the two stacks totaled 34.8 lb/hr or 0.77 lb/T ADP.

Gaseous emissions at two mills were sampled by the EPA test team. Results are summarized in Table 26.

Lime Kilns

The lime kiln is an essential element on the closed-loop system that converts green liquor to white liquor. The kiln supplies calcium oxide (quicklime, CaO), which is wetted (slaked) by the water in the green liquor solution to form calcium hydroxide, $Ca(OH)_2$ for the causticizing reaction. The reaction in the causticizer

$$Ca(OH)_2 + Na_2CO_3 \longrightarrow 2NaOH + CaCO_3$$
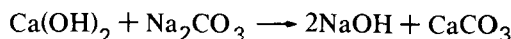
provides sodium hydroxide for cooking liquor and precipitated lime mud, which is recycled through the kiln. The lime sludge enters as a 55 to 60 percent solid-water slurry. The reaction which takes place in the kiln is

$$CaCO_3 + heat \longrightarrow CaO + CO_2$$
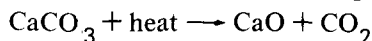
Most lime kilns used by pulp mills are the rotary type, usually ranging from 8 to 13 feet in diameter and 125 to 400 feet in length. The kilns are of steel construction and are inclined at an angle of about 10 degrees to the horizontal. Lime mud is fed in at the elevated end and contacted by hot` gases resulting from the combustion of natural gas or fuel oil and proceding through the kiln in the opposite direction. Large motors (several hundred horsepower) turn the entire kiln at low speeds, causing the lime to proceed downward through the kiln toward the high-temperature zone (1800 to 2000 °F) to discharge at the lower end. As the lime melt and mud move along, they dry in the upper section, which may be equipped with chains or baffles to give the wet mud better contact with the gases. As the lime moves down farther, it agglomerates into small pellets and finally is calcined to calcium oxide in the high-temperature zone near the burner.

Rotary kilns are capable of producing the large quantities of quicklime required by kraft mills (40 to 400 T/day), but heat losses through the long kiln are considerable.

Fluidized bed calciners are presently being used by a few manufacturers, but their production rate at this time is not as great (25 to 150 T/day).

Table 26.   SMELT TANK GASEOUS EMISSIONS, EPA TEST RESULTS[a]

Mill	SO_2, ppm	Reduced sulfur gases, ppm				TRS as H_2S		
		H_2S	CH_3SH	$(CH_3)_2S$	$(CH_3)_2S_2$	ppm	lb/hr	lb/T ADP
B	Tr	3.7	1.1	2.3	0 05	7.0	1.42	0.036
C	0.17	2.0	ND	ND	Tr	2.0	0.27	0.011

[a]ND — not detected, TR — trace.

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Emissions

The rolling and tumbling of the lime in the rotary kiln and the vaporization of sodium compounds (carried into the kiln with the lime mud) in the high-temperature zone and their later condensation are responsible for the formation of most of the particulate matter carried by the kiln exhaust gases. This emission constitutes not only an air pollution problem but also a loss of usable chemical.

The lime dust is made up of particles of sizes ranging from 1 to over 100 microns in diameter, while the soda fume consist of very small particles, most less than 1 micron in diameter. Therefore, the lime dust is removed from the exhaust gas quite easily; but the soda fume is very difficult to remove.

Some odorous sulfur gases are emitted from lime kilns. Hydrogen sulfide is produced in the kiln by the reaction

$$Na_2S + H_2O + CO_2 \longrightarrow Na_2CO_3 + H_2S$$
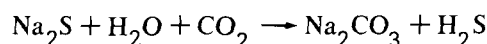
Sodium sulfide entering the system as an impurity in the lime sludge and sulfur bearing process water used as scrubbing liquid in the lime kiln may be sources of reduced sulfur emission.

At some mills, the odorous noncondensable gases from the digesters, blow tanks, and multiple effect evaporators are incinerated in the lime kiln. Burning of these reduced sulfur gases forms sulfur dioxide, which apparently reacts with either the lime in the kiln or the alkaline scrubbing solution in the scrubber, resulting in no significant increase in total sulfur emission.

Control Techniques

Odorous emissions of hydrogen sulfide can be reduced by adequate washing of the lime mud precipitate from the causticizer to remove adherent white liquor containing sodium sulfide. However, a small amount of sodium compounds (about 0.25 percent) is intentionally left in the lime to avoid the formation of large loose balls or rings of lime adhering to the inner surface of the kiln in the agglomeration zone.

Sufficient excess air must enter the kiln for complete combustion of the fuel and for oxidation to sulfur dioxide of some hydrogen sulfide formed in the kiln by the reaction of water, carbon dioxide, and sodium sulfide.

Several types of control equipment are available for the reduction of lime kiln particulate emissions. The water scrubber, usually of the impingement or venturi type, is used exclusively in the kraft industry. The impingement type is a fairly low pressure drop unit (5 to 6 inches of water) in which the exhaust gas flows through wetted baffles with water sprays between them. Nozzles and baffles tend to be obstructed by lime buildup, which may

reduce efficiency and cause maintenance problems. Maximum solids content of the scrubbing medium is usually less than 2 percent.

Venturi scrubbers are generally more efficient (97 to 99 percent) than impingement type scrubbers and operate with a pressure drop of 10 to 20 inches of water. They can use a scrubbing medium of up to 30 percent solids since they have less tendency to sludge up, and thus do not require cleaning as frequently as impingement scrubbers. Water flows down the edges of the vertical venturi, from large orifices, to the throat where an annular ridge causes it to splash outward into the throat. Particulates in the gas flowing through the throat in the same direction as the water are caught by the curtain of water. The extreme turbulence in this area prevents the buildup of sludge. Increasing the water and/or gas velocity increases the pressure drop across the scrubber as well as the efficiency.

If the scrubbing liquor contains sodium sulfide, as it does in some installations, hydrogen sulfide may be formed in the scrubber from the reaction of sodium sulfide, carbon dioxide, and water in the same manner as it is in the direct contact evaporator. Other reduced sulfur compounds in the scrubbing liquor may also be partially stripped from solution.

Other sources of particulate emissions associated with kilns are open conveyors, elevators, slaker vents, and storage facilities for lime. Enclosing these sources and venting them through the kiln control device or a separate air cleaner appears to be the most effective means of control.

Emission Data

Particulate stack emission data for 66 lime kilns were reported by 35 mills on the questionnaire. Rates ranged from 0.08 to 43 lb/T ADP. The median concentration was 0.4 gr/dscf. Stack flow rates ranged from 5800 to 24,500 dscfm, with a median value of 13,800 dscfm or 33 dscfm/T ADP. These data are tabulated in Table A-4 in Appendix A. The distribution of emission ranges is plotted in Figure 11.

Particulate concentrations at the inlet to the scrubber were reported for 15 kilns. These data were separated by scrubber types, efficiencies were computed, and results are tabulated in Table 27.

Gaseous emission data from 22 lime kilns were reported in the questionnaires by 13 mills. These data are tabulated in Table A-5 in Appendix A. Emissions of TRS compounds ranged from 0.015 to 4.0 lb/T ADP hydrogen sulfide as sulfur. The median value was 0.43 lb/T ADP. Values for individual compounds are summarized in Table 28.

Particulate tests on lime kilns were run at two mills by the EPA test team. Both kilns were controlled by venturi scrubbers with pressure drops of about 10 inches of water. Results are summarized in Table 29.

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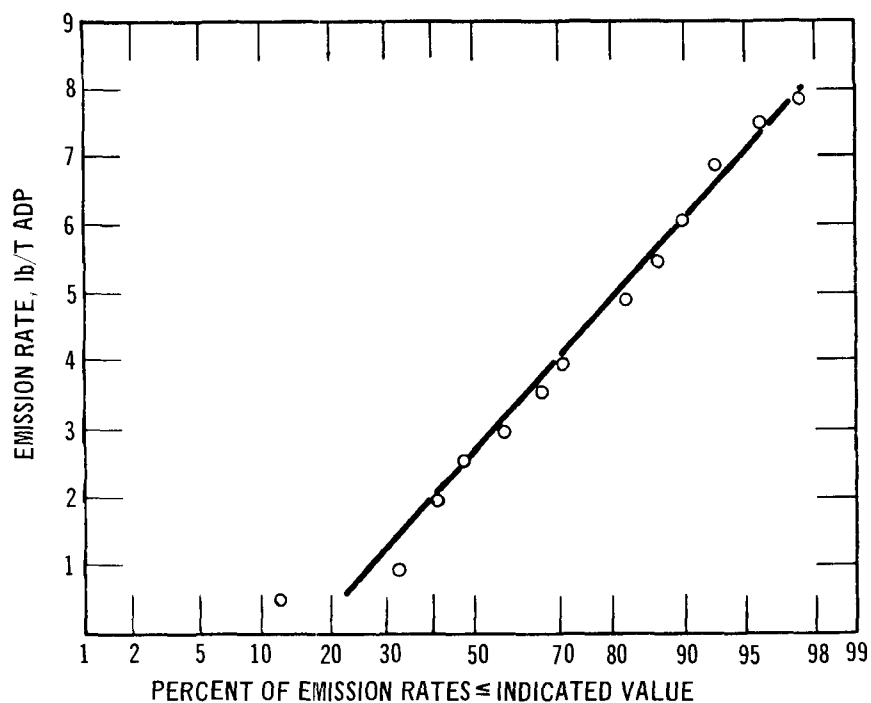
Figure 11. Lime kiln particulate emissions, questionnaire data.

Table 27. LIME KILN SCRUBBER EFFICIENCY,
SUMMARY OF QUESTIONNAIRE DATA

Impingement scrubbers			Venturi scrubbers		
Particulate concentration, gr/dscf		Collection efficiency, percent	Particulate concentration, gr/dscf		Collection efficiency, percent
Inlet	Outlet		Inlet	Outlet	
3 50	0.46	86.9	4.68	0.16	96.5
14.05	0.43	96.9	10.00	1.00	90.0
14.29	0.58	95.9	6.33	0.23	96.4
9.22	1.05	88.6	9.30	0.13	98.6
16.02	0.88	94.5	13.80	0.12	99.1
11.78	1.56	86.8	12.14	0.14	98.9
14.81	0.53	96.4	6.05	0.38	93.7
			2.55	0.37	85.5
Averages					
11.94	0.78	92.2	8.11	0.32	94.8

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Table 28. GASEOUS LIME KILN EMISSIONS,
SUMMARY OF QUESTIONNAIRE DATA

Compound	Emissions				Number of units
	Concentration, ppm		Rate, lb/T ADP as H_2S		
	Range	Median	Range	Median	
SO_2	0 to 140	33.8	0 to 2.35	0.3	13
H_2S	0 to 500	107.9	0 to 4.0	0.5	24
$(CH_3)SH$	0 to 90	14.0	0 to 0.36	0.07	10
$(CH_3)_2S$	0 to 245	27.0	0 to 0.46	0.05	14
$(CH_3)_2S_2$	0 to 11.4	5.4	0 to 0.21	0.03	10

In the EPA testing program, two lime kilns were sampled for gaseous compounds. The water used for scrubbing the gases from both kilns contained only traces of organic sulfur compounds. Both kilns were used to incinerate digester and evaporator noncondensable gases. Only traces of organic sulfur gases were detected. The hydrogen sulfide and sulfur dioxide results are given in Table 30.

Table 29. LIME KILN PARTICULATE EMISSIONS,
EPA TEST RESULTS

Mill	Gas flow rate, scfm	Particulate loading				Scrubber efficiency, percent	Emission rate, lb/T ADP
		Concentration, gr/scf		Rate, lb/hr			
		Inlet	Outlet	Inlet	Outlet		
B	17,610	—	0.322	—	48.7	—	1.42
C	16,500	7.89	0.285	957	40.1	95.9	1.7

Table 30. LIME KILN GASEOUS EMISSIONS,
EPA TEST RESULTS

Mill	Compound	Emissions				Number of tests
		Concentration, ppm		Rate, lb/T ADP as H_2S		
		Range	Mean	Range	Mean	
B	SO_2	Trace	—	—	—	8
B	H_2S	7.2 to 79.9	25.0	0.04 to 0.5	0.16	8
C	SO_2	1.2 to 48.8	20.4	0.027 to 0.44	0.18	10
C	H_2S	30 to 146	67.8	0.15 to 0.72	0.34	12

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Brown Stock Washing Systems and Other Miscellaneous Sources

Emission inventories and special studies have identified the significant emission sources from brown stock washing systems to be those associated with the washing of black liquor from, or screening of, pulp. Such sources include the brown stock washer hood and knotter vents, the exhausts of vacuum pump systems used on brown stock washers, and the brown stock filtrate tanks, which serve to collect the black liquor and air from brown stock washers operated with a barometric leg. Washer hood vents are usually mechanically exhausted, although a limited number of older systems are vented by natural draft and a smaller number yet have no hoods or vents whatsoever. Knotters may be vented singularly, vented in a common washer hood vent system, or operated without a vent system. Few knotter systems are vented singularly. Depending on the system design, vents from other processes where black liquor is violently agitated, such as the salt cake mix tank, could be a miscellaneous source emission.

Lime kiln slaker vents are also commonly listed as a miscellaneous source, although the emission of reduced sulfur, if any is present, is no more than a trace. Both the smelt tank vent and black liquor oxidation tower vents are also commonly characterized as miscellaneous sources. These two processes and their emissions are described elsewhere in this report.

In the past, these miscellaneous sources have been characterized as minor emission sources based on the relative amount of reduced sulfur compounds emitted from them as compared to those from uncontrolled major emission processes such as the recovery furnace system. With application of the technology available for control at major emission points, there can be a major rearrangement in the significance of miscellaneous emissions. Under the conditions of controlled major sources, they may represent the largest source of reduced sulfur emissions.

Emission Data

The data in Table 31 represent the reduced sulfur emissions from 17 mechanically vented brown stock washing systems.[1] The emissions are characteristically dominantly dimethyl sulfide and dimethyl disulfide from the roof vent system and almost exclusively these two compounds from the undervent system (vacuum pump exhausts and filtrate seal tank vents). As shown in Table 32, the median TRS emission level from the roof vent of 14 of the above systems using fresh water on the washers was 0.04 lb/T ADP, compared to 0.35 from five systems using condensate as a washing medium. The median TRS emissions from the undervents on these systems was 0.08 and 0.11 lb/T ADP, respectively. As shown in Table 33, the median TRS emission for the total system was 0.10 when using fresh water and 0.40 lb/T ADP when using condensates as a washing medium in these systems. The most significant difference in emissions between systems using fresh water and those using condensates was at the roof vents, as shown in Table 32. The difference in median levels was 0.31 lb/T ADP, or 9 times greater when condensates were used.

Table 31. BROWN STOCK WASHER SYSTEM TRS EMISSIONS, SPECIAL STUDIES DATA

System	Wash water	Roof vents Rate, lb/T ADP TRS as H_2S	Roof vents Percent H_2S and CH_3SH	Roof vents Percent $(CH_3)_2S$ and $(CH_3)_2S_2$	Under vents Rate, lb/T ADP TRS as H_2S	Under vents Percent H_2S and CH_3SH	Under vents Percent $(CH_3)_2S$ and $(CH_3)_2S_2$	Total TRS, lb/T ADP
1	Fresh	0.1	0	100	0.35	0	100	0.45
2	Fresh	0.21	0	100	0.63	0	100	0.84
3	Fresh	0.07	0	100	0.03	0	100	0.10
4	Fresh	—	0	100	—	0	100	0.03
5	Fresh	0.01	0	100	0.02	0	100	0.03
5	Condensates	0.15	0	100	0.09	0	100	0.24
6	Fresh	0.05	0	100	0	0	100	0.05
7	Fresh	0.10	10	90	0.11	25	75	0.21
8	Fresh	0.05	0	100	0.11	0	100	0.16
9	Fresh	0.04	60	40	0.08	30	70	0.12
10	Fresh	0.01	10	90	0.02	0	100	0.03
11	Fresh	0.04	90	10	0.06	0	100	0.10
12	Fresh	0.01	90	10	0.005	0	100	0.02
13	Fresh	0.01	60	40	0.005	0	100	0.01
14	Fresh	0.08	—	—	0.18	—	—	0.26
14	Condensates	0.41	—	—	0.22	—	—	0.63
15	Condensates	0.03	—	—	0.11	—	—	0.14
16	Condensates	0.35	0	100	0.05	0	100	0.40
17	Condensates	0.60	0	100	0.30	0	100	0.90

Table 32. BROWN STOCK WASHER SYSTEM TRS EMISSIONS, ROOF VENTS AND UNDER VENTS, SPECIAL STUDIES DATA

Number of systems	Wash water	TRS as H_2S, lb/T ADP							
		Roof vents				Under vents			
		Max.	Min.	Median	Mean	Max.	Min.	Median	Mean
13	Fresh	0.08	0.01	0.04	0.05	0.63	0	0.08	0.13
5	Condensates	0.65	0.03	0.35	0.32	0.30	0.05	0.11	0.15

TABLE 33. BROWN STOCK WASHER SYSTEM TRS EMISSIONS, TOTAL SYSTEM, SPECIAL STUDIES DATA

Number of systems	Wash water	TRS as H_2S, lb/T ADP			
		Max.	Min.	Median	Mean
14	Fresh	0.84	0.015	0.10	0.17
5	Condensate	0.90	0.14	0.40	0.46

The bulk of the stripping of reduced sulfurs from condensates in these systems occurs in the washers (Table 34). The difference in median discharge levels from the undervent system when using the two different wash waters was 0.03 lb/T ADP.

A comparison of TRS emission levels from two systems operated alternately on fresh water and condensates is shown in Table 34. Roof vent

Table 34. BROWN STOCK WASHER SYSTEM TRS EMISSIONS, ALTERNATE USE OF FRESH AND CONDENSATE WASH WATER, SPECIAL STUDIES DATA

System number	Wash water	TRS as H_2S, lb/T ADP		
		Roof vents	Under vents	System
5	Fresh	0.01	0.02	0.03
5	Condensate	0.15	0.09	0.24
14	Fresh	0.08	0.18	0.26
14	Condensate	0.41	0.22	0.63

losses increased 0.14 and 0.33 lb/T ADP, representing increases of 15 and 5 times, when condensates were substituted for fresh water at the washers. The undervent system increases were less, being 0.07 and 0.04 lb/T ADP, respectively. System emission increases were 0.21 lb/T ADP, or 8 times, and 0.37 lb/T ADP, or 2.5 times, respectively, for the two systems when condensates were substituted for fresh water.

Walther and Amberg report a reduced sulfur emission of 0.6 lb/T ADP from a brown stock washer system using fresh water.[22] This is higher than the median of 0.10 lb/T ADP found in these 14 systems but less than the maximum found, which was 0.84 lb/T ADP.

The EPA test team made stack measurements at brown stock washer systems and knotter hood vents at two mills. The data are given in Table 35.

Table 35. BROWN STOCK WASHER SYSTEM GASEOUS EMISSIONS, EPA TEST RESULTS [a]

Mill	Operation	Gas flow rate, scfm	SO_2, ppm	Reduced sulfur gases, ppm				TRS as H_2S	
				H_2S	CH_3SH	$(CH_3)_2S$	$(CH_3)_2S_2$	ppm	lb/T ADP
B	Brown stock washer, west	20,000	Tr	2.2	3 9	5 6	2 6	16.9	0 05
B	Brown stock washer, east	10,000	Tr	0.9	3.5	11 1	1 6	18.7	0 03
C	Brown stock washer	34,600	0 25	Tr	Tr	2 1	0 8	3.7	0 03
C	Washer seal tank	760	Tr	268	18 9	382	50 2	769	0 13
C	Knotter hood	15,300	0 20	0 30	0.24	14 1	2 5	19.6	0.06

[a] Tr - trace

Control Techniques

There is no known feasible absorption or chemical oxidation system for brown stock washer system vent gases. A logical control method is thermal oxidation, and the only control system for these sources in the United States uses this method. In this case, the vent gases are burned in the recovery furnace using a specially designed injection system. The large volumes, which range from 35,000 to 50,000 cfm per washing system, limit the existing process equipment suitable for handling such a volume to the recovery furnace or possibly a steam or power boiler. The procedure is not attractive for application in any but new recovery furnace systems due to major engineering and construction changes required. The reasonably low gas volumes from most undervent systems suggest the possibility of burning these in the lime kiln. In those cases where this can be done in conjunction with the use of fresh water in the washers, a reduction of approximately 90 percent emission level for this source would be accomplished.

Kraft (Sulfate) Pulping **61**

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SEMICHEMICAL SULFITE PULPING PROCESSES

INTRODUCTION

Raw Materials

Semichemical pulps can be made by any of the commerical cooking processes by reducing cooking time, temperature, or the amount of chemical charged to the digester. Many types of wood can therefore be pulped using these processes. Semichemical pulping process is used for the most part to produce pulp from hardwoods for use in making corrugated board. About 9 percent of the wood pulp produced in the United States is made in this manner.

Process Description

As pointed out above, semichemical pulps can and are manufactured by variations in other commerical chemical pulping processes. The process most extensively used is the neutral sulfite semichemical (NSSC) process however. Semichemical pulping is a two-stage process that uses a mild chemical treatment of the chips to weaken the intercellular bonding by partial removal of the hemicellulose and lignin, followed by mechanical treatment to separate the individual fibers.

For the manufacture of NSSC pulps, chips, usually hardwood, are cooked in batch or continuous digesters with a nearly neutral solution of sulfite containing a small amount of alkaline agents such as carbonate, bicarbonate, or hydroxide. After cooking, they are blown to a blow tank. The cooked chips are further processed in disk refiners, washed free of cooking liquor, and converted to board or paper. Some NSSC pulp is bleached prior to use, but the practice is limited due to high bleaching costs. Since a number of NSSC mills were converted from other processes, many variations in operating conditions and equipment exist.

The cooking liquor may be prepared either by adding fresh chemicals (sulfite and carbonate) to water or spent liquor or by absorbing sulfur dioxide generated in a sulfur burner in a sodium carbonate solution.

The spent cooking liquor may be discharged as a liquid effluent, burned with heat recovery but no chemical recovery, or burned with heat and chemical recovery. Prior to burning, the liquor is concentrated in multiple effect evaporators similar, if not identical, to those used in the kraft

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process. Chemical recovery may be combined with the kraft recovery process, a process commonly referred to as cross recovery, with soda and sulfur from the semichemical process replacing salt-cake make-up in the kraft process. In cross recovery schemes, the spent cooking liquors are mixed prior to burning.

Semichemical liquor may also be burned alone in a conventional kraft furnace for recovery of chemicals. Green liquor from smelt formed is sulfited directly or indirectly to produce new cooking liquor. There are only a limited number of these systems. The nature and control of emissions from these systems may differ significantly from other semichemical processes, however, since the smelt from which cooking liquor is produced may contain sodium sulfide. The liquor may also be burned under oxidizing conditions in fluidized combustion, forming sodium sulfate, which may be used for make-up in the kraft process.

Product Yield

Pulps that have a yield ranging from about 60 to 80 percent are generally classed as semichemical pulps. Those pulps in the lower semichemical yield range that require only moderate mechanical treatment may be called high yield chemical pulps.

EMISSIONS

Because of the difference in the chemical attack on the lignin when using sulfite liquors, such compounds as methyl mercaptan and dimethyl sulfide are not formed during digestion. The NSSC process should,therefore, be free from these odorous compounds. In addition, the absence of sulfide ions from the cooking liquor will virtually eliminate hydrogen sulfide as a possible emission. Exceptions to this rule might be expected in those systems where liquor is burned in such a manner that the smelt contains sodium sulfide. Atmospheric emission sources from an NSSC mill will include sulfur dioxide absorption towers, if they are used, blow tanks, spent liquor evaporators, and the liquor burning or chemical recovery furnace. In the case of spent liquor recovery in a kraft mill recovery system, the NSSC liquor is said to have an effect upon the emissions from the kraft recovery system.[4] This is not documented however.

Sulfur Dioxide Absorption Tower

Sulfur dioxide absorption towers generally are countercurrent packed towers using soda ash or another alkaline solution as the absorbing medium. Chemical absorption takes place according to the following reaction

$$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2$$
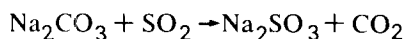
This reaction leads to the emission of carbon dioxide. Sulfur dioxide may also be absorbed in water according to the following reaction

$$SO_2 + H_2O \longrightarrow H_2SO_3$$
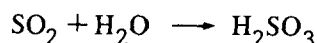
Nearly total absorption of sulfur dioxide in the tower is feasible in a properly designed and operated tower. Emissions are, therefore, dependent on the design and operating conditions of the individual towers. Smelt that is formed when burning the cooking liquor in a converted kraft furnace under a partial reducing atmosphere and then dissolved to form green liquor contains sulfide. If sulfited, it will release hydrogen sulfide.[23]

Blow Tank

When the cooked pulp is blown into the blow tank, large amounts of steam and gases escape from the pulp and spent liquor. Sulfur dioxide is the major gaseous emission. Recently, recovery systems have been installed to recover the sulfur dioxide from the blow pit gases. These installations are based upon the absorption of sulfur dioxide by scrubbing either in the vent stack or by routing the gas to the sulfur dioxide absorption tower. Again, the emissions will be determined by the design and operation of the system.

Chemical and Heat Recovery Furnace

In those situations where semichemical liquor is burned for the single purpose of destroying organic matter with no chemical recovery, a water quality protection measure, the residual sulfur present in the liquor can be expected to be emitted as sulfur dioxide. The mills that follow this practice all produce pulp using an ammonia pulping base.

Where semichemical liquor is burned in conjunciton with black liquor form the kraft process in cross recovery, there is no evidence that the conditions controlling emissions from the furnace are different than when kraft black liquor alone is burned. The potential exists for a pH reduction when the two liquors are mixed in cross recovery systems. This might have an effect on the reduced sulfur emissions from the contact evaporator, although there is no evidence that such a situation occurs.

In theory, the sulfur emissions from fluidized bed combustion systems should be extremely low. Short-term studies show this to be so. The emissions measured on two different systems amounted to no more than 0.1 lb/T ADP, of which 70 percent of the sulfur emission was reduced sulfur, principally hydrogen sulfide, and 30 percent was sulfur dioxide.

When semichemical liquor is burned in a partial reducing atmosphere, some sodium sulfide is reported to exist in the green liquor, white or cooking liquor, and spent cooking liquor. Hydrogen sulfide stripping in a flue gas contact evaporator would be anticipated if one were used. It has been shown that proper and controlled amounts of combustion air can

control the reduced sulfur emissions from these furnaces. Anticipated emission rates of reduced sulfur from the furnace by this control technique are 0.25 lb/T ADP. It has also been demonstrated that the ratio of soda to sulfur present in the cooking liquor is related to the sulfur dioxide emission from these furnaces. [23]

EMISSION DATA

Questionnaires were sent to 60 acid sulfite and nonintegrated neutral sulfite mills. Eleven were returned by the nonintegrated semichemical mills, ten from soda base and one from ammonia base mills.

Information on the use of methods to control sulfur dioxide emissions from absorbers and from digester relief and blow gas are summarized in Table 36. Absorbers were considered controlled if a second absorber was used or if a scrubber was used after the absorber.

Table 36. EXTENT OF CONTROLS USED IN SEMICHEMICAL PULPING OPERATIONS, QUESTIONNAIRE DATA

Operation	Number of mills	Controls used	
		Yes	No
Absorbers	6	3	3
Digester relief gas	11	3	8
Digester blow gas	11	3	8

Relief and blow gases were controlled by venting to the absorber or to a separate scrubber. Three of six mills using absorbers provided controls, and three of the eleven reporting used digester and relief gas control.

The data provided in the questionnaires on the amounts of sulfur dioxide emissions are shown in Table 37. The data are so sparse that a summary is not warranted.

The information on types of cooking liquors used and the types of heat recovery or chemical recovery furnaces is summarized in the following paragraphs.

Ten of the mills use sodium-base liquors. Three of these use fluidized bed recovery furnaces. The chemicals are recovered in the form of sodium sulfate and sodium carbonate and can be used as make-up chemicals in a kraft process.

Table 37. SULFUR DIOXIDE EMISSIONS FROM SEMICHEMICAL PROCESSES, QUESTIONNAIRE DATA

Mill number	Emission rate, lb/T ADP						Type mill
	Absorption		Digester relief		Furnace		
	Before control	After control	Before control	After control	Before control	After control	
21	0.33	ND	—	—	—	—	NH_3
25	ND	0.021	—	—	—	—	NH_3
28	0.365	ND	—	—	—	—	Na
30	0.298[b]	—	0.775[b]	—	26.5	2.4	Na
31	0.192[b]	—	—	—	ND	7.1	Na

[a]No data reported for digester blow or evaporators.

ND — process controlled, but no data reported.

[b]No controls.

Two of the mills using sodium-base liquors use recovery systems designed by the Institute of Paper Chemistry. In this system, the spent liquor is concentrated in multiple effect evaporators and burned in a kraft type recovery furnace. A smelt of sodium carbonate and sodium sulfide is dissolved to make green liquor. This liquor is sulfited in an absorbing tower using sulfur dioxide from a sulfur burner. This produces cooking liquor containing sodium sulfide, sodium carbonate, and sodium hydrosulfide. Hydrogen sulfide and sulfur dioxide are emitted from the sulfiting tower. One of these mills reported total emissions of 20.1 lb/T ADP of hydrogen sulfide and organic sulfur compounds and 5.21 lb/T ADP of sulfur dioxide. The other mill reported total emissions of 24.7 lb/T ADP of hydrogen sulfide and organic sulfur compounds and 13.5 lb/T ADP of sulfur dioxide.

One of the mills reporting uses ammonium-base cooking liquors. This mill concentrates the liquor to 45 percent solids and burns it in a pulverized coal-fired boiler. The resulting sulfur dioxide is vented to the atmosphere.

CONTROL TECHNIQUES

Little information is available on control of emissions from new NSSC mills. The limited information on emission control from semichemical pulping is referred to in other parts of this section. Control of emissions from those unit operations similar to sulfite sources (absorption tower, blow tank) will be described in the following section.

Semichemical Sulfite Pulping Processes   **67**

SULFITE PULPING PROCESS

INTRODUCTION

Raw Materials

Sulfite pulp can be made from several types of wood, but soft woods are generally used. The specific type of wood used depends both on the final product desired and the cooking base employed.

Process Description

Sulfite pulping is an acid chemical method of dissolving the lignin that bonds the cellulose fibers together. Many of the older mills use a sulfurous acid-calcium bisulfite solution for the cooking acid. Calcium-base spent liquor, because of problems associated with evaporation and chemical recovery and its low chemical cost, is not normally recovered. To satisfactorily recover the spent liquor, several other acid bases have been developed, the most important being sodium, magnesium, and ammonium.

Because sulfite pulp is used in a wide variety of end products, pulping conditions will vary considerably between mills. These products can include pulp for making high-grade book and bond papers and tissues, for combining with other pulps, and for making dissolving pulp for producing cellophane, rayon, acetate, films, and related products.

The pulping operation involves cooking wood chips with a low resin content in the presence of an acid within a digester. The heat required for cooking is produced by the direct addition of steam to the digester or by the steam heating of the recirulated acid in an external heat exhanger. The cooking liquor, or acid, is made up of sulfurous acid and a bisulfite of one of the above four bases. The sulfurous acid is usually produced by burning sulfur or pyrites and absorbing the sulfur dioxide in liquor. Normally, part of the sulfurous acid is converted to the base bisulfite to buffer the cooking action. During the cooking action, it is necessary to vent the digester occasionally as the pressure rises within the digester. These vent gases contain large quantities of sulfur dioxide and, therefore, are recovered for reuse in the cooking acid.

Upon completion of the cooking cycle, the contents of the digester, consisting of cooked chips and spent liquor, are discharged into a blow pit or tank. During this operation, some water vapor and fumes escape to the atmosphere from the tank vent. The pulp then goes through a washing

stage, where the spent liquor is separated from the fibers. The washed pulp is either shipped or kept within the plant for further processing.

Product Yield

Wood cooked by the sulfite process has a pulp yield ranging from well below 50 percent for dissolving pulps up to 60 percent, and generally is about 50 percent or below. A pulp yield above 60 percent generally calls for classifying the pulping operation as semichemical even though it may be an acid sulfite or bisulfite cooking process.

EMISSIONS

Sulfur dioxide is the principal atmospheric emission from the sulfite processes. The main sources of sulfur dioxide release are the absorption towers, blow pit or dump tank, multiple effect evaporators, and liquor burning or chemical recovery systems.

Absorption Towers

Industrial absorption towers for sulfite processes are usually packed towers or venturi absorbers. In the case of packed towers, sulfur dioxide gas is introduced in the bottom of the tower while an alkaline solution of the desired base (ammonia, etc.) is introduced at the top of the tower. Where calcium is the base, limerock $(CaCO_3)$ is used as packing into the tower. Sulfur dioxide reacts with water to yield an acidic solution.

Acid fortification towers are also absorption towers. Weak cooking liquor is passed through the tower for the purpose of absorbing additional sulfur dioxide. This replenishment of sulfite in the liquor offsets the sulfite lost through mill emissions as sulfur dioxide or combined as lignosulfonic acids in the spent pulping liquor.

The quantity of sulfur dioxide gas delivered to the absorption tower will depend upon the desired pH and strength of inorganic chemicals in the cooking liquor. The amount of sulfur dioxide emitted will depend on the design and operating conditions of the individual towers.

Blow Pits

There are three methods of discharging the digester; hot blowing, cold blowing, and flushing. In a hot blow, the pressure in the digester is relieved to a predetermined level and the contents are then blown into a blow pit. In cold blowing, the pressure in the digester is relieved to a low level and the contents are then pumped into a dump tank below the digester. Spent liquor is introduced into the bottom cone of the digester to reduce pulp consistency and aid discharge. In the flushing system, after the digester has been relieved, spent liquor or hot water is pumped into the digester for

several minutes at a high rate. The blow valve is then opened and the pulp is discharged while the flushing liquid continues to enter the digester.

The three types of digester discharge affect the amount of sulfur dioxide that is emitted to the atmosphere. Gases that leave the digester during relief are sent to the accumulators, where they fortify the cooking liquor. The gases that pass through the accumulators are sent to other areas in the process, where they may be absorbed. However, blow tanks and dump tanks are usually vented to the atmosphere. Gases carried from the digester to these tanks may, therefore, be sources of emissions. Recent installations of gaseous control devices on blow pit gases will reduce these emissions.

A review of the digester discharge system shows that for the hot blow style, the pressure is only partially relieved before the blow is made. The digester gases that were not relieved will be sent to the blow pit during the blow. Significant quantities of sulfur dioxide are therefore emitted in this style of discharging if no recovery is practiced. In the cold blow and flushing style of discharging the digester, the pressure is almost fully relieved, and the relief gases are routed to the accumulators. That fraction of the gases that remains in the digester may then escape from the system when the pulp is discharged to the dump tanks. Ranges of sulfur dioxide emissions that might be expected from the blow pit vent stack without scrubbing are: [4]

Potential source	SO_2 emissions, lb/T ADP
Blow pit, hot blow	100 to 150
Dump tank	10 to 25

Recovery Units

Practices in the recovery of the base used in sulfite pulping differ widely from mill to mill. Because of the variety of chemical and physical properties exhibited by the base chemicals — calcium, sodium, magnesium, and ammonia—different processes have been developed to satisfy the handling and recovery problems peculiar to each base. In some instances, no attempt is made to recover the chemical or sensible heat of the spent liquors, or in some cases, only the heat is recovered. No attempt is made to recover chemicals from calcium base liquor.

Spent liquor from several magnesium sulfite processes can be burned in a heat and chemical recovery system in which the inorganic salts break down into magnesium oxide and sulfur dioxide. These chemicals can then be recombined directly to produce magnesium bisulfite acid for cooking.

The absorption towers absorb the sulfur dioxide with a solution of magnesium hydroxide. Sulfur dioxide enters the towers from the recovery furnace as well as from the fortification towers and/or the digester. Magnesium hydroxide readily absorbs the sulfur dioxide. Absorption

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efficiencies of the venturi systems range from 95 to 98+ percent. Sulfur dioxide emissions from the absorption system range from 10 to 25 lb/T ADP. [4]

A process for the recovery of pulping chemicals from ammonium-base bisulfite spent cooking liquor has recently been reported to be in operation.[24] The spent cooking liquor is concentrated to about 53 percent solids in multiple effect evaporators. The concentrated liquor is then burned in two conventional oil-fired boilers at a rate of 60 gallons per minute (gpm). About 3 gpm of No. 6 fuel oil is also fired with the liquor as the liquor itself will not support combustion. The combustion gases containing sulfur dioxide are absorbed to produce cooking liquor. The absorbers are of the sieve tray type. One absorber has six trays, and emissions are reported to be 65 ppm sulfur dioxide. The other absorber has four trays, and emissions are reported to be 118 ppm. Total sulfur dioxide released is about 1 T/day, which is about 18 lb/T ADP.

Multiple Effect Evaporators

Multiple effect evaporators, which concentrate spent liquors, may be a source of sulfur dioxide emissions. Such emissions are evolved because of the high-temperature and low-pressure conditions in the effects. The type of condenser has an effect on the sulfur dioxide emissions. Adequate contact between the sulfur dioxide and the cooling water will remove a large portion of the gas. Sulfur dioxide emissions from the multiple effect evaporators are in the range of 5 to 10 lb/T ADP. [4]

CONTROL TECHNIQUES

Little information is available on control of emissions from sulfite mills. Those unit operations that are similar to kraft sources can use control systems similar to those already described.

Sulfiting Tower

The pressure accumulator is usually vented into the acid storage tank because the two tanks are nearby. The acid storage tank is then vented to the absorption tower. This system effectively prevents emissions from these items of equipment, thereby leaving the acid absorption tower as the only significant source of emission in the acid system.

The efficiency of absorption of most sulfiting towers exceeds 90 percent. Some mills have placed a second absorption tower in series with the sulfiting unit for scrubbing exhaust gases. The increase in design efficiency and the required operating conditions are unknown.

Blow Pit

Flash steam, sulfur dioxide, and inert gases are released in the blow pit during a digester blow. These gases then exit from the blow pit, and after

the steam is condensed, the noncondensable gases, mainly sufur dioxide, are generally absorbed in a packed tower. The recovered sulfur dioxide is reused in the process, and the condensate creates a source of hot water. The system is about 95 percent efficient in absorbing sulfur dioxide from the blow pit stacks, where the sulfur dioxide concentration is approximately 4 percent during the initial stage of the blow. This produces recovery water containing 0.85 percent sulfur dioxide. The recovery water is subsequently used directly in the fortifying of the cooking acid, or the sulfur dioxide is stripped from the recovery water and used in the manufacture of cooking acid.

Recovery Furnace Systems

Significant amounts of particulate matter will be generated if sodium or magnesium based liquor is burned in a recovery furnace, but probably not if ammonia based liquor is burned. Sulfur dioxide will be generated in all cases where liquors are burned. The degree of recovery of sulfur dioxide from the recovery furnace for reuse in the liquor making process is a function of (1) the efficiency of liquor collection in the pulp washing process, (2) the efficiency of the sulfur dioxide collection systems on the acid-making system absorbers, digesters, recovery furnace, etc., and (3) the required liquor characteristics for the type of pulp being manufactured. The interrelationship between the above factors and the amount of sulfur dioxide in the tail gas from the recovery furnace system is best understood if it is recognized that the cation base and sulfur may not exist in stoichiometric amounts in cooking liquor. Depending on the type of pulp being manufactured and the cation base used, a certain amount of free sulfur dioxide exits in the liquor. This results, in some situations, in an excess of sulfur dioxide in fresh and spent liquor over that which can combine with the cation in a recovery furnace sulfur dioxide recovery system. Whether there is sufficient cation added in the case of ammonia or recycled and added in the case of magnesium to capture a major portion of the sulfur dioxide in the recovery furnace tail gas and return it to reuse is mainly dependent on the amount of free sulfur dioxide in the liquor going to the recovery furnace. Assuming that sulfur dioxide recovery from miscellaneous sources is equal in all cases, the liquor collection system efficiency dictates how much sulfur (free and combined sulfur dioxide) and how much cation go to the furnace. The amount of cation carried in the system dictates whether sufficient cations are present to capture the sulfur dioxide from the furnace in the tail gas scrubber. The sulfur dioxide emission rates from sulfite recovery furnace systems do not therefore directly reflect the performance of the sulfur dioxide absorbers used on the furnace but may reflect insufficient cation to capture the sulfur dioxide present. This makes it necessary, for example, to distinguish between sulfur dioxide emission capability of the bisulfite systems referred to earlier as compared to sulfite systems. To obtain equivalent sulfur dioxide emission rates from different systems may therefore require special external treatment schemes in one case and not another.

Sulfite Pulping Process

EMISSION DATA

Questionnaires were sent to 60 acid and nonintegrated semichemical pulp mills. Twenty were returned from mills manufacturing acid sulfite pulp.

The information on the control of sulfur dioxide emissions from absorbers, digester relief gas, and blow gas, is summarized in Table 38. Absorbers were considered controlled if a second absorber in series with the main absorber was used or if a scrubber was used after the absorber. Relief and blow gases were considered controlled if vented to the absorber or to a separate scrubber. Fifteen of twenty used some control on absorbers, fifteen of sixteen reporting controlled digester relief gas and four of eighteen controlled digester blow gas.

Table 38. EXTENT OF CONTROLS USED IN SULFITE PULPING OPERATIONS, QUESTIONNAIRE DATA

Operation	Number of mills	Controls used Yes	Controls used No
Absorbers	20	15	5
Digester relief gas	16	15	1
Blow gas	18	4	14

The data given in the questionnaires on the amounts of sulfur dioxide emissions are summarized in Table 39. The information on types of cooking liquors used and the types of heat or heat and recovery boilers is summarized in the following paragraphs.

Table 39. SULFUR DIOXIDE EMISSIONS FROM SULFITE PROCESS, QUESTIONNAIRE DATA

Mill number	Absorption Before control	Absorption After control	Digester relief Before control	Digester relief After control	Digester blow Before control	Digester blow After control	Evaporators Before control	Evaporators After control	Furnace Before control	Furnace After control
4	7 1	0 04	–	–	ND	0.193	–	–	–	–
5	3 5[b]	–	–	–	–	–	–	–	–	–
12	0 13	ND	–	–	–	–	–	–	–	–
13	–	–	–	–	0 335[b]	–	–	–	–	–
14[c]	–	–	0 96	ND	–	–	44.83	ND	ND ND	5 9
15	9 3	ND	–	–	–	–	–	–	–	–
17	–	9.05	–	–	–	–	–	–	–	–
25	ND	0 21	–	–	–	–	–	–	–	–
27	0 3	0.09	–	–	–	–	–	–	–	–
34	ND	1 29	–	–	–	–	–	–	–	–

[a]ND – process controlled, but no data reported.

[b]No controls.

[c]Two furnaces

Seven of the mills used magnesium-base cooking liquor. Of these, two operated recovery furnaces. Magnesium oxide and sulfur dioxide are recovered in these systems and recombined to make the cooking liquor.

Eight of the mills reporting used calcium-based cooking liquors. Two of these mills concentrated their spent liquor and burned it in conventional boilers. Presumably, no use is made of the resulting calcium sulfate.

Six of the mills use ammonia-base cooking liquors. One of these mills burns its spent cooking liquor. It concentrates the weak liquor to 60 percent solids in a quadruple effect evaporator and burns it in a Combustion Engineering Special Liquor Burner.

STEAM AND POWER GENERATION

INTRODUCTION

Pulp and paper mills require large amounts of steam for process heating, utility heating, driving equipment, and genereating electricity. A portion of the steam is generated in recovery furnaces, but much of it is generated in conventional industrial boilers.

A separate questionnaire form was sent to all mills for information on power boilers. Information was requested on the following subjects:

1. Mill production, capacity, and type.
2. Steam generation and use.
3. Boiler and emission control equipment.
4. Fuel types, quantities, and composition.
5. Emission data.
6. Automatic monitoring units.
7. Analytical procedures.

The number, types, and capacities of pulp and paper mills that reported some information are summarized in Table 40. The 288 mills reporting represent 66 percent of the total pulp and paper capacity of the United States.

Fuels Used

The fuels used by the pulp and paper mills are coal, oil, natural gas, and bark/wood waste. The amounts of each fuel used by each of the mill categories are given in Table 41. The portions of the total energy supplied by each fuel are: coal — 35 percent; oil — 27 percent; gas — 26 percent; and bark/wood — 12 percent. Most mills burned combinations of fuels: 31.9 percent of the plants reporting used bark plus other fuels, 39.9 percent used coal plus other fuels, 54.7 percent used oil plus other fuels, and 35.5 percent used gas plus other fuels. A further breakdown of fuel usage is presented in Table 42.

The characteristics of the fuels are tabulated in Table 43. Coal used had an average sulfur content of 1.9 percent and ash content of 8.1 percent. Oil averaged 1.8 percent sulfur, and bark/wood averaged 2.9 percent ash.

Table 40. TYPES OF PULP AND PAPER MILLS REPORTING INFORMATION FOR POWER BOILER QUESTIONNAIRE SURVEY

Production category[a]	Number of mills reporting	Total nominal capacity of mills reporting, T/day		
		Chemical pulp	Mechanical pulp	Paper/ paperboard
C	15	8,367	—	—
C+P	91	58,683	—	58,042
M	6	—	878	—
M+P	13	—	2,965	4,980
C+M+P	22	12,712	7,014	18,511
P	141	—	—	19,974
Total	288	79,762	10,857	101,507
Total U.S. capacity (1968)		114,500	21,000[b]	165,000[b]
Percent of U.S. capacity reporting		70	52	62

[a]C —chemical pulp; M — mechanical pulp; P — paper and/or paperboard.
[b]Estimated.

Table 41. FUEL CONSUMPTION IN PULP AND PAPER MILL POWER BOILERS

Production category[a]	Number of mills reporting	Annual average fuel consumption[b]			
		Coal, T/day	Oil, gal./day	Gas, $10^3 ft^3$/day	Bark/wood, T/day
C	12	1,700 (2)	134,000 (7)	33,000 (5)	2,800 (8)
C+P	80	12,600 (37)	1,773,300 (48)	312,270 (32)	16,890 (50)
M	5	280 (2)	2,710 (2)	750 (1)	80 (1)
M+P	11	1,190 (7)	142,960 (5)	18,140 (5)	93 (4)
C+M+P	18	3,110 (4)	493,420 (12)	100,220 (10)	3,960 (11)
P	124	7,170 (50)	902,540 (67)	33,650 (23)	480 (1)
Total	250	26,050 (112)	3,448,930 (141)	498,030 (76)	24,303 (75)
Approx heat value of fuel used,10^{10} Btu/day[c]		68	52	50	22
Percent of total energy consumption		35	27	26	12

[a]C — chemical pulp, M — mechanical pulp; P — paper and/or paperboard.
[b]Figures in parentheses represent number of mills reporting use of the indicated fuel.
[c]Basis: coal — 13,000 Btu/lb; oil — 150,000 Btu/gal.; gas — 1000 Btu/ft^3, bark/wood — 4500 Btu/lb.

Table 42. FUEL USAGE DATA FOR PULP AND PAPER MILL POWER BOILERS

Fuel usage	Number of mills reporting	Percent of total
Coal	66	24.17
Coal + oil	6	2.19
Coal + gas	3	1.10
Coal + bark	11	4.03
Coal + oil + gas	6	2.20
Coal + oil + bark	10	3.66
Coal + gas + bark	3	1.10
Coal + oil + bark + gas	4	1.47
Oil	67	24.5
Oil + gas	21	7.69
Oil + bark	16	5.86
Oil + gas + bark	20	7.32
Gas	17	6.23
Gas + bark	23	8.42
Bark	0	—

Table 43. CHARACTERISTICS OF FUELS BURNED IN POWER BOILERS AT PULP AND PAPER MILLS

Production category[a]	Number of mills reporting	Heating value[b] Coal, Btu/lb	Heating value[b] Oil, Btu/gal	Heating value[b] Gas, Btu/ft³	Heating value[b] Bark/wood, Btu/lb	Ash content, percent[b] Coal	Ash content, percent[b] Bark/wood	Sulfur content, percent[b] Coal	Sulfur content, percent[b] Oil
C	15	12,100 (2)	149,000 (7)	1030 (7)	4240 (9)	12 5 (2)	1 2 (7)	2 0 (2)	1 7 (7)
C+P	90	13,100 (39)	148,000 (60)	1030 (44)	4810 (53)	8 0 (37)	3 1 (34)	1 7 (39)	2 0 (51)
M	6	14,400 (3)	149,000 (3)	1050 (2)	6200 (1)	5 2 (3)	3 4 (—)	1 1 (3)	2 3 (2)
M+P	13	12,500 (7)	147,000 (7)	1010 (6)	3270 (3)	8 6 (7)	— (0)	2 2 (7)	2 0 (6)
C+M+P	22	13,300 (4)	149,000 (12)	1040 (14)	4140 (12)	9 1 (3)	2 6 (6)	1 9 (4)	2 0 (13)
P	129	13,200 (52)	149,000 (61)	1020 (33)	3150 (2)	8 1 (54)	6 9 (2)	2 0 (51)	1 6 (57)
Total	275								
Overall mean average		13,100 (107)	149,000 (150)	1030 (106)	4590 (80)	8 1 (106)	2 9 (50)	1 9 (106)	1 8 (136)
Range		10,500 to 14,700	122,000 to 155,000	—	—	3 5 to 2 1	0 1 to 20	0 5 to 10	0 1 to 3 9

[a]C — chemical pulp, M — mechanical pulp, P — paper and/or paperboard

[b]Figures in parentheses represent number of mills reporting the indicated data

Steam and Power Generation

Steam Usage

The steam use distribution, by production category, is summarized in Table 44. The overall average use for all plants was as follows:

Process heating	68 percent
Equipment drives	17 percent
Utility heating	13 percent
Electricity generation	10 percent
TOTAL	108 percent

The total is greater than 100 percent because some mills use the exhaust steam from equipment drives and electricity generation for process and utility heating, thus using some steam twice.

Table 44. STEAM USE DISTRIBUTION AT PULP AND PAPER MILLS, POWER BOILERS ONLY

Production category[a]	Number of mills reporting	Average steam use distribution, percent on weight basis								Total
		Electricity generation		Equipment drives		Process		Utility heating		
		Average	Range	Average	Range	Average	Range	Average	Range	
C	14	6	0 to 23	26	3 to 90	75	50 to 99	6	0 to 30	113
C+P	91	9	0 to 67	18	0 to 80	72	30 to 99	8	0 to 40	107
M	6	3	0 to 20	5	0 to 24	46	0 to 97	36	0 to 99	100
M+P	13	9	0 to 25	11	0 to 47	68	40 to 98	14	2 to 28	102
C+M+P	22	12	0 to 50	18	0 to 66	66	24 to 90	6	0 to 20	102
P	138	11	0 to 99	17	0 to 90	66	0 to 99	16	0 to 90	110
Total	284	10		17		68		13		108

[a] C — chemical pulp; M — mechanical pulp; P — paper and/or paperboard.

Types of Boilers

The types, ages, and firing methods of the boilers are summarized in Table 45. The average age for all boilers was 23 years.

The firing methods for the 397 coal-fired boilers included the following:

Pulverized	26.0 percent
Spreader stoker	24.7 percent
Underfed stoker	22.4 percent
Traveling grate	22.1 percent
Cyclone furnace	2.8 percent
Vibrating grate	2.0 percent

PULP AND PAPER INDUSTRY EMISSIONS

Table 45. TYPES OF POWER BOILERS USED IN PULP AND PAPER INDUSTRY

Production category[a]	Number of mills reporting	Boiler size, 10³ lb steam/hr		Boiler age, years		Firing method,[b] number of boilers							Predominant fuel burned, number of boilers				Stack height, feet	
		Average	Range	Average	Range	A	B	C	D	E	F	G	Coal	Oil	Gas	B/W[c]	Average	Range
C	15	155.3	15 to 600	16.5	0 to 41	1	6	–	1	2	1	3	3	26	14	1	161.3	87 to 310
C+P	90	121.4	5 to 600	23.2	0 to 68	30	41	2	44	7	–	62	160	166	65	10	150.0	12 to 475
M	5	40.6	2.5 to 80.0	27.8	7 to 62	–	–	–	4	–	–	–	6	4	–	–	81.2	3 to 0202
M+P	13	79.1	14 to 300	27.1	1 to 49	6	4	–	6	–	1	5	20	19	2	4	125.7	10 to 210
C+M+P	21	178.7	30.0 to 725.0	17.4	0 to 47	–	8	–	4	1	1	6	16	41	30	4	126.1	4 to 250
P	135	49.1	4.5 to 400.0	24 4	0 to 60	52	29	6	39	1	1	25	166	207	16	–	125.3	20 to 250
Total	279					89	88	8	98	11	2	101	371	463	126	19		

[a] C – chemical pulp, M – mechanical pulp, P – paper and/or paperboard.

[b] Firing method of boilers equipped to burn coal and/or bark. A – underfeed, B – travelling grate, C – vibrating grate; D – spreader stoker, E – cyclone; F – pulverized-wet bottom; G – pulverized-dry bottom.

[c] B/W – bark and wood wastes.

EMISSIONS

The sulfur emissions from the burning of coal and oil in power boilers were computed from the total fuels used (Table 41) and the average sulfur content (Table 43). As indicated in Table 46, coal-fired boilers emitted a total of 988 T/day sulfur dioxide and oil-fired boilers a total of 483 T/day sulfur dioxide, for a total of 1471 T/day.

CONTROL TECHNIQUES

On the questionnaires, 320 boilers were reported as having particulate control devices. The data are summarized in Table 47. On all but four boilers, the control devices were multiple cyclone collectors. The other four devices consisted of two scrubbers and two electrostatic precipitators.

From the above group, emission data were reported for 43 boilers. Of these, 17 were fired with coal only. The emission data for these boilers are tabulated in Table 48. The average concentration to the collector was 2.24 gr/ft^3, with an average outlet concentration of 0.39 gr/ft^3, for an average collection efficiency of 78 percent. This concentration is equivalent to an emission rate of 18 lb/T of coal fired. Multiplying the rate by the total amount of coal used from Table 41 gives a total emission rate of 470,000 lb/day of particulates for the mills responding to the questionnaire, assuming that the average emission rate can be applied to all the boilers.

Emission data were reported for 26 boilers that were used to burn bark and wood waste. All but two of these boilers also burned other fuels. The data are tabulated in Table 49.

The average fuel utilization for this group, on a Btu basis, is as follows: bark/wood — 48.5 percent; oil — 31.0 percent; coal — 11.3 percent; and gas — 9.2 percent.

Particulate emissions from all of these boilers were controlled by cyclone collectors. The average emission concentrations were 2.74 gr/scf at the collector inlet and 0.45 gr/scf at the collector outlet. Total emission from the 26 boilers was 7177 lb/hr from the burning of 7337 T/day of bark/wood, plus auxiliary fuels. This is an emission rate of 23 lb/T of bark/wood. Assuming that this rate is valid for the other boilers burning bark/wood, the total particulate emission from the respondents is 560,000 lb/day.

NEW TECHNOLOGY

Since the questionnaires were returned, the installation of an electrostatic precipitator to control fly ash emission from a coal and bark fired boiler has been reported by Nachbar.[25] This is believed to be the first installation of an electrostatic precipitator to control emissions from a combination coal and bark fired boiler. Previously, it was widely believed that the carbon content of the char would cause it to be difficult to collect in an electrostatic precipitator. A pilot study showed that precipitability was "medium to good."

Table 46. POWER BOILER FLUE GAS CHARACTERISTICS

| Production category[a] | Flue gas | | | | Total SO$_2$ emissions, T/day[b,c] | | Atmospheric particulate emissions, gr/scf[c] |
| | Flow, 10³ acfm | | Temperature, °F | | | | |
	Mean	Range	Mean	Range	Oil-fired boilers	Coal-fired boilers	
C	110	43 to 311	428	200 to 750	18.8 (7)	64 (2)	1 08 (5)
C+P	102	4 to 470	463	70 to 100	248 (48)	478 (37)	0.44 (26)
M	124	1 to 460	453	365 to 550	0.4 (2)	10.6 (2)	—
M+P	35	8 to 103	427	300 to 600	20.0 (5)	45.2 (7)	0.21 (1)
C+M+P	92	2 to 504	387	275 to 550	69 0 (12)	118 (4)	0.42 (3)
P	41	—	477	—	126 (67)	272 (50)	0.22 (1)
Total					483 (141)	988 (112)	

[a]C — chemical pulp, M — mechanical pulp, P — paper and/or paperboard.

[b]Emissions calculated from data on average fuel consumption and sulfur content reported in Tables 41 and 43 and assuming 8 pounds per gallon of fuel oil

[c]Figures in parenthesis represent number of mills reporting data.

Table 47. POWER BOILER PARTICULATE CONTROL EQUIPMENT DATA

| Production category[a] | Number of mills reporting | Control equipment, number of boilers | | Pressured drop, inches of water | | Rated efficiency, percent | | Fly ash reinjection, number of boilers | |
		Yes	No	Average	Range	Average	Range	Yes	No
C	15	23	21	2.6	0 6 to 4 0	92 9	85 to 98	19	25
C+P	91	171	231	2 7	0.2 to 6.0	85 6	38 to 99	90	321
M	6	4	6	—	—	92.0	92	4	6
M+P	13	15	28	2 3	0 5 to 3.0	84 2	70 to 90	4	39
C+M+P	22	28	60	3.6	1.0 to 10 0	87.6	80 to 95	13	75
P	139	79	311	2.4	0.3 to 5.9	80.3	20 to 96	52	335
Total		320	657						
Percent		33	67						

[a]C — chemical pulp, M — mechanical pulp, P — paper and/or paperboard.

Table 48. EMISSION DATA FROM POWER BOILERS FIRED WITH COAL ONLY[a]

| Mill number | Boiler number | Collector rating | | Flow, 10³ dscfm | Fly ash reinjection | Particulate concentration, gr/dscf | | Collection efficiency, percent | Emission rate, lb/hr |
		Pressure drop, inches of water	Efficiency, percent			Inlet	Outlet		
031	6	1 5	90	43	No	2 21	0 73	62	269
031	8	1 7	90	104	No	1 58	0 68	57	603
096	2	2 5	92	78	No	—	0 08	—	534
	4	2 5	92	121	No	—	0 65	—	674
107	2	2 3	91	62	No	—	0 24	—	128
	3	3 0	88	111	No	—	0 28	—	264
113	19	—	85	110	No	—	0 19	—	183
	18	—	85	128	No	—	0 59	—	656
119	4	2 6	93	75	No	1 29	0 4	69	257
178	6	3	85	25	No	0 29	0 035	88	8
272	5-6[b]	—	85	140	No	—	0 25	—	300
	9[c]	—	95	140	No	—	0 1	—	120
273	25[c]	2 2	97	183	No	4 89	0 43	91	674
134	2	2 3	86	15 5	Yes	4 93	0 66	86	88
	3	3 9	90	16 6	Yes	2 55	0 28	89	40
178	1-5	3	85	208	Yes	0 21	0 033	84	59
275	7	1 7	93	90	Yes	—	0 28	—	216
Average						2 24	0 39	78	298

[a]Controlled by centrifugal collectors except as noted
[b]Scrubber
[c]Electrostatic precipitator

The precipitator was put into operation in November 1969. Numerous test gave the following average results:

Gas flow rate	387,500 acfm
Inlet dust loading	1.03 gr/scf
Gas velocity, full force	3.78 ft/sec
Collection efficiency	99.5 percent

Precipitator operation and performance are reported as being excellent. Normally there is no visible emission. Condensed water vapor is visible only during the coldest winter days.

Table 49. EMISSION DATA FROM POWER BOILERS FIRED WITH BARK/WOOD PLUS OTHER FUELS

Mill number	Boiler number	Collector rating Pressure drop, inches of water	Collector rating Efficiency, percent	Percent of fuel supplied, Btu basis B/W[a]	Oil	Gas	Coal	B/W[a] T/day	Fly ash reinjection	Gas flow rate, 10^3 dscfm	Particulate concentration, gr/dscf Inlet	Outlet	Collection efficiency, percent	Emission rate, lb/hr
031	7	2	—	75	25	0	0	200	Yes	—	9.90	0.81	92	402
048	4	2.8	90	51	59	0	0	384	Yes	83	—	0.14	—	100
072	1	2.5	88	68	32	0	0	450	Yes	55	0.59	0.12	80	57
096	1	2.5	92	16	18	0	66	30	Yes	51	—	1.1	—	480
107	3	2.5	92	7	13	0	80	31	Yes	51	—	1.2	—	528
113	21	4.8	92	23	1	0	76	136	Yes	91	—	0.18	—	140
144	4	3	93	25	0	0	75	200	Yes	123	—	0.17	—	180
	5		90	73	27	0	0	205	Yes	—	—	0.51	—	—
183	7	3	90	82	18	0	0	305	Yes	—	—	0.30	—	—
185	3	2.5	92	44	—	46	0	26	Yes	76	2.3	0.16	93	104
191	3	—	80	35	65	0	0	65	Yes	56	—	0.43	—	209
217	4	—	93	98	2	0	0	165	Yes	57	0.90	0.32	64	156
218	5	3.6	82	64	36	0	0	250	Yes	48	2.11	0.44	79	183
219	3	3.0	82	57	43	0	0	250	Yes	50	3.01	0.35	88	150
	2	3	93	31	0	69	0	360	Yes	131	—	0.18	—	202
253	3	—	95	100	0	0	0	145	Yes	40	—	0.37	—	127
260	1	3	95	37	63	0	0	215	Yes	50	—	0.10	—	43
	11	2.5	90	28	38	34	0	370	Yes	153	1.7	0.13	92	171
292	12	3	84	39	18	43	0	765	Yes	187	1.83	0.30	84	482
272	3	2.8	84	41	20	39	0	815	Yes	156	2.10	0.51	76	682
026	7-8	0.2	75	100	0	0	0	70	Yes	19	1.4	0.4	71	65
205	BB	—	84	25	75	0	0	400	No	198	—	0.6	—	1020
	2	3	97	44	56	0	0	500	No	60	—	0.94	—	488
284	3	4	96	30	70	0	0	120	No	35.5	—	0.52	—	158
	3	0.6	96	30	70	0	0	120	No	58	—	0.93	—	463
	4	2.1	89	40	60	0	0	750	No	172	4.3	0.4	90	588
Average				48.5	31	9.2	11.3			84	2.74	0.45	83	299
Total								7337						7177

[a]B/W — bark and wood wastes

APPENDIX A: DETAILED EMISSION DATA
FROM QUESTIONNAIRE SURVEY

Table A-1. PARTICULATE EMISSIONS FROM RECOVERY FURNACES CONTROLLEDBY ELECTROSTATIC PRECIPITATORS

Unit	Pulp production rate, T ADP/day	Gas flow rate, dscfm	Ratio of flow rate to production, dscfm T ADP/day	Particulate concentration, gr/dscf Inlet	Outlet	Collection efficiency, percent	Emission rate, lb/T ADP Inlet	Outlet
1	599	119,000	198	6 44	0 0327	99 5	263	1 33
2	870	88,700	102	6.4	0.076	98.8	134	1 59
3	632	135,000	214	4 0	0 04	99 0	176	1 76
4	664	117,000	176	2 32	0 06	97.5	84 2	2 17
5	232	62,500	270	—	0 04	—	—	2 21
6	362	73,800	204	2 59	0.0524	98 0	109	2 21
7	637	65,900	103	2 07	0 11	94 7	44 1	2 34
8	657	110,000	167	—	0 07	—	—	2 41
9	375	52,000	139	—	0.094	—	--	2 7
10	1766	60,500	130	3.4	0 17	95 0	55 3	2 8
11	900	118,000	131	6.42	0 105	98.4	173	2 83
12	821	144,000	175	4 14	0 167	96 0	70 6	2 84
13	902	71,800	80	3 61	0 176	95 1	59 2	2 89
14	340	42,000	124	2.53	0.124	95 1	64	3 14
15	188	29,000	154	—	0 11	—	—	2 49
16	865	146,000	164	5 5	0.1	98.2	191	3 5
17	621	78,000	125	4 07	0.143	96 5	105	3 70
18	225	47,700	209	3.88	0.0955	97 5	169	4 15
19	328	57,000	174	—	0 12	—	—	4 29
20	902	91,800	102	3.03	0.211	93 1	63 5	4 42
21	621	85,300	137	5 26	0.157	97 1	149	4 44
22	95	49,700	520	1 55	0 0424	97 8	167	4 57
23	358	71,400	200	—	0.133	—	´	4 64
24	390	40,300	103	3 22	0.23	92.9	68 5	4 89
25	815	138,000	170	5.0	0 148	97 1	174 3	5 2
26	281	61,700	220	3 454	0 118	96.6	170	5 34
27	160	46,500	295	4 27	0 092	97.9	255	5 49
28	600	114,000	190	2.45	0.15	93.9	95 8	5 87
29	380	61,500	162	2.83	0 178	93.8	94 4	5 93
30	298	86,000	390	—	0 1	—	—	5 94
31	225	54,000	240	3 102	0 124	96 0	153	6 12
32	163	38,000	233	3.26	0.139	95 4	156	6 65
33	350	61,800	176	4.04	0 188	95 4	147	6 84
34	492	103,800	210	—	0 168	—	—	7 37
35	263	70,300	267	3 08	0 14	95 5	170	7 72
36	213	94,500	443	2.41	0.1	95.8	221	9 17
37	626	96,000	153	—	0 3	—	—	9 48
38	569	72,600	128	3.099	0 373	87 9	81 4	9 8
39	315	97,000	308	5.12	0.17	96.7	325	10 8
40	330	89,000	270	4.4	0 2	95.5	245	11 24
41	510	105,000	206	—	0 317	—	—	13 4
42	149	64,500	433	2 71	0 152	94 4	241	13 5
43	379	78,000	206	3.68	0 327	91 1	156	13 9
44	108	24,200	224	1 25	0 307	75 5	58	14 2
45	213	43,000	202	4.1	0 365	91 1	170	15 1
46	139	69,000	568	1.48	0 148	90.0	151	15 1
47	492	114,500	232	1 96	0.33	83.2	93 9	15 8
48	225	93,000	413	—	0 19	—	—	16 2
49	265	43,700	165	3 95	0 49	87 6	134	16 6
50	350	73,700	210	1 42	0 40	72 0	74 6	17 35
51	332	71,000	214	—	0 40	—	—	17 6
52	317	85,300	270	2 69	0 325	88 0	149	18 0
53	200	31,000	155	3 23	0.57	82 4	103	18 2
54	328	57,500	175	4 1	0.51	87 6	148	184
55	250	62,200	249	—	0 362	—	—	18 6
56	359	83,000	231	—	0 4	—	—	19 1

Table A-1. PARTICULATE EMISSIONS FROM RECOVERY FURNACES CONTROLLED BY ELECTROSTATIC PRECIPITATORS (Con't)

Unit	Pulp production rate, T ADP/day	Gas flow rate, dscfm	Ratio of flow rate to production, dscfm T ADP/day	Particulate concentration, gr/dscf Inlet	Particulate concentration, gr/dscf Outlet	Collection efficiency, percent	Emission rate, lb/T ADP Inlet	Emission rate, lb/T ADP Outlet
57	225	42,000	186	2 84	0 51	82 1	109	19 5
58	210	70,000	333	5 0	0 3	94 0	343	20 6
59	260	38,000	146		0 73	—	—	21 9
60	225	61,000	270	2 97	0.394	86 8	166	22
61	287	73,000	256	—	0 413	—	—	22
62	280	100,000	357	6 0	0 3	95 0	442	22 1
63	318	113,000	356	-	0 819	—	-	23 4
64	395	63,400	160	6 23	0 721	88 4	206	23 8
65	150	93,000	620	—	0 19	--	—	24 2
66	206	48,500	235	3 34	0.5	85 1	162	24 5
67	390	76,700	196	4.26	0 68	84 0	173	27 6
68	316	79,000	250	4 14	0.552	86 7	213	28 3
69	160	54,600	340	3.46	0 469	86 5	243	33 0
70	335	66,500	200	3 05	0 87	71 5	125	35 7
71	380	76,500	201	-	0 815	—	—	35 8
72	130	50,000	285	4 0	0.5	87 5	316	39 5
73	130	50,000	385	4.0	0 5	87 5	316	39 5
74	379	86,400	228	—	0 89		—	41 8
75	171	35,000	205	3 96	1 05	73.7	167	44 1
76	239	65,000	272	-	0 8	—	—	44 8
77	165	72,000	437	—	0.5	·	—	44 8
78	437	120,500	276	9.95	0.89	91.1	565	50 5
79	437	120,500	276	9.95	0 89	91 1	565	50 5
80	250	74,700	300	—	0.99	—	-	61
81	120	63,000	525	3.22	0 60	81 4	348	64 8
82	208	58,000	280	2 53	1 04	58 9	145	64 8
83	139	62,200	450	1 35	0.725	47 0	124	66 6
84	560	107,000	190	—	0 366	—	—	15 1
85	239	86,500	350	2 8	1 2	58.0	209	89 5
86	192	82,800	430	2 15	1 05	50 3	191	94 9

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Table A-2. PARTICULATE EMISSIONS FROM SMELT TANKS

Unit	Pulp production rate, T ADP/day	Gas flow rate, dscfm	Ratio of flow rate to production, dscfm T ADP/day	Particulate concentration, gr/dscf as Na$_2$O		Emission rate, lb/T ADP as Na$_2$O	
				Inlet	Outlet	Inlet	Outlet
1	400	6,350	16	1.0	0.16	3.27	0.05
2	902	2,100	2.3	0.39	0.11	0.19	0.052
3	358	2,700	7.5	0.41	0.094	0.64	0.15
4	312	3,450	11	—	0.09	—	0.21
5	388	3,290	8.5	—	0.14	—	0.25
6	294	9,800	33	0.23	0.06	1.58	0.41
7	383	3,100	8.1	—	0.3	—	0.50
8	254	2,400	9.5	—	0.3	—	0.58
9	500	14,000	28	—	0.1	—	0.57
10	308	2,650	8.6	—	0.35	—	0.62
11	266	5,050	19	0.72	0.16	2.82	0.63
12	165	6,200	38	—	0.10	—	0.77
13	280	15,000	54	—	0.09	—	0.99
14	139	2,620	19	—	0.26	—	1.01
15	130	10,000	77	—	0.07	—	1.10
16	130	10,000	77	—	0.07	—	1.10
17	822	37,000	45	1.6	0.13	14.8	—
18	493	9,000	18	4.73	0.31	17.8	1.2
19	316	6,700	21	—	0.33	—	1.44
20	298	6,400	21	—	0.33	—	1.46
21	210	10,000	48	—	0.15	—	1.47
22	232	10,400	45	—	0.17	—	1.57
23	569	9,090	16	1.65	0.48	5.43	1.58
24	225	5,000	22	—	0.38	—	1.74
25	318	11,040	35	—	0.26	—	1.86
26	225	7,900	35	—	0.29	—	2.09
27	318	10,900	34	—	0.30	—	2.11
28	288	5,600	19	5.94	0.58	23.7	2.3
29	225	5,900	26	—	0.44	—	2.38

Table A-3. GASEOUS EMISSIONS FROM SMELT TANKS

Unit	Exit gas Flow rate, acfm	Exit gas Temperature, °F	Pulp production rate, T ADP/day	Ratio of flow rate to production, acfm T ADP/day	SO_2 ppm	Reduced sulfur gases, ppm H_2S	CH_3SH	$(CH_3)_2S$	$(CH_3)_2S_2$	Total reduced sulfur as H_2S ppm	lb/hr	lb/T ADP
1	10,000	150	400	25	—	—	—	5	—	5	0.22	0.014
2	11,300	155	225	50	—	3	—	—	—	3	0.15	0.015
3	4,600	190	254	18	—	—	9	—	—	9	0.17	0.017
4	15,150	200	316	48	9	3	—	—	—	3	0.18	0.002
5	5,000	200	902	6	—	63	—	—	—	63	1.26	0.035
6	9,850	140	225	44	—	9	—	—	—	9	0.39	0.045
7	24,600	160	500	49	—	5	3	1	—	8	0.94	0.048
8	6,000	190	383	16	—	10	34	0	0	44	1.07	0.007
9	6,400	215	139	46	—	10	10	—	—	20	0.50	0.009
10	10,600	220	200	53	1.4	18	1	0	0	19	0.78	0.010
11	15,320	158	620	25	—	22	41	0	4	71	4.65	0.19
12	10,000	166	225	44	2	15	35	0	2	54	2.10	0.23
13	21,000	180	318	66	—	17	3	—	12	43	3.70	0.30
14	18,900	158	318	60	—	24	7	—	14	59	4.77	0.38
15	14,000	168	210	67	10	20	—	80	—	100	5.08	0.61
16	55,000	146	822	67	10	—	25	25	25	100	24.0	0.75
17	14,000	168	130	108	20	40	—	150	—	190	9.63	1.9
18	16,000	180	318	50	385	337	400	38	18	811	48.7	3.9

Table A-4. PARTICULATE EMISSIONS FROM LIME KILNS

Unit	Pulp production rate, T ADP/day	Exit gas flow rate, dscfm	Ratio of flow rate to production, dscfm T ADP/day	Exit concentration, gr/dscf	Emission rate, lb/T ADP
1	294	10,600	36	0.01	0.074
2	520	13,800	28	0.02	0.019
3	498	12,000	24	0.02	0.10
4	804	24,000	30	0.02	0.12
5	793	15,300	19	0.03	0.12
6	498	17,200	35	0.02	0.14
7	294	8,700	30	0.02	0.12
8	308	12,000	39	0.05	0.40
9	422	9,530	25	0.09	0.42
10	338	9,530	28	0.09	0.52
11	900	11,700	13	0.21	0.55
12	706	6,300	9	0.31	0.57
13	475	19,200	40	0.07	0.583
14	350	10,000	29	0.10	0.594
15	700	18,700	28	0.12	0.660
16	950	23,800	25	0.13	0.67
17	735	7,000	9	0.36	0.71
18	280	10,000	36	0.10	0.73
19	593	18,600	31	0.14	0.88
20	873	13,700	16	0.28	0.90
21	225	10,000	44	0.11	0.97
22	420	11,500	27	0.19	1.07
23	200	11,300	56	0.11	1.28
24	270	7,500	28	0.22	1.265
25	262	8,270	32	0.22	1.438
26	560	14,500	26	0.29	1.552
27	540	15,000	28	0.3	1.727
28	437	11,700	27	0.37	2.06
29	355	15,810	45	0.23	2.12
30	550	27,800	50	0.21	2.15
31	320	5,800	18	1.05	2.28
32	686	32,000	47	0.27	2.57
33	262	8,520	32	0.40	2.67
34	363	22,200	61	0.22	2.73
35	540	18,000	33	0.4	2.75
36	490	15,502	32	0.43	2.79
37	309	5,100	16	0.83	2.82

Table A-4. PARTICULATE EMISSIONS FROM LIME KILNS (Con't)

Unit	Pulp production rate, T ADP/day	Exit gas flow rate, dscfm	Ratio of flow rate to production, dscfm T ADP/day	Exit concentration, gr/dscf	Emission rate, lb/T ADP
38	509	4,830	9	1.5	2.93
39	490	12,300	25	0.58	3.00
40	486	4,830	10	1.5	3.07
41	437	13,669	38	0.49	3.14
42	551	9,800	18	0.88	3.22
43	1100	29,500	27	0.59	3.26
44	540	21,500	40	0.4	3.28
45	642	19,980	31	0.53	3.38
46	473	22,900	48	0.38	3.78
47	315	12,300	39	0.48	3.86
48	275	18,700	68	0.29	4.06
49	275	18,700	68	0.29	4.06
50	335	14,750	44	0.46	4.17
51	347	4,830	14	1.5	4.30
52	232	8,500	37	0.57	4.30
53	465	26,400	57	0.37	4.33
54	298	11,000	37	0.59	4.86
55	86	15,300	180	0.13	4.76
56	315	23,000	73	0.34	5.16
57	290	29,200	100	0.25	5.18
58	500	12,600	25	1.0	5.19
59	232	17,080	74	0.38	5.75
60	747	13,900	19	1.56	5.97
61	166	10,000	84	0.51	6.33
62	284	10,000	49	0.98	7.11
63	400	12,100	30	1.2	7.48
64	473	28,170	60	0.65	7.96
65	284	15,100	53	1.28	14.02
66	232	12,000	52	4.0	53.1

Table A-5. GASEOUS EMISSIONS FROM LIME KILNS

Unit	Production rate, T ADP/day	Exit gas Flow rate, acfm	Exit gas Temperature, °F	Ratio of flow rate to production, acfm T ADP/day	SO₂, ppm	Reduced sulfur gases, ppm H₂S	CH₃SH	(CH₃)₂S	(CH₃)₂S₂	Total reduced sulfur as H₂S ppm	lb/day	lb/T ADP
1	338	16,000	156	47	—	—	—	—	—	3	5	0.016
2	400	19,000	150	48	—	0	3	6	—	9	18	0.04
3	350	19,700	170	56	0	6	0	5	0	11	23	0.06
4	500	21,800	158	44	10	15	3	1	0	19	45	0.08
5	950	48,000	170	50	—	10	15	—	—	25	122	0.14
6	262	15,600	170	60	1	60	0	2	2	64	110	0.42
7	262	15,600	170	60	1	60	0	2	2	64	110	0.42
8	593	39,000	223	66	—	3.1	2.4	6.4	11.4	35	133	0.22
9	498	29,000	150	58	55	43	—	—	—	43	138	0.28
10	422	16,000	156	38	15	0	90	48	26	100	174	0.41
11	793	30,150	180	38	37	30	—	0	2	124	391	0.50
12	550	57,000	180	103	10	50	—	—	—	50	300	0.53
13	232	12,000	131	52	—	110	—	—	—	110	157	0.64
14	275	36,500	150	133	5	15	15	5	5	45	180	0.66
15	275	36,500	150	133	5	15	15	5	5	45	180	0.66
16	551	16,600	160	30	—	159	—	—	39	198	356	0.66
17	747	25,100	160	34	—	152	—	—	13	188	573	0.69
18	498	20,000	150	40	80	258	—	—	—	258	568	1.13
19	551	9,500	160	17	—	386	—	245	—	613	632	1.15
20	804	40,000	150	50	80	260	—	—	—	260	1150	1.43
21	298	20,000	165	67	—	500	—	—	—	500	990	3.34
22	166	17,000	160	102	—	386	—	—	—	380	703	4.2

APPENDIX B: SAMPLING AND ANALYTICAL PROCEDURES AND EQUIPMENT

SUMMARY OF PROCEDURES

A variety of sampling and analytical methods were used by the mills replying to the questionnaires, by the National Council of the Paper Industry for Air and Stream Improvement (NCASI) in their special studies, and by the Environmental Protection Agency (EPA) in their field investigations. In the case of gas analysis, significant improvement in precision and sensitivity of gas analysis occurred over the approximate 4-year period during which the data were collected. In the case of particulate analysis, varying efficiencies of the media used to collect particulate matter and the incorporation of a gas washing and condensation step may account for differences in amount of materials referred to as particulate matter in this report.

Gas Analysis

Questionnaire Data

Essentially all the gas emission data reported in the questionnaires were developed during a period when the analytical procedures available for hydrogen sulfide included its collection in (1) a strong caustic solution and subsequent analysis for sulfide ion by potentiometric titration, or (2) zinc acetate and subsequent analysis for sulfide using a methelene blue colorometric procedure, or (3) cadmium chloride and subsequent analysis for sulfide ion by iodometric titration. The latter two procedures are described in References 26 and 27. Methyl mercaptan was also collected in cadmium chloride and subsequently analyzed by iodometric titration after separation of the mercaptide precipitate from the cadmium solution.[2]The method used for alkyl sulfides and disulfides involved collection in benzene and subsequent titrimetric and spectrophotometric measurement of the alkyl sulfides present. A modification of the West-Gaeke method [28] was commonly used during this period for sulfur dioxide determination.

Special Studies

All special studies on recovery furnace systems were conducted using an instrumental coulometric titration (Barton titrator). The procedure is fully described in the basic references cited in the text. Special studies on miscellaneous sources were conducted using a flame photometric chromatographic detector, a flame ionization chromatographic detector,

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and continuous analysis of the sulfur dioxide formed upon oxidation of the reduced sulfur compounds present. The sampling, handling, and instrumental methods are described in detail in the basic references cited in the text.

EPA Field Investigation

A special mobile field sampling laboratory developed by EPA was used for these investigations. This facility and the sampling and analytical procedures used are described later in this appendix.

Particulate Sampling and Analysis

It was common practice during the period that particulate emission data reported in the questionnaires were being generated to use the in-stack alundum thimble collection procedure described in Reference 29 and other sources. In their field investigations, EPA employed procedures, described later in this appendix, developed for compliance testing for new stationary sources and published in the Federal Register.[30] The relative particle collection efficiency of the alundum thimble method and the EPA method has not been fully established, but the limited data available suggest that the EPA procedure has the greater efficiency.

EPA MOBILE FIELD SAMPLING LABORATORY

A mobile source sampling laboratory was developed by the Emission Measurement Branch of the Office of Air Quality Planning and Standards, Environmental Protection Agency. The equipment was mounted in a self-propelled vehicle to facilitate sampling at various locations.

A unique continuous gas sampling system was devised for the mobile laboratory. The gas sample from the source is filtered to remove particulates and delivered through an electrically heated Teflon sampling line at a temperature above its dew point. At the mobile laboratory, the sample is passed through a dynamic dilution system where purified air is used as the diluent. The dilution system provides simultaneous dilution levels up to six orders of magnitude. Teflon components are utilized where possible; and where stainless steel is used, the quantities of gas handled overwhelm the minor surface adsorption effects. The appropriately diluted samples are delivered to various instruments.

Particulate samples are obtained using a modified sample train developed by EPA. The gas meters and draft gauges are located within the mobile laboratory, while the filters, cyclone, and impingers are located with the particulate probe at the sampling site. Two complete sampling trains can be used to simultaneously sample the inlet and outlet of a control device. Pitot tube readings are recorded on a multipoint recorder after being transduced by a transmitting differential pressure manometer.

Remote temperature readings are obtained by thermocouples and are also recorded on a multipoint recorder.

In addition to two electrically traced Teflon gas sampling lines, four 250-foot umbilical cables were prepared. The umbilical cables were fabricated by hand-wrapping the necessary power lines, thermocouple leads, pitot lines, communication lines, and sample lines. All the umbilical cables are reel-mounted to facilitate handling. A voice powered telephone system with electrical buzzers provides communications between all sampling points and the mobile laboratory.

Gas Analysis

Instrumentation

The continuous gas monitoring instrumentation provides on-site analysis for oxygen, carbon monoxide, carbon dioxide, hydrocarbons, and various sulfur compounds. Dynamic dilution permits the use of sensitive laboratory instruments for actual source testing while avoiding problems associated with condensation of moisture in the sample. Instruments installed included two gas chromatographs, a total sulfur analyzer, a Barton titrator, an oxygen analyzer, a carbon dioxide analyzer, and a carbon monoxide analyzer.

Oxygen analysis is performed continuously on the process gas stream by a Beckman Model F3 oxygen analyzer. The F3 analyzer measures the magnetic susceptibility of oxygen. Three ranges were provided: 0 to 5, 0 to 10, and 0 to 25 volume percent. The instrument accuracy is ± 1 percent of full scale.

Carbon monoxide and carbon dioxide are analyzed by Beckman infrared analysis instruments. A Beckman Model IR 315 is used for carbon dioxide with three ranges: 0 to 1, 0 to 10, and 0 to 20 volume percent. Carbon monoxide is analyzed by a Beckman Model IR 315 A with ranges of 0 to 500 parts per million (ppm), 0 to 2 percent, and 0 to 10 percent by volume. Both instruments have accuracies of ± 1 percent full scale and sensitivities of 0.5 percent full scale. The instruments have three panel-mounted sections: an analyzer section, an amplifier/control section, and a constant-voltage transformer.

Total sulfur in the process stream is analyzed by a Melpar sulfur dioxide analyzer. The instrument oxidizes sulfur compounds in a hydrogen flame and uses a flame photometric detector to measure the sulfur dioxide. The output of the flame photometric detector is recorded on a log/linear recorder. Sensitivity of the instrument is 0.01 ppm, and response is linear between 0.01 and 10 ppm. The dilution system extends the useful range of the Melpar to allow analysis of much higher concentrations. Total sulfur is reported as sulfur dioxide concentrations in parts per million by volume. The measurement provides a basis for determining material balances, peak sulfur loadings in the source, and checks on the chromatographs.

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The gas chromatograph systems installed in the mobile laboratory were developed by the Division of Chemistry and Physics, National Environmental Research Center, Research Triangle Park, North Carolina. These systems are described in detail later in this appendix.

Dilution System [31]

This section describes the dynamic serial dilution system developed for the mobile sampling van, and its function in the dilution of stack gases.

Purpose — Stack sampling of gaseous pollutants within a given industry is often complicated by widely varying moisture and pollutant concentrations. The dewpoint temperature is usually greater than the operating temperature of many instruments and consequently must be lowered. In most cases, this has been accomplished with a scrubber or condenser. In order to follow large fluctuations in a pollutant's concentration, individual instruments may have analytical and/or electronic parts in duplicate or even triplicate.

The term "sample conditioning" refers to the process by which the stack gas is rendered acceptable for analysis. Normally this term would include only the removal of moisture and particulates from the sample. In this case, however, the design of the van's entire sample-conditioning system was primarily governed by the need to selectively and continuously identify various gaseous pollutants with instruments whose analytical capabilities are limited to concentrations more typically encountered in ambient air.

This situation meant that some means of diluting the stack gas would be needed. If dry air was used to dilute the sample and lower the moisture content, the sample could be kept above its dewpoint until it had been analyzed and the moisture problem would be solved. Furthermore, it would be solved without using a mechanism that could remove or alter some of the constituents in question.

Since the van would be used later on sources in other types of industry, the fact that the moisture problem could be nullified in a manner that would be almost universally applicable made the dilution concept doubly attractive.

Description — Figure B-1 shows the relationship of the dilution system to the other components of the sampling system, and Figure B-2 shows the actual piping arrangement. In view of the quantity and type of analytical instruments being employed, and in order to keep the entire operation as mobile as possible, it was necessary to permanently mount both the instruments and the dilution system in the van. Consequently, some means of transporting the sampled portion of the stack gas to the van without allowing condensation to form was required. The sample first passes through a heated probe containing glass wool to remove coarse particulates. It then flows through a heated millipore filter and thence into a 3/16-inch-

inside-diameter (i.d.) Teflon sample line 250 feet in length. The sample line temperature, which is monitored as the line enters the van, is maintained at approximately 20°F above the dewpoint of the gas by varying the voltage applied to insulated nichrome wires that have been encased in the sample line.

A stainless-steel bellows pump, which is similarly heated, is one source of sample line vacuum. Stack gas exiting from this pump tees to the first stage of the serial dilution system and to an unrestricted atmospheric vent (denoted as "V" on Figure B-2).
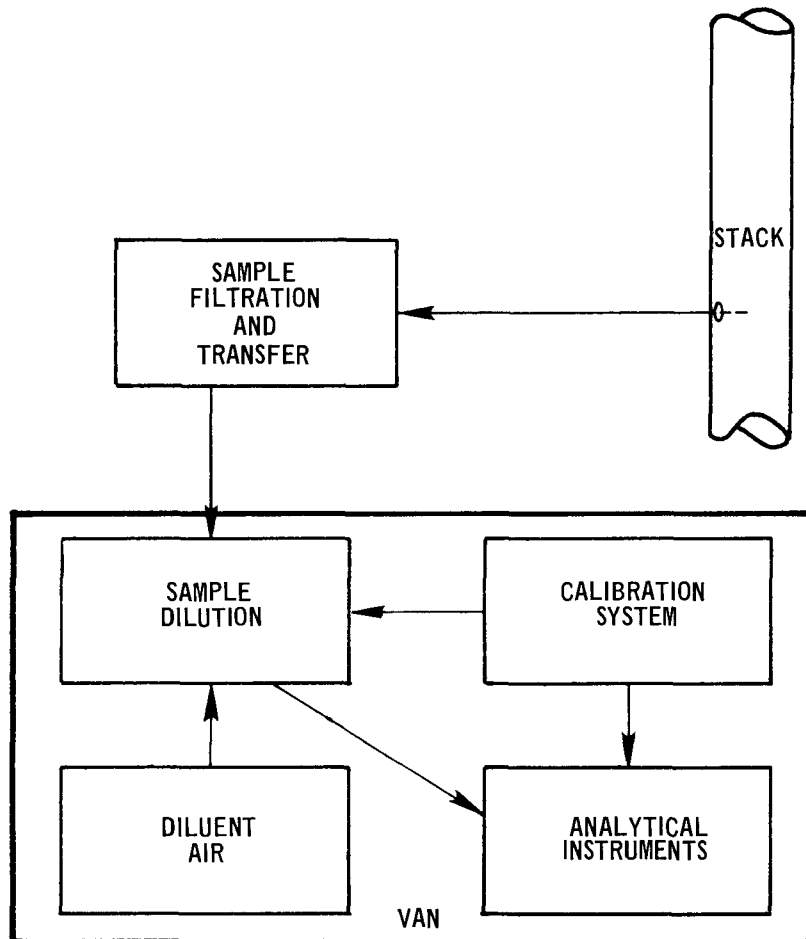
Figure B-1. Arrangement of gas-sampling system of mobile sampling van.
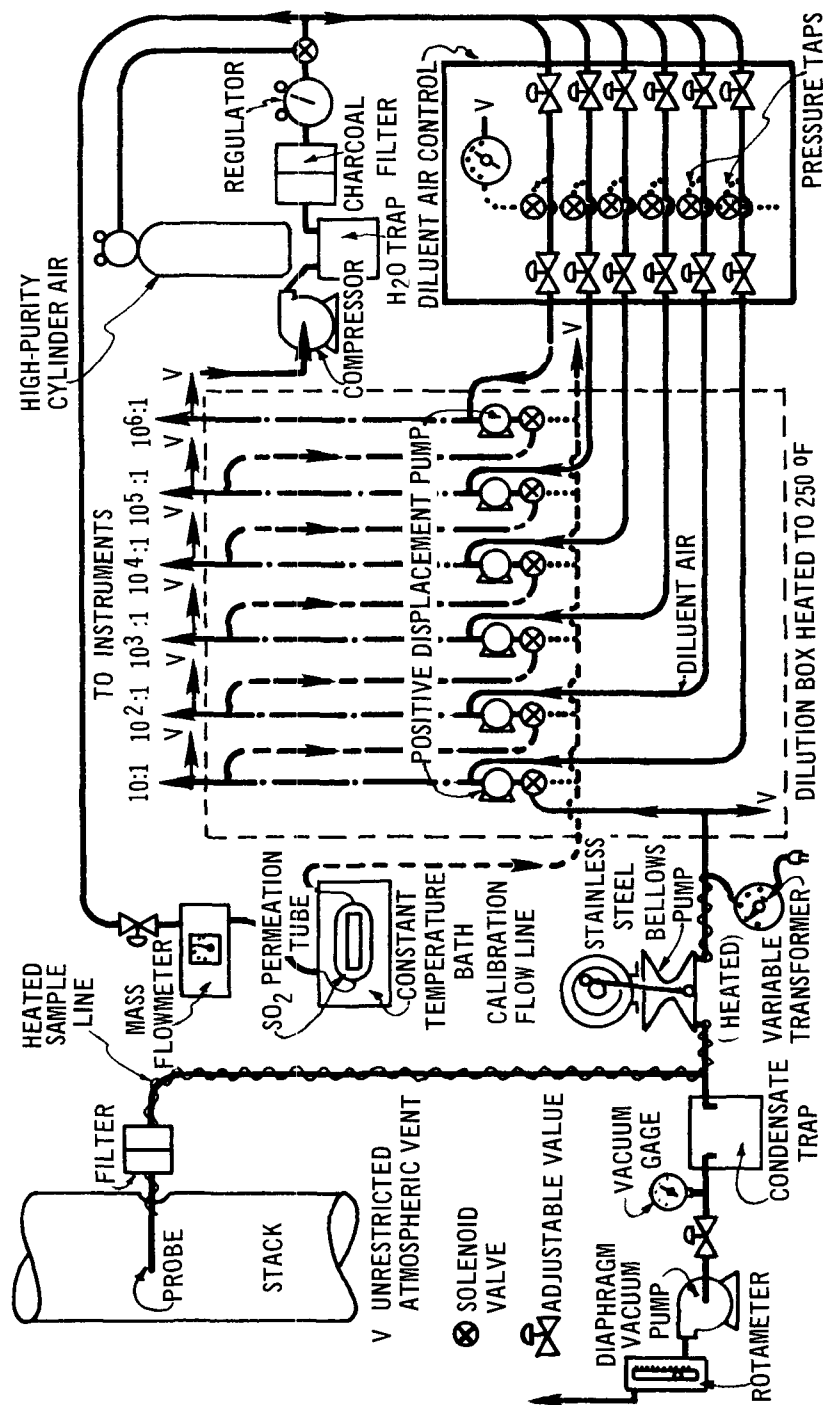
Figure B-2. Sample dilution system and related equipment.

The output of a diaphragm pump that is connected in parallel is monitored to determine the sample residence time in the sample line. This time is kept at a minimum in order to reduce the possible occurrence of interactions between the various constituents. A vacuum gauge located in front of the diaphragm pump is checked periodically to see that the pressure drop in the line does not exceed the value beyond which the bellows pump will no longer deliver the quantity of stack gas required by the dilution system.

The dilution system produces stack gas diluted to six different integral powers of ten. Although most sources require use of no more than the first two or three stages, there are occasions when high pollutant concentrations will warrant use of the higher dilutions.

Each stage of dilution consists principally of a Komhyr model A-150 positive displacement pump, which meters the gas being diluted. Displacement is approximately 150 cubic centimeters per minute (cm^3/min) and is constant within $\pm$ 1.5 percent of mean value. Since both the inlet and outlet of this pump are indirectly vented to the atmosphere, the pressure drop across it remains constant, and a constant mass is delivered per unit of time. Air that is dried and then filtered through activated charcoal is used as the diluent. The diluent air is teed into the pump's outlet line after passing through a monitoring orifice. The quality of this air is periodically verified by comparison with high-purity cylinder air. Assuming each stage is diluting by a factor of ten, 90 percent of the resulting mixture then exits the dilution system through an unrestricted atmospheric vent, with the remaining 10 percent going to the next dilution pump. Thus the quantity of gas available for analysis under these circumstances is approximately 1350 cm^3/min for each power of dilution.

The entire dilution system is presently contained in a box about 18 inches square. Refinements in the pump design could reduce this size considerably. The box is maintained at 250°F to prevent condensation in the first stage of dilution and to ensure that the mass pumped per unit of time will not change due to temperature fluctuations.

Each stage is initially adjusted to the required dilution ratio by supplying it with gas from a sulfur dioxide permeation tube [32] calibration system that has been adjusted to deliver a sulfur dioxide concentration of 10.0 ppm. The output of that stage is then monitored with a Melpar sulfur dioxide analyzer, which employs a Microtek flame photometric detector [33] that has been previously calibrated with the permeation tube. For example, if a dilution ratio of 10:1 is desired, the valve controlling the flow of diluent to that stage is adjusted until a reading of 1.00 ppm of sulfur dioxide is obtained. This procedure is then repeated for the remaining stages. Once the system has been calibrated, a Bourdon tube pressure gauge that is connected to a manifolded solenoid valve arrangement (Figure B-2) is used to periodically monitor the diluent flows through their respective orifices.

Accuracy and Reliability — The dilution system as described has been operated for as long as 12 hours without developing any measurable changes in the dilution ratios. Fluctuation in the barometric pressure during the course of operation, however, will directly affect the mass of stack gas being diluted per unit of time.

The accuracy of the system is principally dependent on the sensitivity of the analytical instrument used in the calibration. Since the flame photometric detector used for calibration has been found to be accurate to within ± 1 percent for a given reading, the accuracy of the calibration of a single dilution calibrated with this instrument is within ± 2 percent.

Utility—Since all dilution factors are simultaneously available in sufficient quantity to meet the sample requirements of all the instruments from a single stage of dilution, the instruments can be independently transferred from one stage of dilution to another. Thus, the flame photometric detector employed in the calibration of the dilution system can thereafter be used to measure total sulfur, and two gas chromatographic systems that employ identical flame photometric detectors can be used to identify various sulfur compounds.

The use of the dynamic dilution system has several secondary benefits with regard to the analytical instruments, the principal one being that the extra analytical and electronic parts that were previously required in order to extend the instruments' ranges are no longer necessary. Instead, the instruments are switched from one dilution stage to another when the pollutant concentration moves beyond the range of detection. Thus, it is possible to confine the pollutant values delivered to an instrument to its most sensitive detection range, and thereby eliminate the expendature of time required to calibrate the instrument beyond that range.

Gas Chromatographic-Flame Photometric Systems[34]

The flame photometric detector (Figure B-3) measures sulfur compounds by detecting the chemiluminescent emission from the excited S_2 molecules formed whenever sulfur compounds are burned in a hydrogen-rich air flame. A narrow-band-pass interference filter between the flame and the photomultiplier tube isolates a particular band of the S_2 emission at 394 microns. The interference filter allows the virtual elimination of interferences from non-sulfur-bearing constituents. The background flame noise is also reduced by viewing only the chemiluminescent emission above the flame.

Low-molecular-weight Sulfur Compound Detector — The gas chromatographic-flame photometric system shown in Figure B-4 was developed to measure low-molecular-weight sulfur compounds in kraft mill effluents. The analyzer consists of a Varian 122 gas chromatographic oven, a Meloy flame photometric detector, a Tracor power supply and electrometer, and a modified Beckman 10-part sliding plate valve equipped

HEATED EXHAUST

INTERFERENCE
FILTER

PHOTOMULTIPIER
TUBE

HEATER

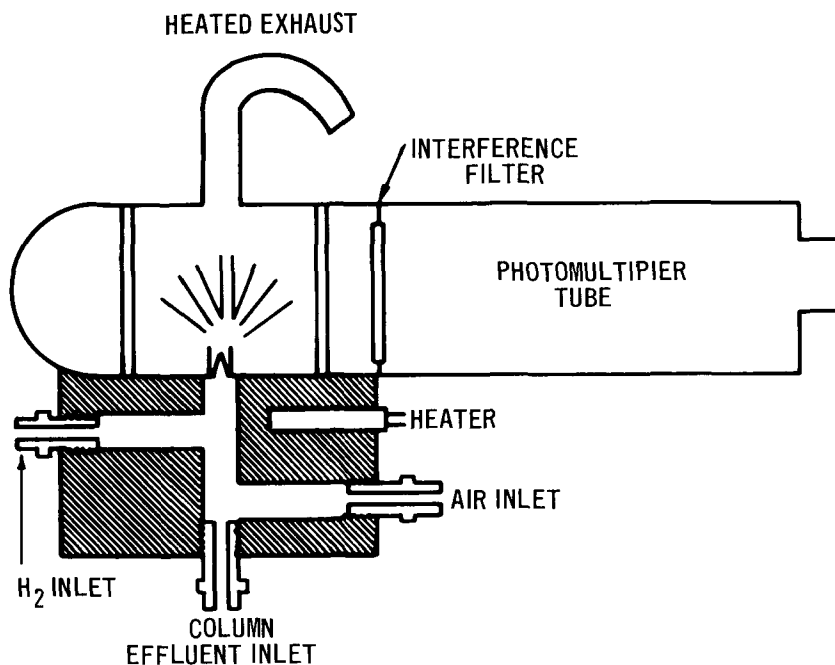AIR INLET

H_2 INLET

COLUMN
EFFLUENT INLET

Figure B-3. Flame photometric detector.

with a 10-cm³ Teflon sample loop, stripper column, and analytical column. The function of the stripper column is to prevent heavier sulfur compounds from reaching the analytical column by backflushing them to vent. The analytical column is 36-foot by 0.085-inch-i.d. Teflon tubing packed with 30/60 mesh Teflon and coated with 6 grams of polyphenyl ether and 500 mg of orthophosphoric acid. The 2-foot by 0.085-inch-i.d. stripper column is packed with the same material as the analytical column.

Two solenoids and an industrial cam timer automatically actuate the sampling valve at 10-minute intervals. The timing sequence to actuate the valve for sample injection, foreflushing, and backflushing is as follows:

1. Valve energized for 1 minute while sample is injected into stripper column and analytical column.
2. Valve de-energized for 9 minutes while stripper column back-flushes heavy sulfur compounds to vent, analytical column continues to be foreflushed, and sample loop is refilled.

The 10-port sample valve was modified to minimize sample-to-metal contact, which can cause severe losses at levels below 10 ppm. The 1/16-inch pipe to 1/8-inch tube fittings on the valve were drilled out so that the
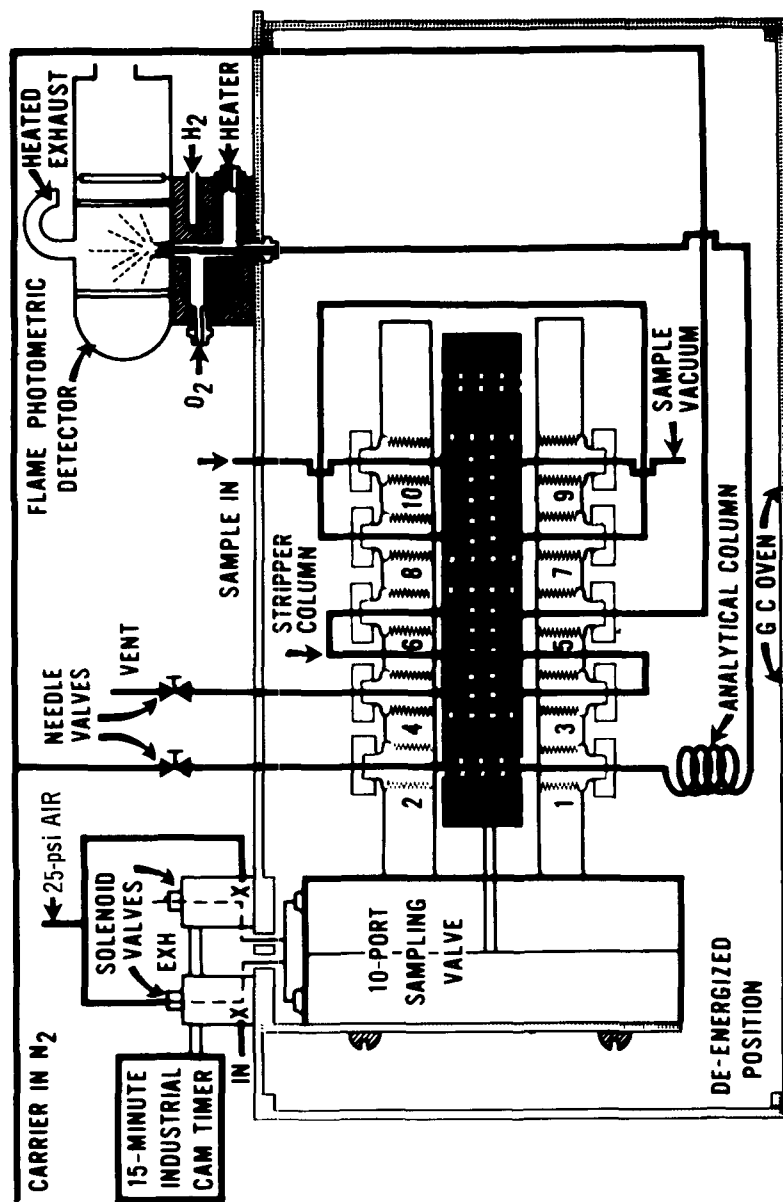
Figure B-4. Chromatographic-flame photometric detector for low-molecular-weight sulfur compounds.
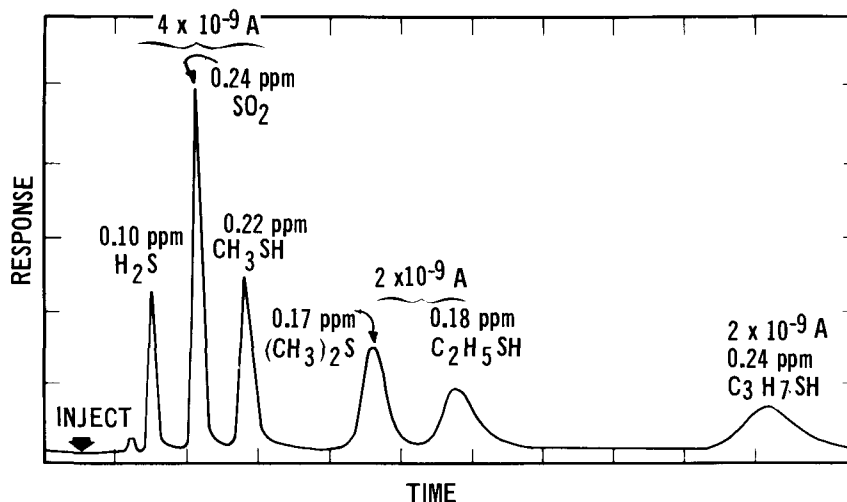
Figure B-5. Chromatogram of low-molecular-weight sulfur compounds.

Teflon lines would go through the fitting and into the body of the valve up to the Teflon slider, thus making the valve essentially all Teflon. The column exit was also fitted into the base of the detector to further minimize sample-to-metal interaction.

A chromatogram of a sub-ppm mixture of sulfur compounds obtained utilizing permeation tubes as a source of sulfur compounds is shown in Figure B-5. Hydrogen sulfide, sulfur dioxide, methyl mercaptan, ethyl mercaptan, dimethyl sulfide, and propyl mercaptan were resolved in 10 minutes on the 36-foot by 0.085-inch-i.d. polyphenyl ether Teflon column. Chromatographic conditions were as follows:

1. Nitrogen carrier gas flow, 100 cm^3/min.
2. Detector temperature, 105°C.
3. Exhaust temperature, 110°C.
4. Column temperature, 50°C.
5. Flame conditions: hydrogen flow, 80 cm^3/min; oxygen flow 20 cm^3/min.

High-molecular-weight Sulfur Compound Detector—The analytical system developed for the heavier sulfur compounds is shown in Figure B-6. A Chromatronia Teflon six-port gas sampling valve equipped with a 10-cm^3 Teflon sample loop was used since backflushing was not necessary. The analytical column is 10-foot by 0.085-inch-i.d. Telfon tubing packed with 30/60 mesh Teflon coated with 10 percent Triton-X 305. The lighter sulfur compounds will emerge rapidly from this column as one peak, followed by heavy sulfur compounds that elute separately.
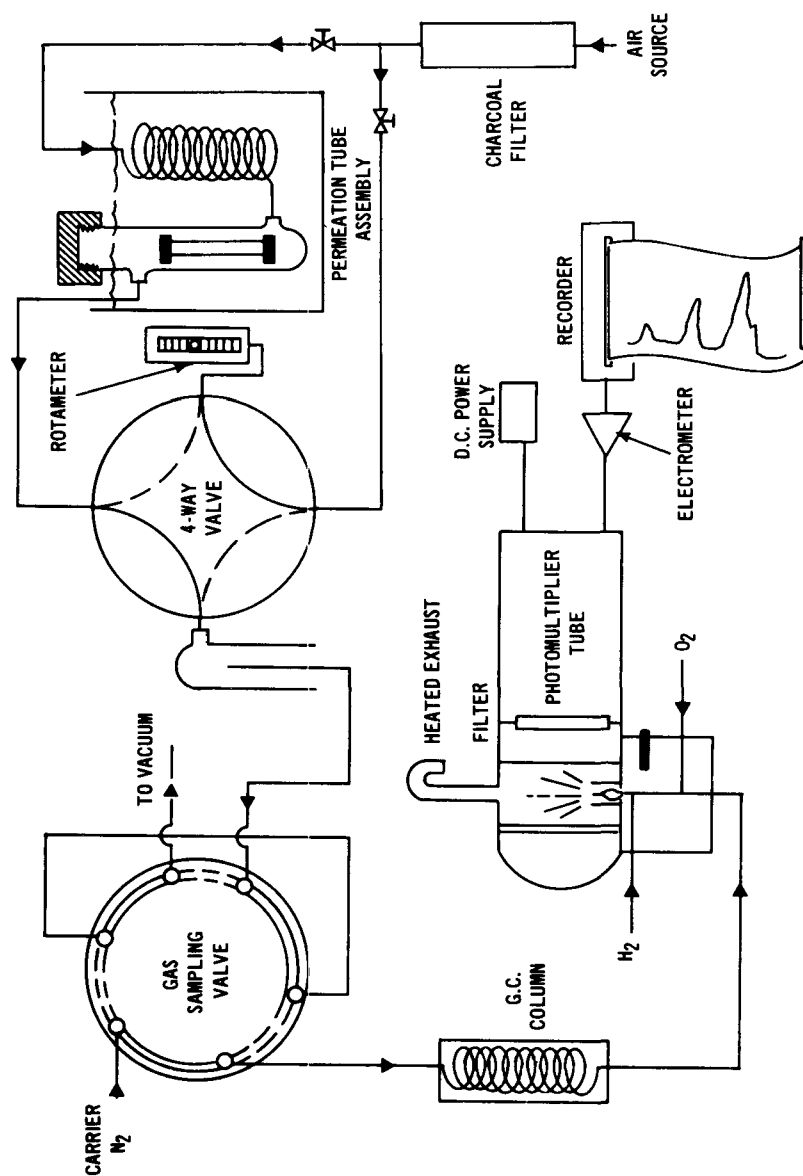
Figure B-6. Gas chromatographic-flame photometric detector for high-molecular-weight sulfur compounds.
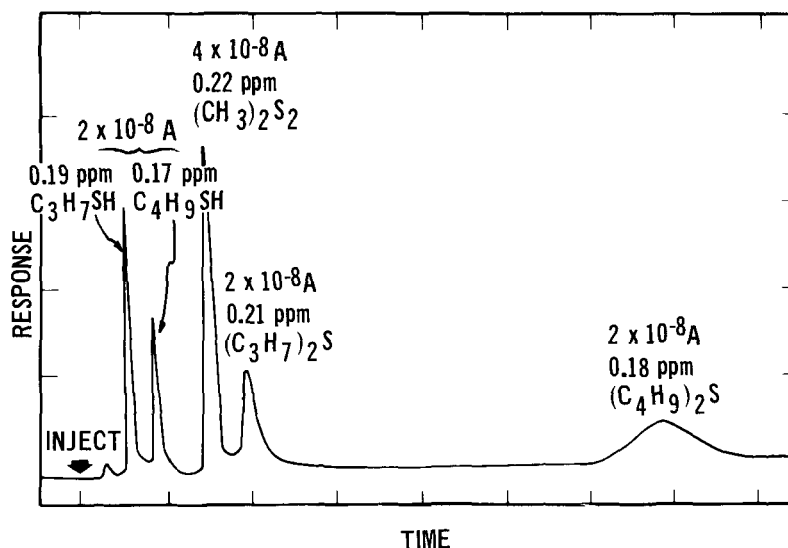
Figure B-7. Chromatogram of high-molecular-weight sulfur compounds.

A chromatogram of a sub-ppm mixture of high-molecular-weight sulfur compounds is shown in Figure B-7. Butyl mercaptan, dimethyl disulfide, dipropyl sulfide, and dibutyl sulfide were resolved in 10 minutes on the 10-foot by 0.085-inch-i.d. Triton-X 305 column. Chromatographic conditions were as follows:

1. Nitrogen carrier gas flow, 100 cm^3/min.
2. Detector temperature, 105°C.
3. Exhaust temperature, 110°C.
4. Column temperature, 70°C.
5. Flame conditions: hydrogen flow, 80 cm^3/min; oxygen flow 20 cm^3/min.

Teflon permeation tubes gravimetrically calibrated according to the procedure of O'Keeffe and Ortman[35] were used as primary standards. The permeation tube assembly is shown in the upper right of Figure B-6. The instruments are calibrated by injecting aliquots of an air stream flowing over the tubes into the chromatographic column. The concentration of the sulfur compound is inversely proportional to the air flow over the permeation tube.

Sampling Procedure — When kraft mill stack effluents are sampled directly, special sampling techniques are required to reduce losses because of high moisture content and a wide concentration range of the sulfur compounds present (ppb to percent levels). The dynamic dilution system

described earlier was used to bring the effluent samples into the inherently limited dynamic range of the flame photometric detectors.

To determine if the chromatographic peaks represent the total volatile sulfur introduced into the chromatographs, a Meloy total sulfur analyzer was used to continuously monitor the diluted sample.

Particulate Sampling and Analysis

The mobile van also includes facilities for particulate sampling and analysis. The procedures employed are detailed in the Federal Register.[30] The following sections briefly describe the major features of these procedures.

Sampling Site and Traverse Points

When possible, a sampling site at least eight duct diameters downstream and two diameters upstream from any flow disturbance such as a bend, expansion, contraction, or visible flame is selected. For a rectangular cross section, an equivalent diameter, equal to 2(length) (width)/(length+width), is calculated. For a sample site meeting these criteria, a minimum of 12 traverse points are sampled. For circular stacks, the traverse points are located on perpendicular diameters; for rectangular stacks, on the centroids of equal rectangular areas.

In some cases, it is necessary to sample at points that do not meet the criteria mentioned in the preceding paragraph. In such cases, the number of traverse points sampled must be increased to ensure a representative sample. Figure B-8 shows the minimum number of traverse points for various distances from a disturbance.

Sampling Train

The EPA particulate sampling train is shown in Figure B-9. Stack gas velocity is determined from gas density and from velocity head as measured by a Type S (Stauscheibe or reverse type) pitot tube. The sampling probe is Pyrex (or stainless steel, if necessary) and employs a heating system capable of maintaining a temperature of 250°F. The particulate sample is collected by glass fiber filters and impingers. The first two impingers contain water, the third is empty, and the forth contains silica gel. The metering system includes a vacuum gauge, leak-free pump, thermometers, dry gas meter, and related equipment as required to maintain an isokinetic sampling rate and to determine sample volume.

Analysis

The following samples are placed in individual containers for analysis:

1. Filter.
2. Loose particulate matter and acetone washings from all sample-exposed surfaces prior to the filter.
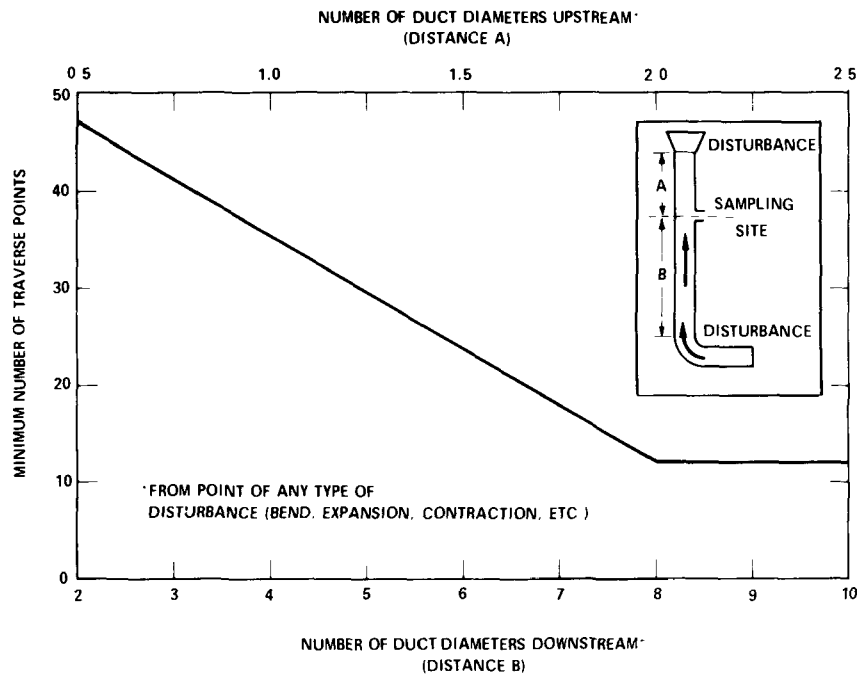
Figure B-8. Minimum number of traverse points.

3. Water from the first three impingers and water washings of all sample-exposed surfaces between the filter and the forth impinger.

4. Silica gel from the forth impinger.

5. Acetone washing of all sample-exposed surfaces between the filter and the forth impinger.

After appropriate sample conditioning, as detailed in the referenced procedure, the weight of particulate in each sample and the total particulate weight are determined.

The total particulate weight and the sample gas volume, adjusted to standard conditions (70°F and 29.92 inches of mercury), are used to calculate the sample concentration by two methods, referred to as the sample concentration method and the ratio of area method. If the concentrations determined by the two methods fall within acceptable limits, the concentration is reported as the average of the two values. If the concentrations do not fall within acceptable limits, the test is repeated.
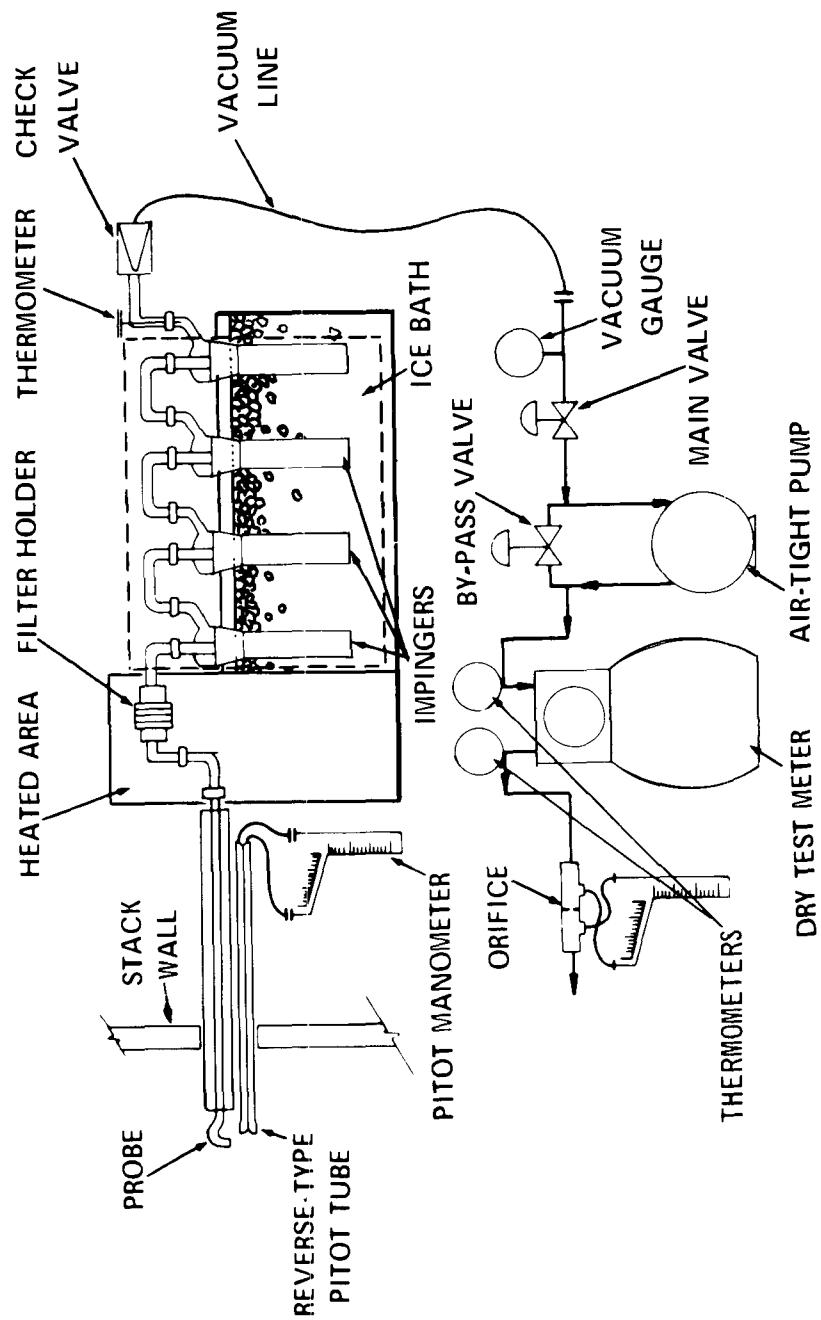
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Figure B-9. Particulate sampling train.

PULP AND PAPER INDUSTRY EMISSIONS

APPENDIX C: ODOR SURVEY

INTRODUCTION

One of the original objectives of this study was to make a comprehensive organoleptic assessment of the odorous emissions from major sources in a pulp mill and to relate the organoleptic measurements to the measured concentrations of the individual compounds in the emissions. This survey was to be conducted by an experienced Environmental Protection Agency (EPA) odor investigator, with a carefully selected and trained panel of odor observers. However, because of the pressure of other assignments, the odor investigator was unable to do more than initiate the odor survey. A greatly curtailed odor survey was then carried out by the principal EPA investigator. The restrictions imposed on the investigation resulted in data with many inconsistencies. The data are reported here to illustrate a method of odor measurement and for the limited significance that may be attached to the results.

EQUIPMENT AND PROCEDURES

The gas sampling system in the mobile van contains a tap for collecting odor samples. At this tap, the sample was diluted approximately 10:1. Samples were drawn through a hypodermic needle into 100-milliliter (ml) syringes. The samples were subsequently further diluted with odorless air in glass syringes and presented to odor panelists directly from the syringes. The method is basically that of ASTM Method D 1391-57.[36] The odor threshold is reported as the number of dilutions at which 50 percent of the panel can detect the presence of an odor. Panels were composed of mill personnel and EPA test crew members. Panels were composed of three to six members.

Odor panel members were screened by the use of hydrogen sulfide from a lecture bottle. A 100-ml syringe was filled from the lecture bottle and injected with air into a 2-cubic-foot plastic carboy, producing a dilution ratio of 567. Samples from the carboy were then diluted by multiples of 10 by using successive syringes. The results of the screening tests at Mill B are given in Table C-1. The dilution ratios are from the carboy.

The response of some of the panelists was rather erratic, but there was no opportunity to obtain any other panelists.

Table C-1. ODOR PANEL SCREENING TESTS[a]

Panel member	Dilution ratio (trial number)						
	B (2)	B (4)	10^8 (5)	10^8 (7)	10^7 (1)	10^7 (6)	10^6 (3)
P	−	−	+	+	−	+	+
H	−	−	−	−	−	−	+
F	−	−	−	−	+	−	+
A	−	−	−	−	−	−	+
O	+	−	−	−	−	−	+
E	−	−	−	−	−	−	+

[a]+ odor detected; −, no odor detected; B, blank consisting of pure air.

Odor samples were taken at the times when samples for gas analysis were being run. Because of the limited time the odor panel was available for evaluation of samples, an odor sample was not taken for each sample analyzed. However, at least one odor sample was evaluated from each point at which a series of samples were analyzed for components. Samples were taken at various times during the day. They were stored in the dark until presented to the odor panel. It was felt that the panelists should be in nonodorous surroundings for at least 2 hours before a panel was held. Since the panelists were not available in the evening, it was necessary to postpone the panel sessions until the following morning. Some tests with a limited panel indicated no deterioration on storing overnight.

RESULTS

The response of the odor panel to one sample is presented in Table C-2. The percent response at each dilution was plotted on log probability paper, as shown in Figure C-1, to estimate the dilution level for 50 percent panel response. The odor dilution thresholds of the other odor samples were obtained in the same manner. The results are tabulated in Table C-3 and Table C-4. The total reduced sulfur (TRS) values are the sum of the reduced sulfur compound readings obtained from the gas chromatograph. The TRS concentrations at the dilution threshold are obtained by dividing the stack TRS concentrations by the dilution threshold.

Table C-2. EXAMPLE OF ODOR PANEL RESPONSE[a]

Panel member	Dilution ratio (trial number)										
	B (2)	B (9)	10^5 (3)	10^5 (6)	10^4 (1)	10^4 (5)	10^4 (7)	10^4 (10)	10^3 (4)	10^3 (8)	10^2 (11)
O	−	−	−	−	−	−	+	−	+	−	+
P	−	−	−	−	−	+	−	+	+	−	+
E	−	−	+	−	+	+	+	+	−	+	+
F	+	−	−	−	−	−	+	−	+	+	+
Percent response	12		12		67				/5		100

[a]+, odor detected, −, no odor detected, B, blank consisting of pure air

Table C-3. ODOR PANEL RESULTS, MILL B

Sample	Source	Odor dilution threshold[a]	TRS emission, ppm	TRS concentration at odor threshold, ppb
	Recovery furnace			
6B	Electrostatic precipitator inlet	5×10^3	4.1	0.8
6C	Electrostatic precipitator inlet	3×10^4	3.4	0.1
6D	Electrostatic precipitator inlet	3×10^4	4.9	0.2
10B	Electrostatic precipitator inlet	5×10^3	4.3	0.8
9B	Electrostatic precipitator outlet	1×10^3	5.9	5.9
13A	Electrostatic precipitator outlet	1×10^4	6.2	0.6
15	Electrostatic precipitator outlet	1×10^4	3.1	0.3
11A	Smelt tank	5×10^3	3.3	0.7
12A	Smelt tank	5×10^4	8.1	0.2
12C	Smelt tank	5×10^3	3.8	0.8
16A	Washer vent	5×10^3	14.5	2.9
16B	Washer vent	7×10^3	10.1	1.4
16C	Washer vent	7×10^3	16.0	2.3
	Lime kiln			
17A	Scrubber, outlet	1×10^2	7.2	70
17B	Scrubber, outlet	1×10^2	11.1	110
18A	Scrubber, inlet	1×10^2	15.6	150
19	Scrubber, inlet	1×10^2	31.2	310
20	Black liquid oxidation	1×10^4	13.6	1.5
	Multiple effect evaporator vents			
21	Scrubber, outlet	5×10^9	14,000	0.003
22	Scrubber, inlet	3×10^7	14,000	0.5
23	Scrubber, inlet	1×10^8	36,000	0.4
24	Vapor line to lime kiln	1×10^{10}	46,600	0.005

[a]Dilution level detectable to 50 percent of the panel.

EVALUATION

An examination of the odor levels reported in Table 2 of the main text for the compounds composing TRS would lead one to expect that the odor threshold level of TRS would be in the range of 1 to 5 parts per billion. Many of the results in Table C-3 do fall in or near this range, but those in Table C-4 are generally well below it. The greatest deviation is in samples from lime kilns, and the deviation is fairly consistent. No reasons can be advanced for this deviation from expected levels.

Odor measurements in general are not capable of a high degree of precision. Chromatographic measurements of gaseous components, on the other hand, are capable of a considerable degree of precision. The deviations in the calculated TRS concentrations at the odor dilution threshold are therefore believed to be due to imprecision in the odor measurements. The fact that the TRS mixtures from the different sources are not the same could possibly account for some deviations. It is not believed, however, that it could account for the large deviations.

Table C-4. ODOR PANEL RESULTS, MILL C

Sample	Source	Odor dilution threshold [a]	TRS emissions, ppm	TRS concentration at odor threshold, ppb
	Recovery furnace			
1	Direct contact evaporator inlet	3×10^2	0.26	0.87
2	Direct contact evaporator inlet	1×10^3	0.28	0.28
3	Direct contact evaporator outlet	4×10^4	0.26	0.0065
4	Direct contact evaporator outlet	4×10^4	0.26	0.0065
12	Direct contact evaporator outlet	1.4×10^4	1.59	0.11
5	Electrostatic precipitator outlet	4×10^4	0.10	0.0025
6	Electrostatic precipitator outlet	4×10^3	0.10	0.025
14	Electrostatic precipitator outlet	5×10^3	1.01	0.2
7	Scrubber outlet	3×10^4	0.11	0.0037
9	Scrubber outlet	9×10^4	1.3	0.015
10	Scrubber outlet	2×10^4	2.74	0.14
11	Smelt tank	2×10^2	2.0	10
13	Black liquor oxidation	2.6×10^5	7.9	0.03
	Lime kiln			
15	Scrubber outlet	2.5×10^3	85.4	34
16	Scrubber inlet	4×10^2	33	82
17	Scrubber outlet	2.5×10^2	59.7	240
18	Brown stock washer	6×10^2	2.65	4.5
19	Knotter vent	6×10^2	12.9	21
20	Brown stock seal tank	1.7×10^4	626	38

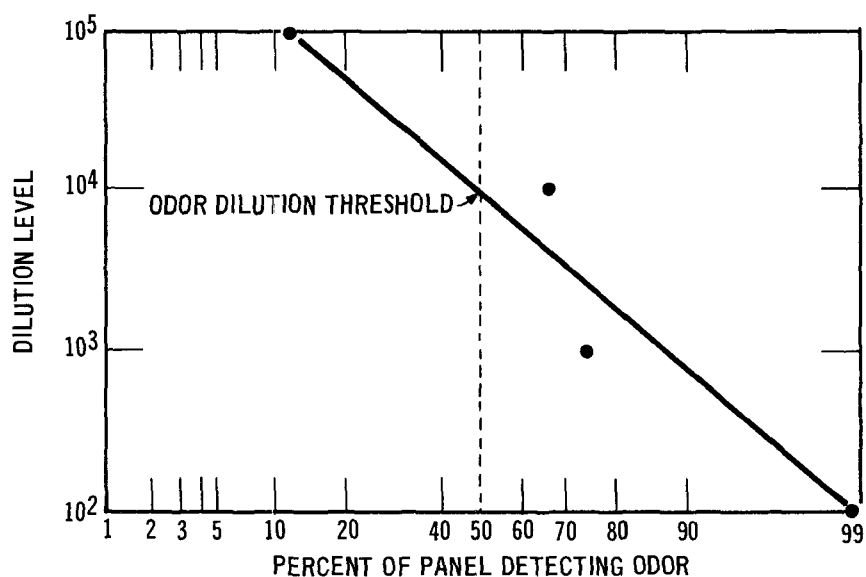[a] Dilution level detectable to 50 percent of the panel.

Figure C-1. Example of method of estimating dilution level for 50 percent response.

The results of this survey illustrate the care that must be exercised in organizing and conducting an odor survey. It is believed that the greatest inadequacy of this study was the lack of opportunity to screen a considerable number of people in order to select odor panelists who have a consistent response to odors. It appears that mill personnel and people who are at the mill for testing purposes do not make good panelists because they may suffer from "odor fatigue." Securing an adequate panel is the greatest difficulty in conducting an odor survey.

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