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Combined Nitrogen Oxides/Sulfur Dioxide Control in a Spray-Dryer/Fabric-Filter System

Interim Report for the Field Research Program

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Interim Report for the Field Research Program

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April 1987

Work sponsored by United States Department of Energy,
Assistant Secretary for Fossil Energy, Pittsburgh Energy Technology Center

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**Farber is affiliated with Chemical Waste Management, Inc., Oakbrook, Illinois.*

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The field test described in this report required ANL staff participation on a 24-hour-per-day, seven-day-per-week basis for more than three weeks. The authors want to acknowledge the ANL team members who participated in this effort and without whom the work would not have been possible: John W. Allen, John L. Anderson, Anthony J. Gorski, John B.L. Harkness, Sherman D. Smith, and Alvin S. Wantroba. The cooperation and assistance of the ANL boilerhouse personnel under the supervision of Raymond Fox were essential to the effort and are gratefully acknowledged.

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COMBINED NITROGEN OXIDES/SULFUR DIOXIDE CONTROL IN A SPRAY-DRYER/FABRIC-FILTER SYSTEM

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ABSTRACT

Caustic soda was evaluated for its value as an additive in combined nitrogen oxides/sulfur oxides (NO_x/SO_x) removal from coal combustion gases in a four-week field test at a 22-MW (electric) industrial-scale spray-dryer facility at Argonne National Laboratory (ANL). A combination of modified process conditions and addition of caustic soda to the lime-based spray-dryer system yielded some removal of NO_x from the flue gases, but an increased sorbent ratio was needed to maintain the SO_2-removal ability. The higher concentration of NO_2 at the system outlet than at the inlet indicated that the oxidation of NO to NO_2 was a key step in the overall removal process; a large increase in the concentration of nitrates was correlated with the increased oxidation of NO to NO_2. The test data also indicated that the outlet temperature from the spray dryer was a key factor in simultaneous NO_x/SO_x removal. Above 190°F, a relationship for NO_x removal was found between the equivalence ratio of the reactants and the pollutants, the thickness of the filter cake, and the ratio of SO_x to NO_x at the system entrance. The existence of a temperature "window" ideal for NO_x removal could not be verified during the field tests, primarily due to an upper temperature limit of 210-215°F. Also, as the filter-cake thickness increased, so did NO_x removal. NO_x removal (up to 45%) was enhanced by high ratios of SO_x/NO_x (>5:1) in the flue gas. At low SO_x/NO_x ratios (<2:1), virtually no NO_x removal (<10%) took place, even when SO_x removal was well over 90%.

1 INTRODUCTION

During the past decade, acid precipitation (less precisely, "acid rain") has emerged as a significant environmental issue with international implications. The mechanisms behind acid-precipitation formation and deposition are very complex and not yet fully understood. However, emissions of sulfur oxides (SO_x) and nitrogen oxides (NO_x) from fossil-fuel-fired boilers have generally been recognized as precursors to the formation of acid precipitates. (The term "acid precipitate" refers both to wet acidic deposits from the atmosphere and to dry deposits that behave like acid rainfall when they come in contact with surface moisture.) In response to concern over these precipitates, the federal government has established a research program to develop cost-effective processes for the simultaneous control of SO_x and NO_x from fossil-fuel-fired (particularly coal-fired) facilities. This program is managed by the U.S. Department of Energy (DOE) through its Pittsburgh Energy Technology Center (PETC). A significant portion of the program is being carried out by Argonne National Laboratory (ANL).

1.1 BACKGROUND

The research program on simultaneous NO_x/SO_x control at ANL during 1985-86 focused on the development of combined NO_x/SO_x removal capability in either spray-dryer/fabric-filter flue-gas-cleaning (FGC) systems or duct injection systems. The goal of this work was to identify and evaluate process modifications, chemical additives, or combinations of the two that can achieve 90% SO_x removal, together with 50% NO_x removal for retrofitted systems to 90% NO_x removal for new systems.

Earlier work in the ANL program focused on additives and process modifications for aqueous scrubber chemistries, such as lime and double alkali chemistries. This work, built upon fundamental studies of organometallic compounds, sought new approaches through development of an improved understanding of the important removal mechanisms and chemical reactions; significant improvement in NO_x removal was achieved in this research.[1-3]

Since their introduction in the late 1970s, spray-dryer/fabric-filter FGC systems have been rapidly achieving acceptance by electric utilities and other industries as an excellent control technology for low-sulfur coal. This class of systems avoids most of the problems associated with more conventional FGC systems -- production of large quantities of wet wastes, build-up of soluble salts (resulting in corrosion of system components), high rates of water and energy consumption, and the necessity of reheating flue gases for proper plume buoyance. However, uncertainties about system performance with high-sulfur coal have generally prevented the penetration of spray-dryer/fabric-filter technology into the market. The only commercial-size (22-MWe equivalent), high-sulfur spray-dryer/fabric-filter FGC system in the United States is the one recently put into operation at ANL. This system was extensively instrumented during its construction in order to ensure its usefulness not only as a pollution-control system, but also as a research tool.[4-8]

The current ANL research program on spray-dryer/fabric-filter systems comprises three integrated tasks, designed to develop the required NO_x/SO_x control technology and transfer information about this technology to the private sector in the most efficient way. Task 1 involves laboratory-scale research capable of screening a wide variety of additives and a wide range of process modifications; toward this end, a highly instrumented, laboratory-scale spray-dryer system has been developed. Results from experiments carried out with the small-scale system are expected to provide necessary guidance for selecting process conditions, chemical additives, or some combination of the two for large-scale tests in the 22-MWe spray-dryer FGC system under Task 2; these tests should provide valuable data at a scale adequate for private industry to make decisions regarding further commercialization. Task 3 is intended to complement Tasks 1 and 2 by ensuring, through a vigorous program of technology transfer, that information from the research program reaches potentially interested parties. All three tasks have proceeded in parallel, with differing degrees of emphasis, as the program has developed.

1.2 PURPOSE OF TESTS

The purpose of the first series of tests was twofold: (1) to fully characterize the commercial-scale, lime-based, spray-dryer/fabric-filter FGC system, with no process modifications or chemical additives, in order to establish a system-performance baseline against which the effects of process modifications and additives can be assessed, and (2) to evaluate the NO_x/SO_x-removal performance of the system with the addition of caustic soda (NaOH) to the lime slurry. Tests on the effect of caustic soda addition were motivated by results achieved by Niro Atomizer in simultaneous NO_x/SO_x removal in a spray-dryer-based FGC system[9] and by a report of brown plumes (NO_2) from a western utility plant operating a spray-dryer FGC system that uses soda ash as the sorbent.[10] Tests with caustic soda addition, therefore, were intended to confirm the results reported by Niro Atomizer, ascertain the proper conditions for optimal combined NO_x/SO_x removal, and elucidate the key reactions responsible for this combined removal.

1.3 REPORT ORGANIZATION

This report is organized into six sections. Section 1 introduces the body of the report. Sections 2-5 discuss in detail the testing approach and results of the first series of field tests. Section 6 presents the main conclusions from the field tests. The appendixes provide further information on procedures and techniques used in the preparation and analysis of process stream samples (App. A) and on the relative accuracy of continuous emission monitors used in the field program (App. B). Appendix C gives metric conversion factors for the English-system units commonly used in the power-generation industry.

2 TEST FACILITY

2.1 OVERALL PROCESS FLOW SCHEME

Figure 2.1 is a process flow diagram of ANL's industrial-scale spray-dryer/fabric-filter FGC system. The system was designed for and attached to a traveling-grate stoker with a maximum continuous rate (MCR) of 170,000 lb/h of steam at 200 psig* pressure. Flue gas exits the economizer of the boiler at about 330°F and is sent by the boiler's induced-draft fan to the stack. At the stack entrance is a guillotine bypass damper. When this damper is open, the flue gas passes directly up the stack. In normal operation, the damper is closed, and the hot flue gas is directed into the spray-dryer/fabric-filter FGC system.

Gaseous species in the flue gas are absorbed in the spray dryer. A spray of fine droplets of lime-water slurry is injected through a rotary atomizer at the top of the dryer chamber. The fine droplets react rapidly with the gaseous species in the flue gas flowing through the spray dryer. At the same time, the hot flue gas causes the water in the slurry droplets to evaporate, thus producing a fine dry powder that contains the reaction products (sulfites, sulfates, and carbonates), unreacted calcium hydroxide [$Ca(OH)_2$], and fly ash. A fraction of this dry powder drops out in the spray dryer and is removed by means of flapper dump valves at the bottom of the chamber. The flue gas carries the remaining powder into a baghouse for particulate-matter collection and then passes through a booster fan into the stack. The solid powders from the spray dryer and the baghouse are transferred by drag-link conveyors to a silo for recycling back to the slurry preparation tank or disposal in an on-site landfill.

2.2 PROCESS EQUIPMENT

2.2.1 Spray-Dryer Scrubber

The 24.5-ft-diameter spray dryer is a Niro Atomizer, Inc., unit equipped with dual flue-gas inlets (see Fig. 2.2). About 60% of the flue gas enters through the roof gas disperser, while the remainder enters through the central gas disperser. Directional vanes in the roof and central gas dispersers impart a swirling motion to the gas stream (counterclockwise, viewed from the top of the chamber). The atomizing disk is a 210-mm-diameter steel disk with eight 6.4-mm-diameter holes, rotating cocurrently with the gas flow at a speed of 14,000 rpm.‡ Lime slurry from the head tank flows through the temperature control valve into the atomizer, where it is dispersed into a spray of fine droplets of about 70 μm mean diameter. Mixing with the gas stream, these fine droplets are simultaneously being dried and reacting with the gas species in the hot flue

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*psig = pounds per square inch, gauge.

‡rpm = revolutions per minute.

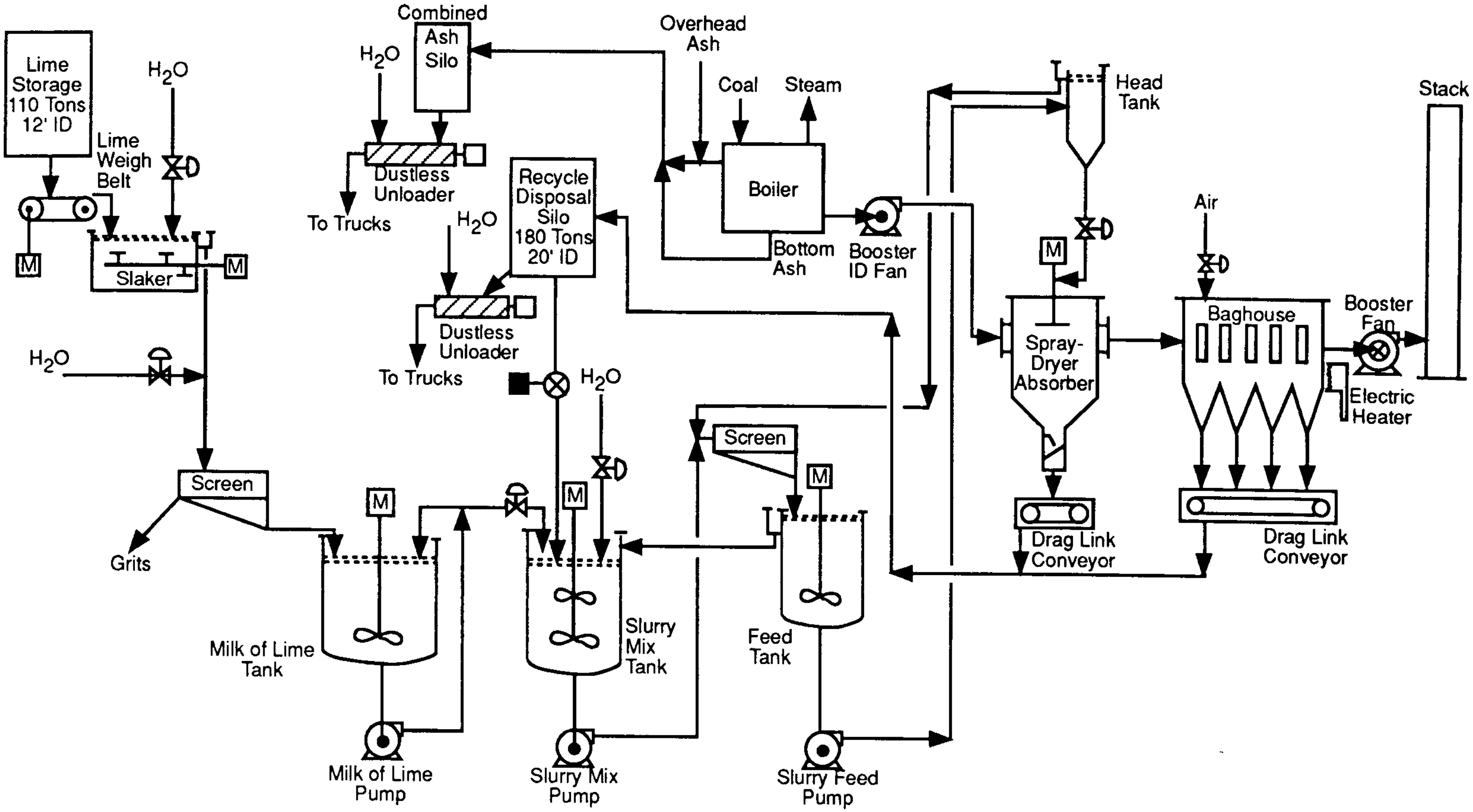

FIGURE 2.1 Process Flow Diagram for ANL Spray-Dryer System

gas. Depending upon the gas flow in the dryer, about one-fourth to one-third of the dry powder formed falls to the bottom of the chamber and is removed by a conveyor. The remainder of the dry powder remains entrained in the cooled flue-gas stream, which exits the spray dryer and enters the baghouse.

2.2.2 Baghouse Filter

The fabric-filter system used to collect particulate matter (as well as to provide additional sulfur oxides control) is a four-compartment, pulse-jet system provided by Joy Manufacturing Co. Each compartment consists of 28 rows of 10 bags each, with a

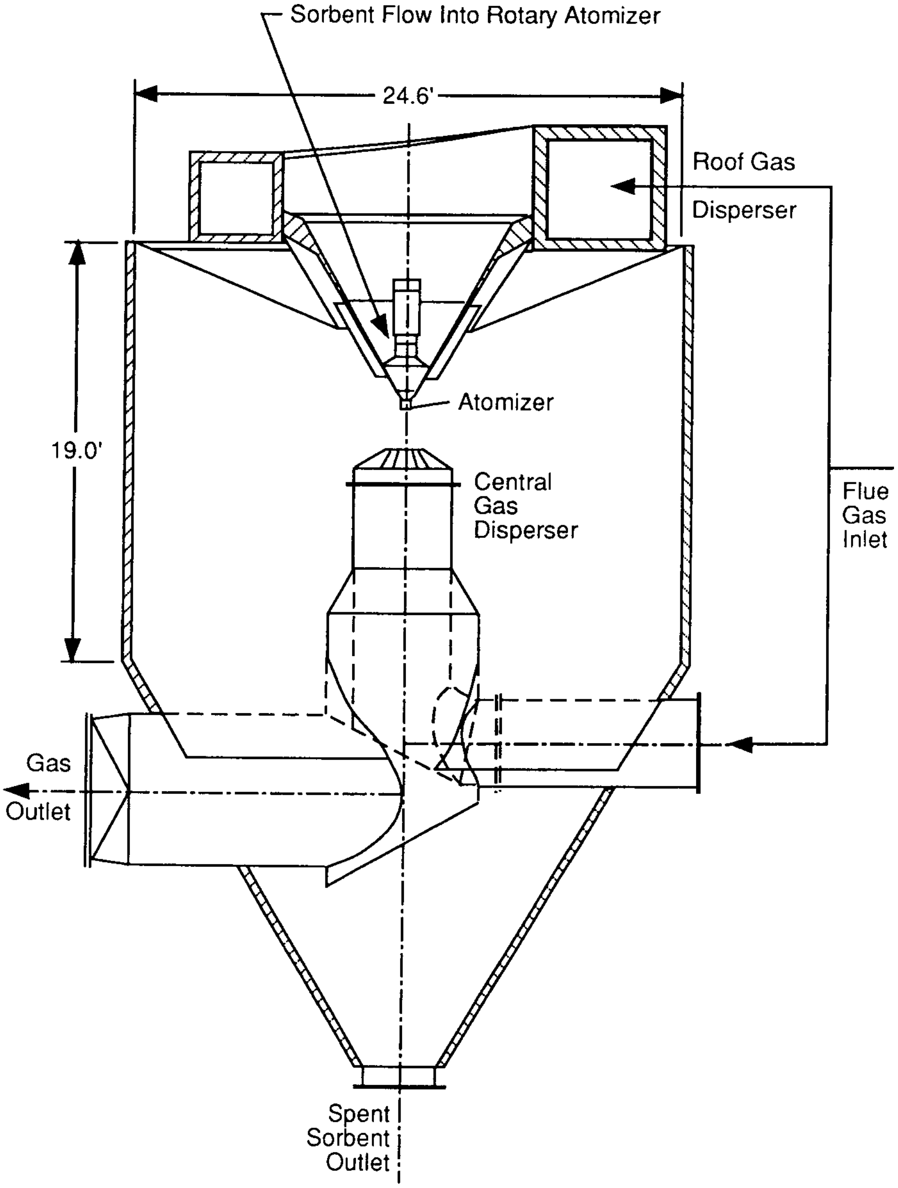

FIGURE 2.2 Spray-Dryer Unit

filtration area of 5,277 ft^2, for a total area of 21,000 ft^2. This corresponds to an air-to-cloth ratio of 3:1 at the design flue-gas flow rate into the filter, or a ratio of 4:1 with one compartment off-line for cleaning. Problems encountered with the original felted fiberglass bags have been overcome using 16.5-oz woven fiberglass bags of the snap-ring design. In addition, the cleaning system has been modified to include a programmable controller and converted from the original on-line cleaning mode to a pressure-drop-actuated off-line cleaning mode.

During operation, the particulate matter in the flue gas is filtered out on the outside of the bags, and the cleaned gas exits through the gas plenum to the booster fan. As the particulate matter is filtered, the sulfur oxides in the flue gas react with the unreacted lime in the solid cake built up on the filter bags. The extent of this reaction depends upon several factors, including the moisture content of the flue-gas stream, the amount of unreacted alkali in the powder cake, and the thickness of the powder cake on the filter bags. Consequently, the overall SO_x removal should be less just after the cleaning cycle than it would be right before cleaning, as has been observed at ANL.

2.2.3 Reagent and Slurry Preparation and Handling

The reagent used in the spray-dryer FGC system is a pebble lime with a high calcium oxide content (>90%). This pebble lime is stored in a silo with a seven-day capacity (based on 100% MCR). From the silo, the lime flows by gravity to a weigh-belt feeder, which (prompted by a level signal from the milk-of-lime tank) feeds the slaker. The slaker, a paste-type unit with a capacity of 2000 lb/h of pebble lime, produces a slurry of 22 weight percent (wt%) calcium hydroxide. After it is screened for grits removal, the 22-wt% $Ca(OH)_2$ slurry flows into the milk-of-lime storage tank. This storage tank is a carbon-steel vessel equipped with baffles and a mixer and sized for a 30-min residence time (750 gal) with respect to the maximum system flow rate. The milk of lime is transferred from the storage tank by rubber-lined centrifugal pumps to a slurry mixing tank.

Inside the slurry mixing tank, the milk of lime is combined with the recycled powders and additional dilution water to form the feed slurry. The amount of milk of lime introduced into the slurry mixing tank is controlled either automatically (by a signal from the SO_2 monitor at the stack) or manually (by setting the lime feed rate with the milk-of-lime controller on the control panel). The spent powder is partly recycled to improve the extent of lime utilization; the amount of recycled powder varies with the slurry mixing-tank level and the slurry density. Like the milk-of-lime tank, the slurry mixing tank is also a carbon-steel vessel equipped with baffles and a mixer and sized for a 30-min retention time at the maximum system flow rate.

From the mixing tank, the slurry is pumped to the slurry feed tank, which continuously overflows back into the mixing tank to ensure a uniform composition between the two tanks. A slurry transport loop, including two centrifugal pumps, circulates slurry from the slurry feed tank up to the head tank, located above the rotary atomizer, and back down to the slurry feed tank.

2.2.4 Booster Fan

The booster fan, located at the end of the FGC system, serves to move the gas through the entire system, overcoming the pressure drops of the spray dryer, fabric filter, dampers, and all associated ductwork. A vortex damper at the fan inlet, controlled automatically by the inlet system pressure signal, ensures that the system exit pressure is the same as the system inlet pressure in the event of an emergency upset. Should such an event occur, the guillotine damper at the FGC system inlet will open automatically, diverting all of the flue gas directly to the stack. The pressure balancing is necessary in order to avoid adverse pressure fluctuations within the boilers when such a gas diversion occurs.

2.2.5 Instrumentation and Process Control

The ANL FGC system was extensively instrumented during construction so that plant operations personnel would have complete, continuous information on system operation and performance. For the combined NO_x/SO_x-control research program, additional instruments have been installed to acquire data important for a thorough understanding of system operation.

Gas temperatures are monitored at the system inlet, at the spray-dryer outlet (two determinations), at the baghouse outlet (two determinations), and at the stack (two determinations). The gas temperature at the spray-dryer outlet is also used to control the total amount of lime slurry injected into the atomizer. In addition, a humidity sensor (the Ondyne, Inc., DT-111S probe, along with the Model 1731 moisture analyzer display) installed downstream of the baghouse monitors the wet bulb and dry bulb temperatures of the cleaned flue gas coming out of the baghouse. Wet and dry bulb temperatures can also be sampled manually at a port in the baghouse exit duct.

Gas pressures are monitored both remotely (with differential pressure cells) and locally (with pressure gauges). Originally, pressures monitored remotely included the system inlet pressure and the pressure drop across the entire baghouse, whereas local pressures were monitored at the spray-dryer outlet and the baghouse outlet, as well as in each of the four fabric-filter compartments. For the purpose of field testing, six differential-pressure cells (manufactured by Dwyer Instruments, Inc.) have been added to the system. Two of the cells are used to monitor remotely the static pressures of the flue gases at the spray-dryer outlet (or the baghouse inlet) and at the baghouse outlet. The remaining cells are used to monitor the pressure drop across each of the four fabric-filter compartments, supplementing the local gauges already in place. These new additions allow continuous monitoring and recording of the tubesheet pressure drop of each compartment, which should help in quantifying the contribution of the filter cake's buildup to the removal of NO_x and SO_x. In addition, the monitored pressure drop across the entire baghouse is used as the "trigger" that initiates the automatic cleaning of the fabric filter itself.

Flows of all important liquid and solid streams were instrumented during construction, both for monitoring purposes and -- in some cases -- for process control. The pebble-lime feed to the slaker is controlled by the level of milk of lime in the milk-of-lime storage tank, from which a signal is sent to the weigh-belt feeder. The weigh-belt feeder, located between the lime silo and the slaker, is equipped to indicate the instantaneous flow rate and the total amount of lime fed into the slaker. The flow of the milk of lime to the slurry mixing tank is monitored with a magnetic flowmeter (manufactured by Foxboro Co.) and controlled by a combination of the slurry mixing tank's level and the signal from the SO_2 emission controller. A second Foxboro magnetic flowmeter is used to monitor the flow of lime slurry from the head tank to the atomizer. Two radiation-based densitometers are used to monitor the densities of the milk-of-lime flow to the slurry mixing tank and the lime/recycled-powder slurry flow to the head tank. The amount of the recycled spent powder sent to the slurry mixing tank is determined by the slurry level in the tank, as well as by the density of the resultant slurry, and is controlled by varying the speed of a rotary valve located underneath the spent-sorbent storage silo. All water flows into the system are monitored. For field testing, counting devices are installed on the rotary valve, the two coal-feed scales, and the weigh-belt-feeder scale, so that the total amounts of spent sorbent recycled, the coal feed, and the fresh lime feed can be continuously recorded by the data-acquisition system (Sec. 2.4). In addition, a gas flowmeter (Kurz Instruments, Inc., Model 455T) has been installed at the stack to determine the volumetric flow rate of the cleaned flue gas.

2.3 FLUE-GAS ANALYSIS SYSTEM

The flue-gas analyzer installed on the stack during construction was capable of monitoring the compositions only of flue gases inside the stack. For the present research program, a Thermo Electron Corp. (TECO) gas sampling and analysis system was installed in order to determine the compositions of the flue gases at both the inlet and outlet of the FGC system. The TECO system, based on the Model 200 in-situ sample-conditioning probe, is a multipoint gas monitor capable of measuring gas compositions in flue gases of very high opacity. Two sets of probes and sample-transfer lines, placed at the FGC system inlet (or the boiler outlet) and the system outlet (the stack), are sequenced into a single analyzer package. Inside the analyzer, the concentrations of SO_2, carbon dioxide (CO_2), nitric oxide (NO), and combined oxides of nitrogen (NO_x) in the flue gas are determined. The oxygen concentration of the flue gas at the boiler outlet is also monitored with an in-situ zirconia-based analyzer; this instrument has been used to monitor overall boiler efficiency. In addition, manual sampling of the flue gases could be performed using sampling ports installed during construction at the FGC system inlet (three 3-in. ports), between the spray dryer and the baghouse (three 4-in. ports), and in the stack (four 3-in. ports).

2.3.1 In-Situ Sample-Conditioning Probe

The TECO Model 200 is an extractive gas monitor that performs in-situ sample conditioning in the probe tip at flue-gas temperatures. The sample is conditioned by diluting a sample of the filtered flue gases drawn through a sonic orifice with dry instrument air from which the CO_2 has been removed. This method of sample conditioning in the probe tip lowers the dew point of the sample gas to a temperature below the extreme minimum ambient temperature at the installation site, thereby eliminating condensation in the sample-transfer line. In addition to eliminating potential problems associated with nondiluting, heat-traced sample-transfer lines, this conditioning method results in the determination of gas compositions on a wet basis, the basis preferred by the U.S. Environmental Protection Agency (EPA).

All sampling-probe parts that are exposed to the flue gases are constructed of Inconel 600 (probe tip), Hastelloy C276 (probe extension), and Pyrex®* glass (sonic orifice). The flue gases are filtered by a coarse filter and two fine filters before they enter the sonic orifice. The coarse filter is a 0.0625-in.-mesh screen of Hastelloy, and the fine filters comprise a replaceable bed of quartz wool and fritted ceramic filters. (No adsorption of SO_2 or NO_x on the quartz wool and ceramic filter had been reported.)

The probe is mounted to the stack or duct using a 3.5-in.-ID (inner diameter) pipe nipple and a mounting flange. Typical operations require a flow of 1-3 $in.^3$/min (20-50 mL/min) of flue gas through the sonic orifice. Since the extracted flue gas is diluted by a ratio of approximately 200:1 with dry air, the sample is rapidly transported under pressure to the analyzer (in about 30 s).

2.3.2 Sample-Transfer Line

The line that transfers the flue-gas samples from the probe to the analyzer consists of two Teflon®‡ lines and two polyethylene lines, all encased in a fire-retardant polyethylene jacket. The Teflon® lines transport the diluted flue-gas sample to the analyzer and the calibration gas to the probe tip. The two polyethylene lines transport the dry instrument air to the probe and are also used to monitor the vacuum generated by the aspirator in the probe tip on the downstream side of the sonic orifice. All the gases in the sample-transfer lines are under positive pressure (except the vacuum line), which eliminates any error caused by leakage of gas.

2.3.3 Gas Analyzers

The gas-analyzer cabinet consists of one SO_2 analyzer, one NO/NO_x analyzer, one CO_2 analyzer, the probe controller, and one TECO M200R display panel. The SO_2 analyzer is a TECO Model 43-200 pulsed fluorescent type, modified for fast response and internal range-switching, slaved to the controller to permit time-sharing between the inlet and outlet probes. For the ANL FGC system, the analyzer would run on a nominal scale of 0-5 ppm§ for the inlet gas samples and 0-3 ppm for the stack-gas samples, with an output of 4-20 mA.

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*"Pyrex®" is a registered trademark of Corning Glass Works, Corning, New York.

‡"Teflon®" is a registered tradename of E.I. Du Pont de Nemours and Co., Wilmington, Delaware.

§ppm = parts per million.

The NO/NO_x analyzer is the TECO Model 14B-200 chemiluminescent type, also with an output of 4-20 mA. The unit would run on a nominal scale of 0-5 ppm for both the inlet and the stack-gas samples. It is equipped with an ozone generator and a carbon bed to permit determination of both the NO and the total NO_x in the gases.

The CO_2 analyzer is the Model 3300 nondispersed infrared (NDIR) type, manufactured by Automated Custom Systems, Inc. It would run on a nominal scale of 0-500 ppm, with an output of 4-20 mA.

The probe controller -- the unit that controls time-sharing between the probes -- contains controls for dilution air pressure, manual calibration, and probe selection. It shows which probe has been selected and displays the pressure and vacuum for each probe, as well as the sampling mode (normal, cal span, or cal zero).

The M200R remote-display unit is operated with the TECO Model 200 gas emission monitor. The M200R unit is a microprocessor-based system that performs the calculations required for EPA compliance reporting and activates alarms for plant operating personnel. The unit provides front-panel control and digital displays for up to six parameters, relay outputs for remote indications, analog outputs for strip-chart recording, and a digital/serial output to communicate with a plant computer. The six parameters displayed on the M200R at ANL are SO_2 (ppm), NO (ppm), NO_x (ppm), CO_2 (%), SO_2 (lb/10^6 Btu), and NO (lb/10^6 Btu).

2.4 DATA-ACQUISITION SYSTEM

The data-acquisition system installed for research on combined NO_x/SO_x control was designed by ANL's Electronics Division to provide ease of operation and maximum flexibility. The heart of the system is an International Business Machines (IBM) XT microcomputer equipped with 640 kilobytes (K) of random access memory (RAM) and an Intel 8087 math coprocessor. Storage of acquired data is accomplished with a 10-megabyte, built-in hard disk; periodically, for data reduction, files are transferred onto floppy disks (5.25 in.). In addition to being used for data storage, the microcomputer can also be used for some of the data reduction.

Signal outputs from all the instruments used for monitoring the FGC system and the boiler operations are fed to interfacing hardware manufactured by the Metrabyte Co. This interfacing unit consists of one eight-channel board (DASH-8), four 16-channel cards (Exp-16), and one five-channel counter-timer card (CTM-05). System inputs to the interfacing board are assigned to each card, as shown in Tables 2.1-2.5. The LabTech Notebook™* data-acquisition software is used to accept input data from the interfacing board, transfer the data to the IBM microcomputer, and control sampling times and frequency of sampling. (Currently, the system is set up to do sampling on a per-minute

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*"LabTech Notebook™" is a registered trademark of Laboratory Technologies Corp., Wilmington, Massachusetts.

TABLE 2.1 Data-Acquisition System, Card 0[a]

Channel No.	Item[b]	Range
	Temperature (°F)	
0	SDA inlet	100-500[c]
1	SDA outlet 1	0-200[c]
2	SDA outlet 2	0-500[c]
3	BH outlet	100-500[c]
4	BHA outlet	0-300[c]
5	BHB outlet	0-300[c]
6	BHC outlet	0-300[c]
7	BHD outlet	0-300[c]
8	Dew point	0-200[d]
9	Dry bulb	0-300[d]
10	Stack	0-300[e]
11	Stack velocity (ft/min)	0-3000[e]
12-15	--	--

[a] Basis: 4-16 channel cards, 1-5 channel counter-timer card.

[b] SDA = spray-dryer absorber; BH = baghouse, with compartments A-D.

[c] Input signal = 0-10 V.

[d] Input signal = 0-5 V, 4-20 mA.

[e] Input signal = 0-5 V.

TABLE 2.2 Data-Acquisition System, Card 1

Channel No.	Pressure[a]	Range (in. H_2O)
0	SDA inlet	-2 - +2[b]
1	SDA outlet	0 - -10[b]
2	BH outlet	0 - -15[b]
3	BH	0 - 10[b]
4	BHA TS	0 - 4[c]
5	BHB TS	0 - 4[c]
6	BHC TS	0 - 4[c]
7	BHD TS	0 - 4[c]
8-15	--	--

[a] SDA = spray-dryer absorber; BH = baghouse, with compartments A-D; TS = tubesheet.

[b] Input signal = 0-10 V.

[c] Input signal = 4-20 mA.

TABLE 2.3 Data-Acquisition System, Card 2[a]

Channel No.	Concentration	Range[a]
	Inlet	
0	SO_2 (ppm)	0-3000
1	CO_2 (%)	0-20
2	NO (ppm)	0-700
3	NO_x (ppm)	0-700
	Outlet	
4	SO_2 (ppm)	0-1000
5	CO_2 (%)	0-20
6	NO (ppm)	0-700
7	NO_x (ppm)	0-700

[a] Input signal = 4-20 mA for all channels.

TABLE 2.4 Data-Acquisition System, Card 3

Channel No.	Item	Range[a]
0	Boiler exit oxygen (%)	0-25
1	Steam production (lb/h)	0-170,000
2	Atomizer current (A)	0-100
3	Combustion air (ft^3/min)	0-50,000
	Flow rate (gal/min)	
4	Lime to slurry mix	0-24
5	Slurry to SDA[b]	0-24
6	Water to slurry mix	0-24
7	Water to slaker	0-20
	Density	
8	Slurry density	0-1.5
9	Milk of lime	0-1.5
	Tank level (%)	
10	Milk of lime	0-100
11	Slurry	0-100
12-15	--	--

[a] Input signal = 0-10 V for all channels.

[b] SDA = spray-dryer absorber.

TABLE 2.5 Data-Acquisition System, Card 4 (counter-timer)[a]

Channel No.	Item	Unit of Measure
0	Coal feed A	Dump[b]
1	Lime feed	lb/count
2	Recycled solids	0.4 ft^3/count
3	Coal feed B	Dump
4	--	--

[a] Input signal = 0-10 V for all channels.

[b] 1 dump = 200 lb.

basis.) By indicating in the software the actual units that each channel is measuring (e.g., °F, gal/min) and the appropriate measurement ranges, one can record the data in their actual scales and units.

Table 2.6 shows how the data are grouped for file transfer to floppy disks for data reduction and permanent storage. Data reduction can be carried out either by using an integrated computer program (such as Lotus 1-2-3™ or Symphony™*) or by loading all of the data files into a larger computer (such as the Digital Equipment Co. VAX or the IBM mainframe) for more extensive data processing. Data reduction using Lotus 1-2-3™ and other programs is discussed in more detail in Sec. 3.

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*"Lotus 1-2-3™" and "Symphony™" are registered trademarks of Lotus Development Corp., Cambridge, Massachusetts.

TABLE 2.6 Data-Acquisition System Files

File Name	Card-Channel	Item[a]	File Name	Card-Channel	Item[a]
UTILITY A	0-9	Dry bulb temp.	UTILITY A	3-10	Milk-of-lime tank level
	0-8	Dew-point temp.	(cont'd)	3-11	Slurry tank level
	0-0	SDA inlet temp.			
	0-1	SDA outlet temp. 1		4-1	Pebble-lime feed rate
	0-2	SDA outlet temp. 2		4-2	Recycled solids rate
	0-3	BH outlet temp.			
	0-10	Stack gas temp.	UTILITY B	0-4	BHA outlet temp.
	0-11	Stack gas flow rate		0-5	BHB outlet temp.
				0-6	BHC outlet temp.
	2-0	SO_2 inlet		0-7	BHD outlet temp.
	2-1	CO_2 inlet			
	2-2	NO inlet		1-0	SDA inlet pressure
	2-3	NO_x inlet		1-1	SDA outlet pressure
	2-4	SO_2 outlet		1-2	BH outlet pressure
	2-5	CO_2 outlet		1-4	BHA TS pressure drop
	2-6	NO outlet		1-5	BHB TS pressure drop
	2-7	NO_x outlet		1-6	BHC TS pressure drop
				1-7	BHD TS pressure drop
	3-0	Boiler exit oxygen			
	1-3	BH pressure drop		3-1	Steam production rate
	3-4	Lime to slurry mix		3-2	Atomizer current
	3-9	Milk-of-lime density		3-3	Combustion air flow rate
	3-5	Slurry to SDA			
	3-8	Slurry density		4-0	Coal feed (A) rate
	3-6	Water to slurry tank		4-3	Coal feed (B) rate
	3-7	Water to slaker			

[a] SDA = spray-dryer absorber; BH = baghouse, with compartments A-D; TS = tubesheet.

3 TEST PROGRAM

The ANL field research program is aimed at determining, through parametric tests conducted on an industrial-scale FGC scrubber, (1) the NO_x/SO_x-removal performance of the unmodified system and (2) the combination of modified process conditions and added sorbents that yields optimal NO_x/SO_x removal. These determinations will provide data needed to develop predictive correlations and to identify optimal operating conditions. The field research program is based primarily on results of laboratory-scale investigations (and parallel pilot-scale work at PETC), which in turn provide feedback to guide further work in the laboratory.

During the second half of FY 1985 and the first half of FY 1986, activities in the field research program were centered on the following areas:

1. Specification development, acquisition, installation, and testing of the TECO Model 200 flue-gas analysis system;
2. Acquisition and installation of additional sensors, probes, and signal-conditioning equipment;
3. Development, acquisition, installation, and testing of an appropriate data-logging system to permit collection of process operating data on a continuous and flexible basis;
4. Acquisition and evaluation of appropriate data-handling and data-analysis software;
5. Development of sampling and analysis procedures for the various solid and liquid process streams; and
6. Evaluation of existing data on the ANL 22-MWe FGC system to determine what additional data were required to adequately characterize the normal operation of the system, as a baseline for the series of parametric tests.

Information concerning the data-logging system, the TECO Model 200 flue-gas analysis system, and the additional sensors and probes installed (Activities 1-3) is given in Secs. 2.2.5, 2.3, and 2.4.

In Secs. 3.1 and 3.2, we describe the procedures developed for sampling and analysis of the solid and liquid process streams and for handling and analysis of the (expected) enormous quantities of data acquired during the tests. After the evaluation of the existing short-term data on the ANL FGC system, it was decided that a long-term test of the system under normal operating conditions would be conducted during the second half of FY 1986 to fully characterize the system and to provide an adequate baseline for future parametric tests; the test plan for this characterization test is discussed in Sec. 3.3. Finally, a general description of the parametric tests of process modifications and chemical additives is presented in Sec. 3.4.

3.1 SAMPLING AND ANALYSIS PROCEDURES FOR PROCESS STREAMS

Continuous data acquisition was supplemented by sampling of relevant liquid and solid process streams. The sampling was concentrated on the feed slurry to the atomizer, the dry powder discharge from the spray dryer, and the recycled powder. These three samples, when analyzed, provided information on the internal stoichiometry and the extent of reactions within the spray dryer, as well as in the baghouse. This information would be needed not only for system characterization and development of a process model, but also for evaluation of the effectiveness and mode of operation of additives to be tested for combined NO_x/SO_x removal. In addition to these three samples, samples from other parts of the FGC system were also acquired periodically. Table 3.1 lists all of the solid and liquid process samples taken during testing, as well as the initial sampling interval (which was subject to modification on the basis of sample and data analysis).

All samples, with the exception of coal samples, were taken in wide-mouth glass bottles with plastic screw caps. Approximately 250 mL in an 8-oz bottle provided a sufficient sample while preventing contact of the samples with air, which could affect the samples during the period of storage before analysis. Spray-dryer-powder samples were first collected in plastic bags, and representative samples were then transferred into the 8-oz glass bottles. About 30 lb of spray-dryer powder was collected to ensure that a representative sample could be obtained, and the sampling period was timed to establish the flow rate of the dry powders from the spray dryer by weighing the collected dry powders. Coal samples were collected periodically over a one-day period, and a representative lot of the coal was then taken as the sample for analysis. It was estimated that a 5-lb sample of coal would be representative of the material collected over the day.

Each sample was labeled (see Fig. 3.1) and assigned a number (Fig. 3.2) to identify the type of sample collected and the time and date of collection. This information was recorded in a bound notebook designated for the field program only. The samples were conveyed, on the same day they were collected, to the ANL Analytical Chemistry Laboratory (ACL) for analysis. The procedures and techniques used by ACL personnel for the preparation and analysis of these process stream samples are described in App. A. The results of this very extensive sample analysis have been reported by the ACL and used in the reduction and analysis of data.

3.2 DATA REDUCTION AND ANALYSIS

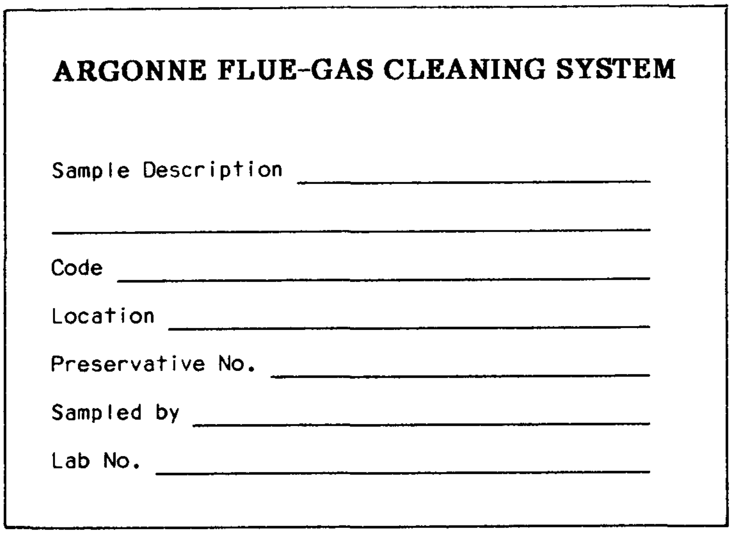
The on-line, continuous acquisition of FGC system-performance data on a per-minute basis generated an enormous number of measurements of the process parameters each day. To develop a manageable data base and smooth out potential fluctuations in process parameter measurements over a short time span (fluctuations normally associated with a large-scale FGC scrubber unit), a computer program, AVEDATA, was written. The function of AVEDATA was to statistically treat the data to eliminate "out-of-bound" data points and then average the process data over a specified period of time. On the basis of these averaged results, tables of all process parameters monitored and

TABLE 3.1 Process Stream Sampling

Sample	Location	Frequency[a]	Analysis
Pebble lime	Weigh-belt	Weekly	% available alkali, % total alkalinity, % Ca^{++}, % $CO_3^=$
Milk of lime	Milk-of-lime pump	Weekly	% solids, % available alkali, % total alkalinity, % Ca^{++}, % $CO_3^=$
Slurry	Slurry feed pump	Daily	% solids, specific gravity, % total alkalinity, % available alkali, % Ca^{++}, % Na^{+}[b], % S, % $CO_3^=$ % $SO_4^=$ % $SO_3^=$, % NO_2^-, % NO_3^-, % SiO_2
Recycled powder	Above mixing tank	Daily	% moisture, % total alkalinity, % available alkali, % Ca^{++}, % SiO_2, % Na^{+}[b], % S, % $CO_3^=$, % $SO_4^=$, % $SO_3^=$, % NO_2^-, % NO_3^-
Spray-dryer powder	Spray dryer	Daily	% moisture, % available alkali, % total alkalinity, % Ca^{++}, Na^{+}[b], % S, % $CO_3^=$, % $SO_4^=$, % $SO_3^=$, % NO_2^-, % NO_3^-, % SiO_2
Baghouse powder	Baghouse conveyor	Weekly	% moisture, % available alkali, % total alkalinity, % Ca^{++}, Na^{+}[b], % SiO_2 % S, % $CO_3^=$ % $SO_4^=$ % $SO_3^=$, % NO_2^-, % NO_3^-
Coal	Weigh scales	Weekly (composite)	Ultimate analysis, heating value, % Cl^-

[a] Sampling frequency may vary, depending upon variations in results from earlier samples.

[b] To be carried out only in NO_x-reduction tests.



ARGONNE FLUE-GAS CLEANING SYSTEM

Sample Description ____________________

____

Code ____________________

Location ____________________

Preservative No. ____________________

Sampled by ____________________

Lab No. ____________________

FIGURE 3.1 Sample Label

graphs of certain key process parameters (e.g., SO_2 and NO_x concentrations in the scrubber inlet and outlet gas streams) as a function of elapsed experimental time were generated. In addition, calculations were carried out with sets of the averaged data and with ACL results on the analysis of the solid and liquid process stream samples collected during the experiments; these calculations generated a separate block of data suitable for subsequent performance-modeling efforts. This block of data includes information on fractional removal of gaseous species, internal stoichiometric ratio, approach to gas saturation temperature, operating temperature, pressure drop across the fabric filter, amounts of additives, and other process parameters determined to be significant. Finally, mass-balance calculations were performed to check whether the system was operated under steady-state conditions during the period of process data acquisition and stream samples collection.

The large amounts of experimental data acquired can be analyzed by any of several personal-computer software packages, such as Lotus 1-2-3™, Reflex™, and the built-in, nonlinear regression program within the Labtech Notebook™, as well as the Statistical Analysis System (SAS) software available on the ANL mainframe computer. Most of the data analysis, graphics preparation, and curve-fitting completed so far has been done using Lotus 1-2-3™ in combination with the Labtech Notebook™; taken together, these two packages can be used effectively to organize the data acquired into tabular format for subsequent data reduction and analysis. The Reflex™ program has been used to generate numerous cross-comparison plots in order to demonstrate the effects of individual process parameters on the removal of SO_2 and NO_x from the gas streams and to investigate plausible mechanisms for the removal of these gaseous species.

One of the objectives of the field testing program has been the development of a simulation model that can be used to predict the performance of the spray-dryer/fabric-filter FGC system. Argonne investigators and other researchers have identified some of

Stream Codes

PL - Pebble lime
ML - Milk of lime
FS - Feed slurry
RP - Recycled powder
SP - Spray-dryer powder
FA - Fly ash
BA - Bottom ash
CL - Coal

Codes for All Samples

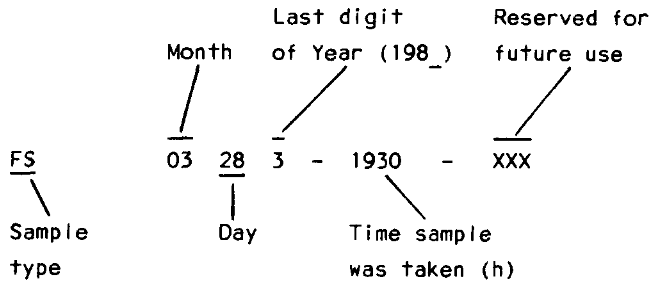


FIGURE 3.2 Coding of Process Samples

the key process parameters responsible for the removal of SO_2 (and probably NO_x as well) in a spray-dryer-based FGC system. These parameters are as follows:

- Inlet SO_2 concentration,
- Inlet flue-gas temperature,
- Spray-dryer exit gas temperature,
- Flue-gas dew-point temperature,
- Spray-dryer exit gas humidity,
- Internal stoichiometric ratio,
- Spray-dryer flue-gas residence time,

- Fabric-filter dust-cake thickness,
- SO_2/NO ratio in the flue gas,
- NO_2/NO ratio in the flue gas, and
- Additive feed rate (for NO_x removal).

Preliminary investigations conducted in developing the process models for NO_x removal are discussed in Sec. 5.

3.3 SYSTEM CHARACTERIZATION

Because performance tests of the ANL spray-dryer FGC system carried out in previous years (using Illinois high-sulfur coal) were of short duration, these tests did not provide an adequate data base to fully characterize the performance and operation of the system. The system characterization study, the first of a series of studies under the field testing program, was designed to acquire extensive system operating data and necessary process stream samples (under baseline operating conditions). These could then be used to (1) evaluate the normal performance and operation of the system and (2) quantify the removal of SO_2 and NO_x (if any), as well as reagent use and utility consumption rates under baseline conditions.

Typical system operating conditions for the ANL FGC unit are given in Table 3.2. Illinois high-sulfur coal used at the ANL boiler house contains about 3.1 wt% sulfur, with a heating value of about 12,000 Btu/lb on a wet basis. To meet the SO_2 emission standard imposed by the State of Illinois, an SO_2-removal efficiency of at least 66% (with a normal removal efficiency of 73-77%) should be attained. (The maximum allowable emission is 1.8 lb $SO_2/10^6$ Btu heat input to the stoker/boiler; for normal operation, the emissions range is 1.2-1.4 lb $SO_2/10^6$ Btu heat input to the boiler.) The actual SO_2-removal requirement during the characterization tests (determined by fuel analysis) was about 75%. Because of the high collection efficiency attained with the baghouse filter, particulate emissions from the system have been well below the state's standard under normal operating conditions. No Illinois standard on NO_x emissions bears upon the operation of the ANL boiler; the normal NO_x emissions from the ANL boiler have been about 0.4-0.5 lb $NO_2/10^6$ Btu heat input to the boiler, which is below the federal emission standards recently promulgated for industrial and small utility boilers.[11]

In addition to FGC system performance, another issue of increasing importance to potential users is reliability of operation. A major attraction of spray-dryer-based systems has been their simplicity -- and thereby, their potentially greater reliability -- in comparison with wet FGC scrubbing systems. The characterization and subsequent parametric tests of the ANL system offer the opportunity to determine whether such systems are indeed simple to operate and less troublesome in terms of maintenance, relative to their wet FGC counterparts.

TABLE 3.2 Normal Operating Conditions for Argonne Spray-Dryer Scrubber

Parameter	70% Boiler Load	82% Boiler Load
Spray-dryer inlet temperature (°F)	334	340
Spray-dryer inlet flue-gas flow rate (acfm)[a]	90,800	106,000
Flue-gas residence time in spray dryer (s)	14	12
Solids in atomizer feed slurry (wt%)	35	35
Recycling ratio	2:1	2:1
Approach to adiabatic saturation (°F)	22-25	22-25
Baghouse air-to-cloth ratio (acfm/ft^2)	3.5:1	4.0:1

[a] acfm = actual cubic feet per minute.

The characterization test was originally to have been conducted over a 60-day period, with the boiler load maintained at as constant a level as possible. However, due to problems with the newly installed monitoring instruments, this test started late and lasted only about three weeks before the caustic-addition tests commenced. In addition, it was initially suspected from the flue-gas analysis, and later confirmed by the fuel analysis, that the sulfur content of the coal being fired was uncharacteristically low (about 2.1 wt%). Nevertheless, this first medium-term test served to familiarize participating staff members with the operation of the system and the procedures for collection of solid and liquid process stream samples. Results from this baseline test are discussed in Sec. 4. Another one-month characterization test of the system using high-sulfur coal has been planned for FY 1988.

3.4 CHEMICAL-ADDITION TESTS

Tests of the effects of chemical additives on the removal (or enhanced removal) of NO_x and SO_2 from combustion flue gases were guided by the results from the laboratory-scale spray-dryer scrubber system and by the pilot-scale studies at PETC.

The tests were carried out with careful control and variation of the chemical-addition rate, the spray-dryer outlet temperature, and the pressure drop across the fabric filter so as to duplicate as closely as possible for promising additives the optimal operating conditions attained at the laboratory-scale and pilot-scale units. Because the optimal operating conditions may vary with the chemical additives to be tested, and because the practical ranges of operating parameters for the ANL commercial-scale FGC system are constrained, individual test plans were to be prepared for review and comment prior to the formal start of testing to evaluate each selected additive. The test plan for the first chemical-addition test, which was used to evaluate the effect of caustic soda addition on combined SO_2 and NO_x removal, is discussed in Sec. 5.1.

To perform the chemical-addition tests, a simple piece of equipment for feeding the chemicals evaluated to the lime slurry tank was constructed. The equipment consisted of a chemical storage tank, a metering pump, and sections of chemical transfer hoses. The storage tank used for the caustic-addition tests was a trailer tanker, rented from the caustic soda supplier. The tanker was a heavily insulated, unheated stainless steel tank equipped with a flow-control valve. The pump used was a Gelber stainless steel gear pump (Model MCP-221/56C), which was mounted on a Graham motor (Model 302E-M1) with a 0-5-V direct-current (DC) special reference processor controller. The purpose of the reference processor controller was to adjust the flow of caustic soda to a predetermined percentage of the lime feed rate, which is controlled by a DC signal of 0-5 V. A problem with the electrical grounding to the processor controller, however, prevented the use of this option during the caustic-addition tests. (An isolation circuit, built subsequently, will be used in future tests.) Instead, the lime slurry feed rate was kept constant, and the caustic feed rate was manually adjusted using the bucket-and-stopwatch method. The transfer hoses used for the caustic-addition tests were 0.5-in.-ID, Buna-N-rubber-lined Weatherhead H9 hoses. The entire hose was heated with Chemlex (10BTV1) autotrace self-regulating heater, which supplies heat at a rate of 33 W/m at 70°F, but only 3.3 W/m at 150°F. A thermocouple-controlled temperature controller was used to maintain the caustic soda flow at 80°F. The hoses and the Chemlex heater were covered with Armstrong sponge-rubber insulation. A flowmeter made of polysulfone, with a range of 0.25-2.5 gal/min, was used to check the flow. All of the fittings and piping used in the system were stainless steel, and the pump/motor assembly was placed inside an enclosure.

4 BASELINE CHARACTERIZATION TESTS

The primary purpose of the characterization tests was to generate an adequate data base under baseline operating conditions, against which the results from subsequent parametric tests of chemical additives and modifications to process operating conditions could be evaluated to determine the effectiveness of these techniques or combinations of techniques. To accomplish this purpose, the first characterization test of the ANL spray-dryer FGC system was carried out over a period of about three weeks (from mid-July to early August 1986) before the scheduled caustic-addition tests commenced. During this period, information from all monitored points, with the exception of those for the coal feed, lime feed, and recycled powder rates, was continuously collected on a per-minute basis and stored on the hard disk of an IBM XT personal computer; the information was transferred onto two floppy disks every other day for safe storage and later analysis.

Due to problems encountered with the interfacing counter-timer card, flow rates of the three solid streams -- coal, pebble lime, and recycled spent sorbent -- could not be monitored. In addition, the gas flowmeter was installed and put into operation only in the second week of the testing period (as is evident in Fig. 4.1), and the dew-point meter was received, installed, and made operational only in the last week of the testing period.

As may be seen in Figs. 4.1-4.4, the ANL stoker/spray-dryer FGC system was carefully controlled to operate in a narrow range. (As a commercial system, it had to be responsive to the fluctuations in actual on-site steam requirements.) The gas flow rates were maintained at about 54,000 standard cubic feet per minute (scfm), plus or minus 10% (Figs. 4.1 and 4.2), while the stoker-boiler was actually operated in a range of about

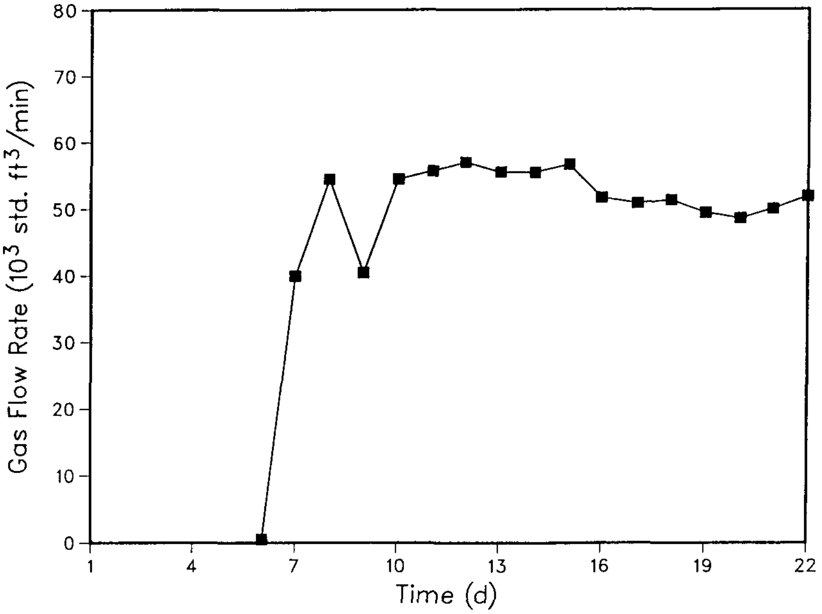


FIGURE 4.1 Baseline Gas Flow Rates (experiment initiated July 12, 1986)

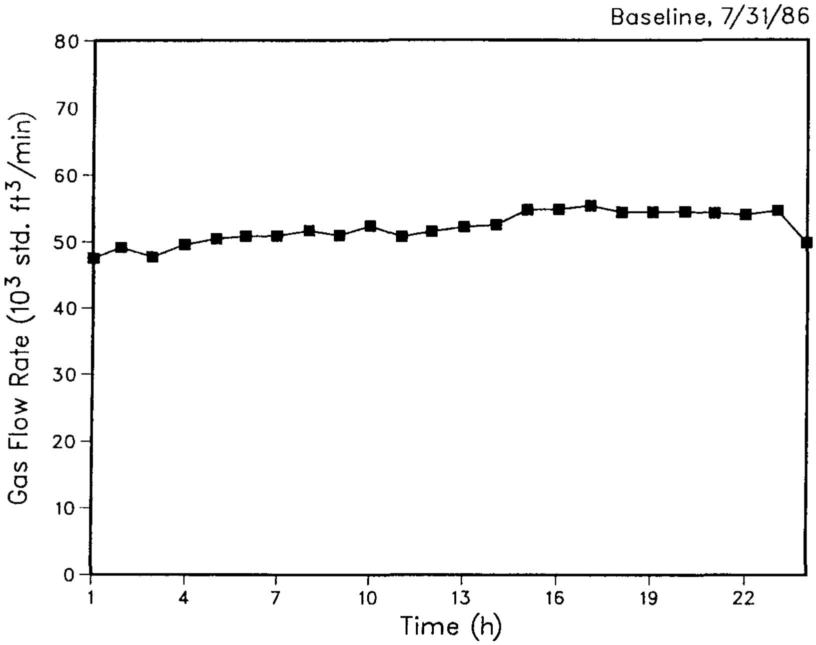


FIGURE 4.2 Hourly Gas Flow Rates

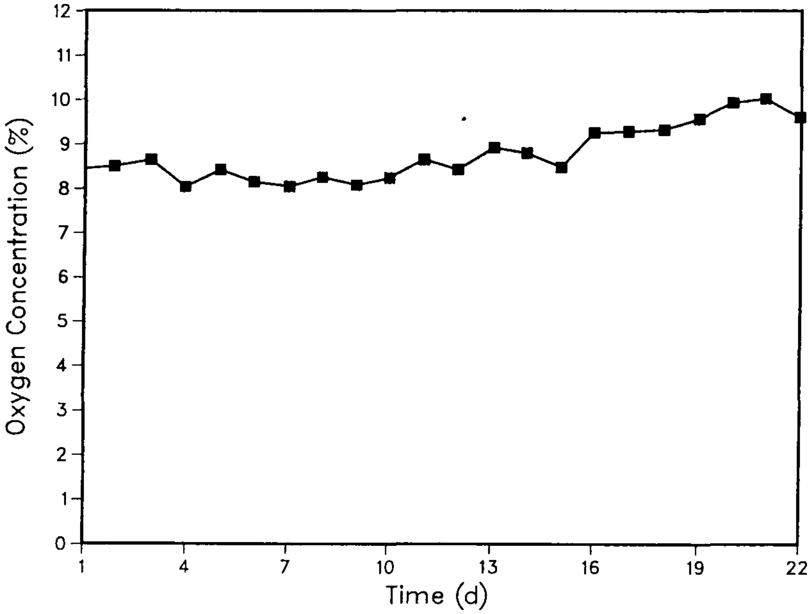


FIGURE 4.3 Baseline Oxygen Levels (experiment initiated July 12, 1986)

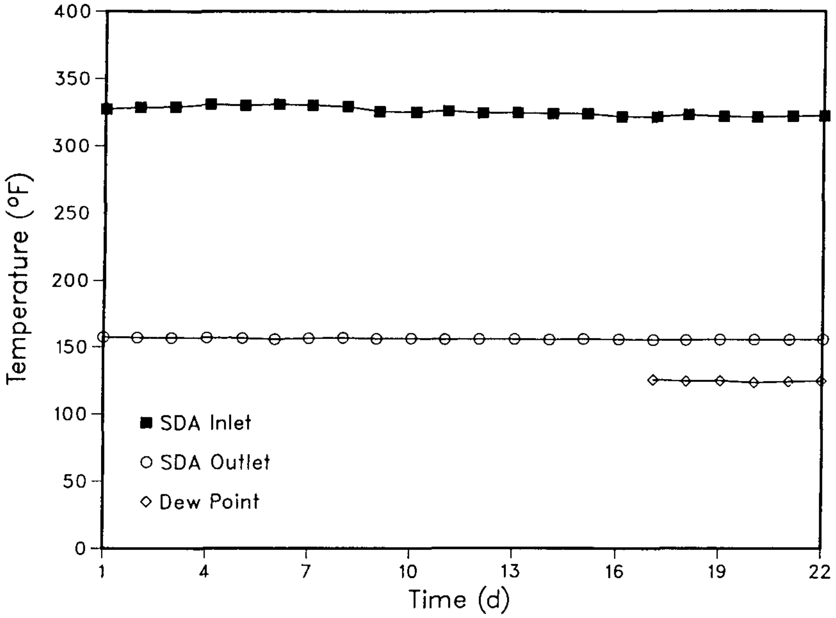


FIGURE 4.4 Baseline Temperatures (experiment initiated July 12, 1986)

50 to slightly over 70% of its maximum operating load. Additional combustion air had to be admitted into the stoker to ensure complete combustion of coal as the boiler load dropped; this measure somewhat offset the expected decrease in the total flue-gas flow rate at low boiler loads. However, the oxygen concentrations in the flue gases at low boiler loads, because of the higher combustion-air admission, were higher than the concentrations at high boiler loads. This is evident in Fig. 4.3; as the boiler load started to decrease during the last week of the testing period, there was a clear upward trend in oxygen levels. The increase in the combustion air, and the resulting increase in oxygen levels in the flue gases, however, resulted in no significant increase in NO/NO_x concentrations in the flue gases coming out of the stoker/boiler.

Results for the flue-gas temperatures at the spray-dryer inlet and outlet (upstream of the baghouse filter) are shown in Fig. 4.4. Again, the flue-gas temperature at the spray-dryer outlet was carefully controlled within a fairly narrow range, even though the flue-gas temperatures at the inlet varied. The flue-gas dew-point temperature, as measured at the baghouse outlet with the new Ondyne meter, clearly indicated that the approach to adiabatic saturation temperature was about 30°F, a fairly high value.

4.1 NITROGEN OXIDES EMISSIONS

Results for NO_x concentrations in the flue gases entering and exiting the ANL FGC system during the characterization tests are shown in Fig. 4.5. The figure shows that total NO_x emissions at the FGC system inlet and outlet did not vary significantly during the testing period (a slight upward trend may be seen in the last three or four

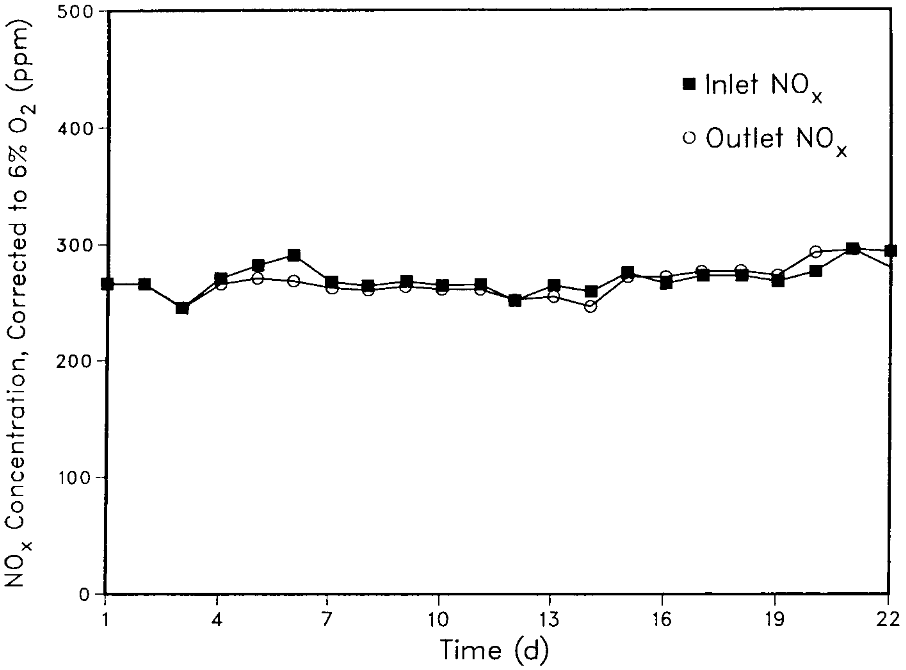


FIGURE 4.5 Baseline Nitrogen Oxides Levels (experiment initiated July 12, 1986)

days). The results of NO measurements are about 10 ppm below the NO_x results, indicating an NO_2 content in the boiler flue gases of less than 5% of the total NO_x content -- an expected result with the stoker-type furnace. At constant boiler loads, the higher oxygen levels shown in Fig. 4.3 for the last six or seven days normally would result in higher NO_x emissions (about 60-80 ppm), which would be about 20-25% higher than the results shown for the preceding two weeks. The actual NO_x emission results shown in Fig. 4.5, however, are only about 30 ppm (10%) higher. This is probably due to the dependence of NO_x emissions from the furnace not only upon oxygen levels in the flue gases, but also on the heat-release rates in the furnace.[12] Because of the decrease in the furnace heat-release rates in the last six or seven days of the testing period, the NO_x emissions from the furnace show no strong dependence on the oxygen concentrations in the flue gases.

The difference between NO_x concentrations in the flue gases at the FGC system inlet and the system outlet, as shown in Fig. 4.5, is also minimal, suggesting that no significant NO_x removal was accomplished during the characterization tests. The results for NO and NO_x removal, calculated from the raw data for the period of the characterization tests, are shown in Figs. 4.6 and 4.7 for the entire period and for a single day, respectively. The curves in these two figures hover slightly above and below the 0% removal lines, confirming that no significant NO or NO_x removal took place during the test period. This observation agrees with expectations that no NO or NO_x removal would be realized under baseline operating conditions (without chemical additions, modifications to process operating conditions, or both).

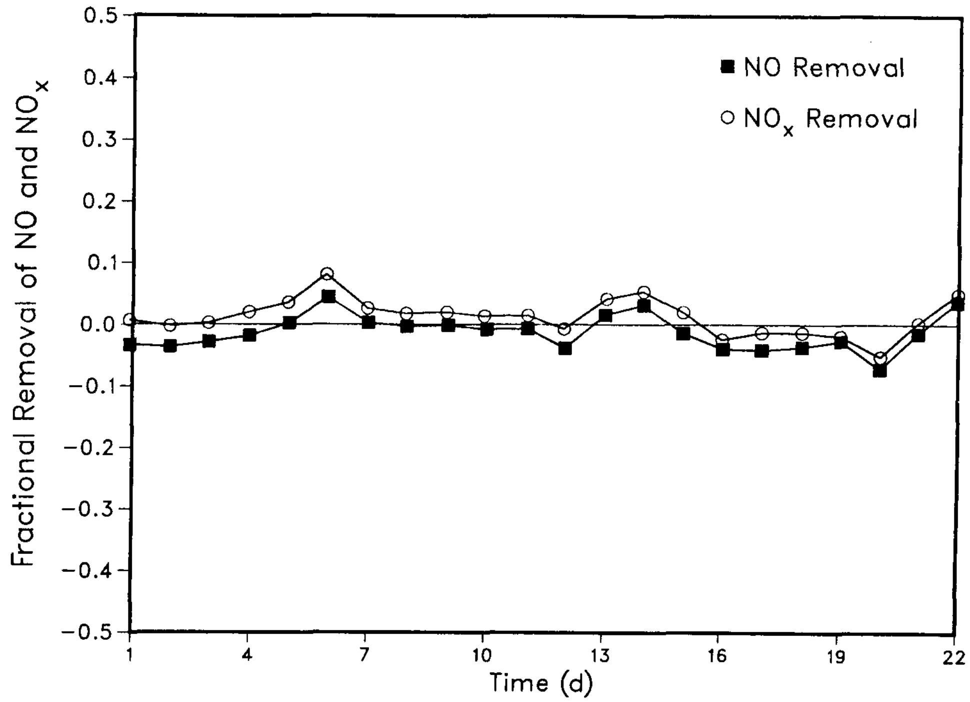


FIGURE 4.6 Baseline Removal Levels for Nitric Oxide and Nitrogen Oxides (experiment initiated July 12, 1986)

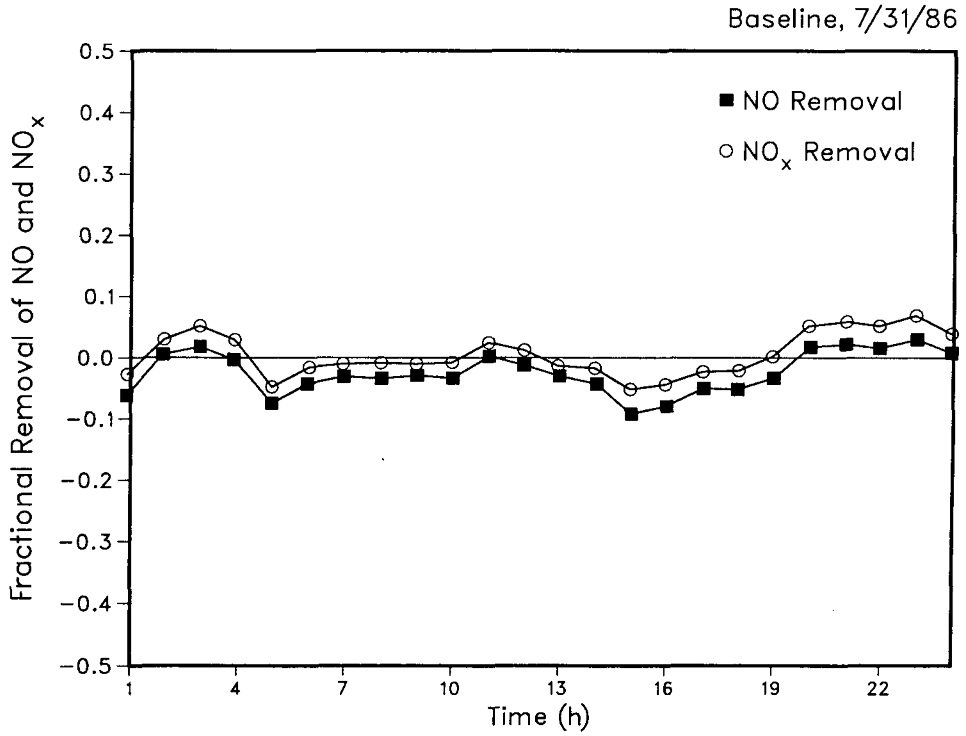


FIGURE 4.7 Hourly Nitrogen Oxides Removal

The fairly random nature of the curves, within a narrow range, over the entire testing period suggests that a system variation in NO/NO_x removal of about ±10% is typical of the ANL spray-dryer FGC system. In the subsequent parametric tests of chemical additives and process modifications, NO and NO_x removals of 10% or less were considered statistically insignificant.

4.2 SULFUR DIOXIDE EMISSIONS AND REMOVALS

Sulfur dioxide concentrations in the flue gases at the spray-dryer FGC system inlet and outlet during the characterization-test period are shown in Fig. 4.8. The figure shows that SO_2 levels in the flue gases from the stoker/boiler did not vary much over the testing period. Over the same period, however, SO_2 levels in the flue gases exiting the FGC system did vary somewhat; this variation was particularly marked during the end of the first week and the beginning of the second week. Compliance with the state requirement limiting maximum SO_2 emissions to 1.8 lb $SO_2/10^6$ Btu heat input (corresponding to emissions of about 800 ppm at 6% O_2) was readily achieved over the entire testing period.

Levels of SO_2 removal for the FGC system, calculated from the raw test data, are indicated in Figs. 4.9 and 4.10 for the entire testing period and for a single day, respectively. The SO_2 removals achieved in this testing period fluctuated between 60 and 80%, not only over the entire period, but also over a single-day span. As was pointed

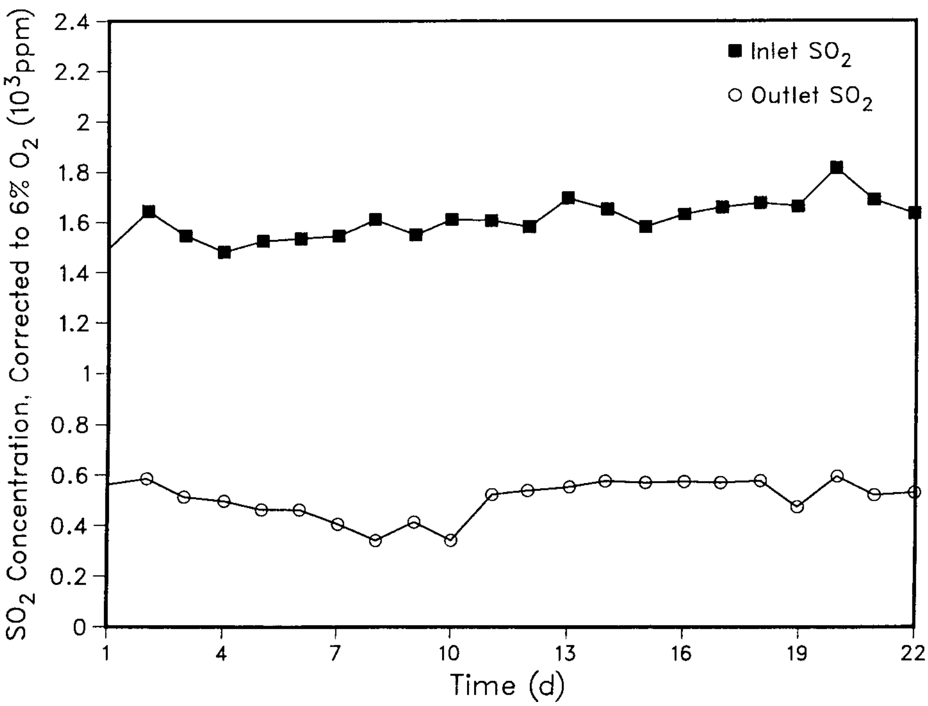


FIGURE 4.8 Baseline Sulfur Dioxide Levels (experiment initiated July 12, 1986)

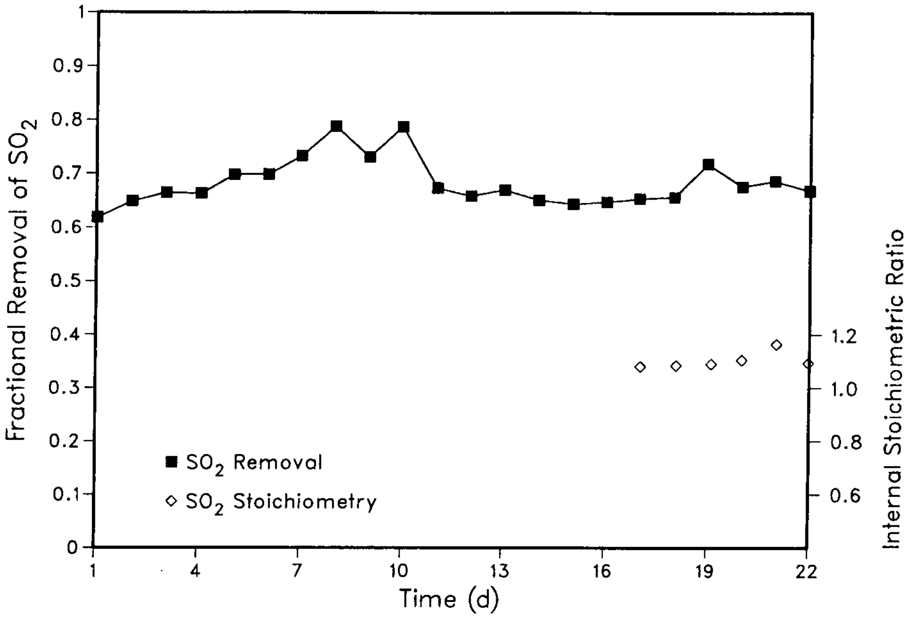


FIGURE 4.9 Baseline Sulfur Dioxide Removal (experiment initiated July 12, 1986)

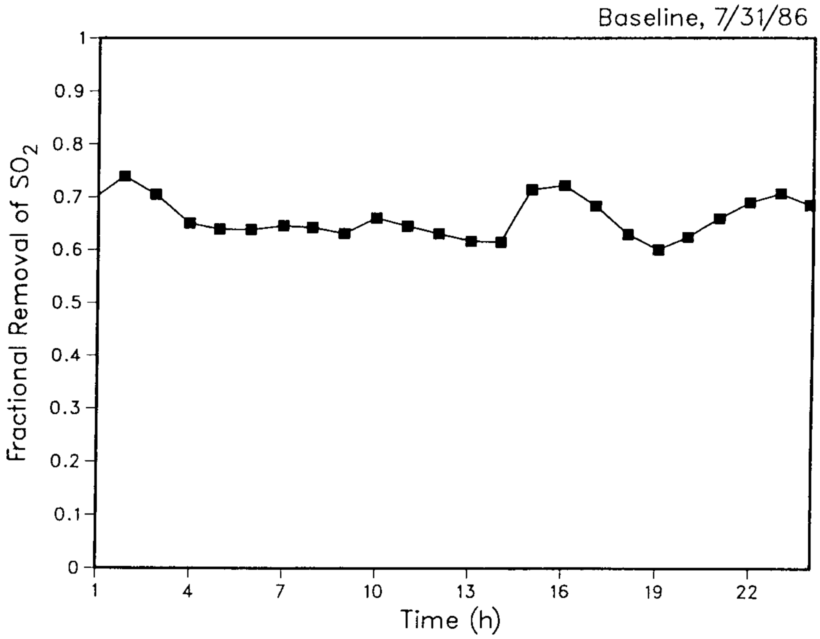


FIGURE 4.10 Hourly Sulfur Dioxide Removal

out above, the sulfur content of the coal fed into the stoker was later found to be 2.1 wt%, about 1 wt% lower than expected. With a heating value of about 11,800 Btu/lb for the coal, an SO_2 control level of greater than 51% would be needed to meet the maximum state emission requirement. (The normal SO_2 removal would be 60-70%.) Figure 4.9 shows that the state requirement was met in all of the days during the testing period. However, the fluctuations that characterize the curve in Fig. 4.10 suggest operating problems with the FGC system. Indeed, immediately after the caustic-addition tests of the following two weeks and before the restart of the system, the spray-dryer atomizer was found to be functioning poorly and was replaced with the standby unit to avoid formation of chunk aggregates inside the spray-dryer chamber.

Test results on overall pressure drop across the baghouse also reveal substantial fluctuations over the entire testing period (Fig. 4.11). The high SO_2-removal points shown in Fig. 4.9 correspond to the high baghouse pressure-drop points in Fig. 4.11. In a spray-dryer/fabric-filter FGC system, a significant amount of the SO_2 removal takes place on the filter cake: The greater the baghouse pressure drop (which implies a thicker filter cake), the greater will be the SO_2 removal, other operating parameters being the same. Of these operating parameters, the reagent-to-sulfur ratio and the approach of the flue gases to adiabatic saturation have been recognized as being the most influential for SO_2 removal. However, the dew-point temperatures of the flue gases were not monitored during the first two weeks of the characterization-test period. Also, collection and analysis of the solid and liquid process streams started only in the last week of this period. The reagent consumption during this last-week period is discussed below.

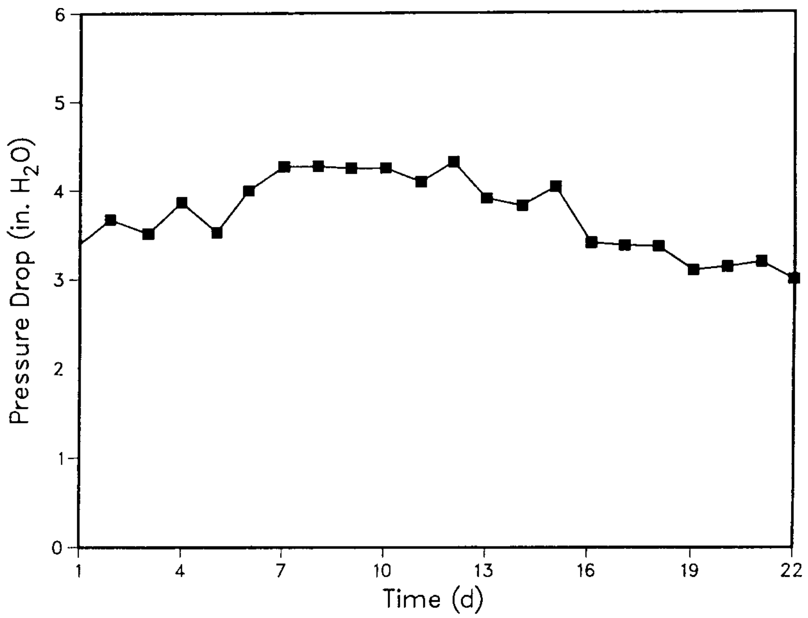


FIGURE 4.11 Baseline Baghouse Pressure Drop (experiment initiated July 12, 1986)

4.3 REAGENT CONSUMPTION AND UTILIZATION

Along with the capital investment required for an FGC system, the reagent consumption rate is among the most important considerations in selection of a system for control of gaseous emissions from combustion facilities. Collection of solid and liquid process streams started in the last week of the baseline characterization tests of ANL's spray-dryer FGC system. As can be seen in Fig. 4.9, the calculated internal stoichiometric ratio (SR) of calcium to sulfur ranges from 1.05 to 1.16, based on the analysis of the collected process stream samples. The internal SR is defined as the ratio of total alkali (fresh lime, recycled powder, and fly ash) to SO_2 (both in moles) in the flue gas entering the FGC system. This internal SR is related to the external SR, defined as the ratio of fresh lime to inlet SO_2 (again, both in moles), via the following equation:

$$SR(in) = SR(ex)[1 + RR \cdot RP(alkali)] \quad (4.1)$$

where RR is the recycle ratio, a measure of the amount of the recycled spent sorbent relative to the fresh lime feed, and RP(alkali) is the available alkali content in the recycled spent sorbent. Knowledge of the internal SR is needed to understand the extent of recycling, the sorbent utilization, and the reaction kinetics; knowledge of the external SR would help in determining the amount of sorbent to be purchased.

The external SR during the last week of the baseline tests was calculated to be 0.80-0.90. This range, in combination with the results for alkali content in the spent sorbent, indicates that the recycle ratio of spent materials to fresh lime feed was about 1.2 during the last week of the tests, which is consistent with (but somewhat lower than) the results previously obtained with high-sulfur coals. The results for the external SR, taken together with the results for SO_2 removal (Fig. 4.9), suggest that the extent of fresh sorbent utilization was about 80%.

4.4 SYSTEM OPERATION

The spray-dryer FGC system at ANL ran reasonably smoothly during the month in which the baseline characterization tests were carried out. The greatest single problem encountered was the lock-out of the conveyor at the bottom of the spray-dryer chamber during the second week of testing. This problem, which caused a system outage of about 17 h, was resolved by plant maintenance personnel. Also during this period, the conveyors connected to the spray-dryer chamber and the baghouse compartments had to be run manually every four to eight hours to prevent overflow of the collected solid materials.

Other, minor problems experienced included the following:

- The tripping of the atomizer by high vibration,
- A broken airline in the baghouse B damper,
- The hanging-up of the baghouse A damper after pulsing,

- A system bypass caused by a power surge,
- A one-time occurrence of high baghouse pressure drop caused by a plugged air line,
- Loss of service of the baghouse B air compressor caused by a deteriorating motor bearing,
- Vibration in the slaker motor,
- Low output in one of the slurry feed pumps, and
- Failure of the low-level alarm of the slurry mixing tank.

These problems were resolved in timely fashion by plant personnel without any unexpected system outages.

5 CAUSTIC-ADDITION TESTS

5.1 TEST PLAN

During 1985-1986, much of the ANL spray-dryer FGC work focused on the role of sodium-based additives in combined pollutant removal with lime-based systems. This line of research was spurred by initial data from Niro Atomizer[9] on the effect of caustic soda addition on combined NO_x/SO_x removal in a calcium-based spray-dryer, as well as by reports of brown plumes (NO_2) from a western utility operating a spray-dryer system that uses soda ash as the sorbent.[10] Initial efforts at ANL were aimed at confirming the Niro Atomizer data, ascertaining the proper conditions for a combined pollutant-removal process, and identifying the key reactions associated with combined removal. In order to accomplish this, a field testing program with a staged approach was implemented and carried out in August 1986. The field tests were designed for parametric study of the combined NO_x/SO_x-removal process at a scale sufficient to produce results that would be acceptable to industry. As conceived and executed, the ANL caustic soda field tests consisted of three tasks:

- Temperature ramp-up,
- 5% caustic addition, and
- 10% caustic addition.

Computerized data acquisition was used in all tasks to ensure completeness of data records and to aid in data reduction (see Table 5.1). Sampling and analysis of selected process streams (see Table 5.2) was used in the development of process material balances, as well as in the investigation of the overall reaction pathway.

5.1.1 Task I — Temperature Ramp-Up

During the first week of the test program, the outlet temperature from the spray dryer was increased in 20°F increments from approximately 150°F to a final temperature of about 210°F. There were two reasons for gradually ramping-up the spray-dryer outlet temperature. First, the ramp-up was needed in order to gather data on system operation with no addition of caustic soda at different spray-dryer outlet temperatures. This was especially important in differentiating the effects of caustic addition from those of high outlet temperature (i.e., the existence of the "temperature window"). Second, the ramp-up needed to be gradual to ensure that no unforeseen occurrences upset the system operation. All variables normally acquired by the data-acquisition system were logged into the computer, and the standard samples were taken.

5.1.2 Task II — Injection I

At the conclusion of Task I, the spray-dryer outlet was at the predesignated test temperature of 210°F, chosen on the basis of laboratory work by ANL and PETC. Once

TABLE 5.1 Process Parameters Monitored by Data-Acquisition System during Field Tests (August 1986)[a]

Temperature	Pressure
Spray-dryer inlet	Spray-dryer inlet
Spray-dryer outlet	Spray-dryer outlet
Baghouse outlet	Baghouse outlet
Stack	Baghouse differential
Baghouse outlet dry bulb	BH Comp. A tubesheet delP
Baghouse outlet dew point	BH Comp. B tubesheet delP
	BH Comp. C tubesheet delP
	BH Comp. D tubesheet delP
Gas composition[b]	**Flow rate**
SO_2 inlet (SDA)	Stack gas
SO_2 outlet(BH)	Steam production
CO_2 inlet (SDA)	Combustion air
CO_2 outlet (BH)	Lime to slurry mixing tank
NO inlet (SDA)	Slurry to spray dryer
NO outlet (BH)	Water to slurry mixing tank
NO_x inlet (SDA)	Water to slaker
NO_x outlet (BH)	
Boiler exit O_2	
Density	**Miscellaneous parameters**
Slurry density	Atomizer current
Milk-of-lime density	Milk-of-lime tank level
	Slurry mixing tank level

[a] SDA = spray-dryer absorber; BH = baghouse, with compartments A-D; TS = tubesheet; delP = differential pressure.

[b] The NO and NO_x levels at the spray-dryer exit were monitored, but the data were manually recorded.

this temperature was reached and the system stabilized (about 6-12 h), initial caustic injection commenced and continued for a period of two days.

During this task, the caustic-addition rate was 5% of the lime-slurry addition rate [as $Ca(OH)_2$] by weight (i.e., 5 wt%). Caustic soda was introduced into the slurry mixing tank, using a precision rotary pump, as a 50 wt% solution. This tank is well-mixed, and since it has a residence time of one hour, we considered additional mixing unnecessary.

TABLE 5.2 Process Samples and Analytical Chemistry Tests in Caustic-Addition Field Tests

Samples	Frequency	Analysis
Feed slurry	Daily[a]	% solids, % available alkali, % total alkalinity, specific gravity, % $SO_3^{=}$, % $SO_4^{=}$, % $CO_3^{=}$, % Na^+, % Ca^{++}, % S, % NO_2^-, % NO_3^-, % SiO_2
Recycled powder	Daily[a]	Same as feed slurry
Spray-dryer powder	Daily[a]	Same as feed slurry
Milk of lime	Weekly	Same as feed slurry
Coal	Weekly	Ultimate and proximate analysis
Caustic soda	Once per truck	% $CO_3^{=}$, % NaOH, % Cl^-

[a] Sample frequency was changed to once per shift during the ramp-up task.

5.1.3 Task III — Injection II

At the conclusion of Task II, the spray-dryer outlet remained at the predesignated test temperature. The caustic-addition rate was then increased to 10 wt% with respect to the lime-slurry addition rate [as $Ca(OH)_2$] for the duration of the test program.

Precautions were taken to ensure the accuracy of the data obtained during the field test. The gas analysis system (SO_2, NO, NO_x, and CO_2) was automatically calibrated in both zero and span every 12 h. Deviations from either zero or span were noted in the bound project notebook, and the appropriate analyzer was adjusted to correct the deviations. Instead of "normal" calibration gas, ANL installed tanks of EPA Protocol Calibration gases having accuracies within ±1% of NBS-traceable values.* As a further check on the accuracy of the gas analyzers, a continuous-emission-monitor (CEM) relative-accuracy test was performed on August 8, 1986, by Clean Air Engineering of

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*The National Bureau of Standards (NBS) is now the National Institute for Standards and Technology (NIST).

Palatine, Illinois (see App. B). The monitor certification was performed according to procedures outlined by the EPA.[13] These procedures include the following:

- *Method 3* -- "Gas Analysis for Carbon Dioxide, Oxygen, Excess Air, and Dry Molecular Weight"
- *Method 4* -- "Determination of Moisture Content in Stack Gases"
- *Method 6* -- "Determination of Sulfur Dioxide Emissions from Stationary Sources"
- *Method 7* -- "Determination of Nitrogen Oxide Emissions from Stationary Sources"

The test results indicated that the relative accuracy of the NO_x monitor was 2.8%, while that of the SO_x monitor was 5.3%.

5.1.4 Stoichiometry and Equivalence Ratio

The introduction of additives, some of which may also participate in the removal of sulfur and nitrogen oxides, into a lime-based spray-dryer system requires some redefinition of terms. For conventional wet and dry scrubbers, which remove only SO_2, the term "stoichiometry" (the ratio of the moles of active sorbent to the moles of SO_2 entering the system) is sufficient to describe one of the main driving forces. The introduction of an additional sorbent with a different valence state, together with the addition of NO_x as a pollutant being reacted, requires a definition that encompasses all of these factors. In discussing research involving combined NO_x/SO_x removal, the term "equivalence ratio" is used here. Equivalence is defined as "having the same chemical combining capacity." Two moles of sodium are the equivalent of one mole of calcium, and two moles of nitrogen oxides (NO or NO_2) are the equivalent of one mole of SO_2. Therefore, the equivalence ratio is defined as follows:

$$\frac{(\text{Moles of Available Ca}) + \tfrac{1}{2}(\text{Moles of Na})}{(\text{Moles of } SO_2) + \tfrac{1}{2}(\text{Moles of } NO_x)}$$

This quantity is used in place of stoichiometry in order to better express the role of the chemical driving forces in the combined removal of NO_x and SO_x, as opposed to the physical factors (such as temperature or filter-cake thickness).

In addition, the use of recycling requires that the stoichiometry (or equivalence ratio) be specified as internal or external. The external stoichiometry is simply the molar ratio of fresh sorbent to pollutants at the inlet to the system, whereas the internal stoichiometry also includes the available alkali in the recycled material and, in some cases, in the incoming fly ash as well. This internal stoichiometry (or equivalence ratio), corresponding to the total amount of available alkali entering the spray dryer, is the actual driving force for the removal of pollutants. The external stoichiometry, a valuable guide to system economics (because it indicates the amount of fresh sorbent that must be purchased), is generally equal to the internal stoichiometry (excluding alkali in the fly ash) when straight-through systems are used.

5.2 EFFECTS OF TEMPERATURE

Normal operation of the spray-dryer/fabric-filter system involves outlet temperatures from the spray dryer that are 20-40°F from the adiabatic saturation temperature. Normally, under these conditions, no noticeable removal of NO_x from flue gases being treated by a lime-based spray dryer takes place. Sulfur dioxide removal has, of course, been shown to be directly affected by the approach temperature to adiabatic saturation.[13] In the case of SO_2, as the outlet temperature from the spray dryer decreases and the approach to saturation concurrently decreases, the SO_2 removal increases at constant stoichiometry (Ca-to-S molar ratio). For effective removal of NO_x from flue gases, combined with SO_x removal, the temperature dependence appears to vary inversely.

At the beginning of the caustic-addition field tests, we increased the exit temperature of the spray dryer in 20°F increments. At each temperature "step," the system was operated for two days to permit it to attain steady-state operation. During each of these two-day periods, ANL continued to take data and process samples for analysis. The purpose of this portion of the field test was to determine the degree of dependence of NO_x removal on the temperature of flue gases exiting the spray dryer. Especially important was the ability to separate any NO_x removal that might have occurred strictly as a consequence of the flue-gas temperature from removals attributable to the addition of caustic soda to the lime.

In addition to studying the removal of NO_x from flue gases, the ANL field test also permitted observation of changes in SO_x removal. System performance was found to vary with the spray-dryer outlet temperature (as observed many times by previous researchers in this field) and with the addition of caustic soda to the lime sorbent. At a spray-dryer outlet temperature of 150°F, the ANL system removed 70% of the incoming SO_2 at an internal equivalence ratio of 1.02. When the outlet temperature was raised to 190°F, the removal decreased to 58%, while the internal equivalence ratio rose to 1.10. At 210°F, prior to the start of caustic soda addition, an increase in the internal equivalence ratio to 1.30 resulted in only a minor increase in the SO_2 removal (to 61%).

At the onset of caustic soda addition (at a rate of 5 wt% of the lime being added), the external stoichiometry decreased to 0.74, while the internal equivalence ratio increased only slightly and removal of SO_x from the flue gases showed little change. When the rate of caustic soda addition was increased to 10 wt%, the external stoichiometry decreased by an average of 8% (even though the internal equivalence ratio increased slightly at the same level of SO_2 removal). Of course, at the time the temperature was raised to 190°F at the spray-dryer exit, substantial quantities of NO_x began to be removed. This removal was enhanced by the addition of the caustic soda to the slurry feed.

As the spray-dryer outlet temperature was increased from 150 to 170°F, no noticeable change in NO_x removal or overall gas composition was observed. Analysis of the recycled powder produced at 150°F indicated an average of 200 ppm each of nitrates and nitrites (Fig. 5.1). This amount of nitrates and nitrites suggests that some NO_x removal had been occurring during normal operation; more important, it provides a "baseline" value that can be used to evaluate system operations at different temperatures. As the spray-dryer outlet temperature was increased to 190°F, some changes in system operation were observed. The NO_2 concentration in the boiler exit remained at approximately the same level, but the outlet NO_2 emissions increased (Fig. 5.2). This increase continued as the exit temperature of the spray dryer was increased to 210°F. (At the time that this increase in net NO_2 emissions was observed, no caustic soda had been added to the system.) Chemical analysis of the recycled powder has shown (Fig. 5.1) that the nitrate and nitrite levels increased at the same time that the increase in the exit NO_2 concentration was observed. The increase in the concentration of nitrates in the recycled powder was much greater than the increase in nitrites.

Analysis of the data has uncovered an apparent increase in flue-gas temperature during certain parts of the test. This temperature increase (on the order of 5 to 10°F, although it was not a consistent phenomenon) did not become evident until the spray-dryer outlet temperature had reached 190°F. This is the same temperature at which we began to observe the net production of NO_2, the substantial removal of NO_x, and the concurrent buildup of nitrates and nitrites in the waste materials.

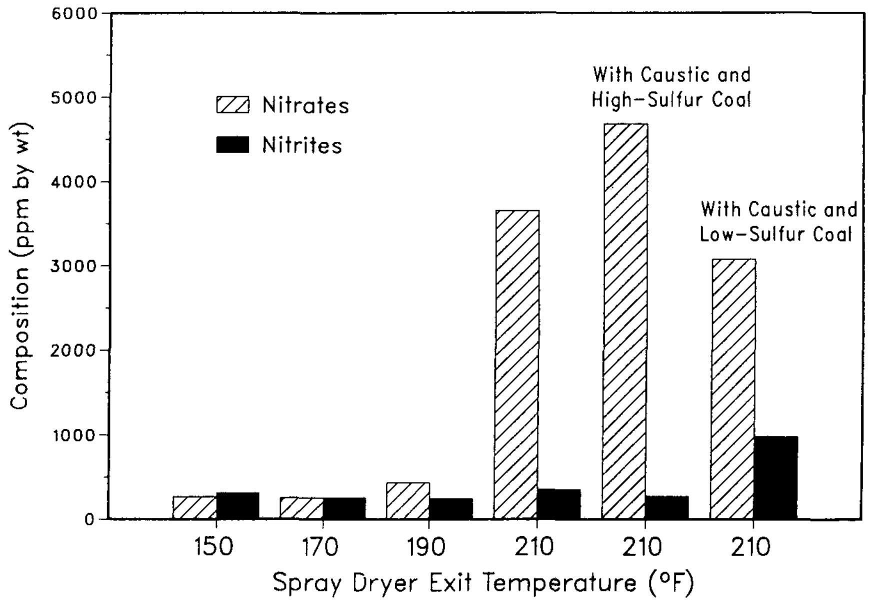

FIGURE 5.1 Nitrates and Nitrites in Recycled Powder

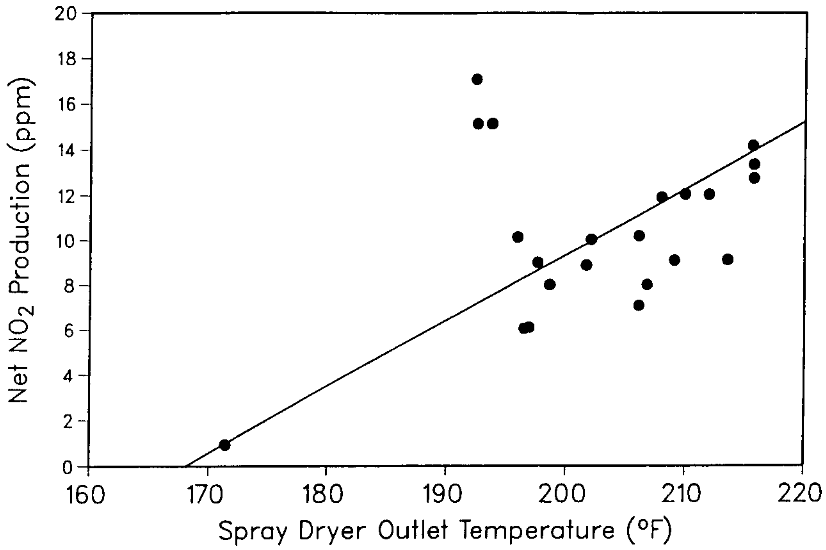

FIGURE 5.2 Net Increase in Nitrogen Dioxide Emissions with Temperature

5.3 EFFECTS OF CAUSTIC ADDITION

5.3.1 Sulfur Dioxide Removal

The field test demonstrated some effect of caustic addition on SO_2 removal. At the beginning of caustic addition (5 wt%), a 17% decrease in the external stoichiometry was observed at a constant level of SO_2 removal. A simple chemical contribution by the sodium to the SO_2-removal level would be insufficient to account for this decrease in the external stoichiometry. The ANL FGC system uses the outlet SO_2 concentration (in lb/10^6 Btu) as its main control over emissions. Should the SO_2 emissions being monitored in the stack start to decrease, the control system automatically decreases the amount of lime fed to the slurry mixing tank. Consequently, with the control system in operation (as is necessary to ensure compliance with State of Illinois standards), it was difficult to precisely determine the effect of caustic addition on SO_2 removal.

5.3.2 Filter-Cake Porosity

The most noticeable effect of caustic soda addition was the increase in filter-cake porosity, which became significant at a spray-dryer outlet temperature of 190°F. This increase in porosity evidenced itself by increased times between cleaning of the filters (about 2 h at 190°F and 3 h at 210°F; see Fig. 5.3). Following caustic soda addition at the 5 wt% level, the time between cleaning of filters increased to 6 h (Fig. 5.4), and then to 8 h when the caustic addition was increased to 10 wt%. An analysis of the particles composing the filter cakes indicated that part of the reason for this increased cake porosity was a change in the surface area of the cake material. The particles produced in the spray dryer at an exit temperature of 210°F prior to caustic

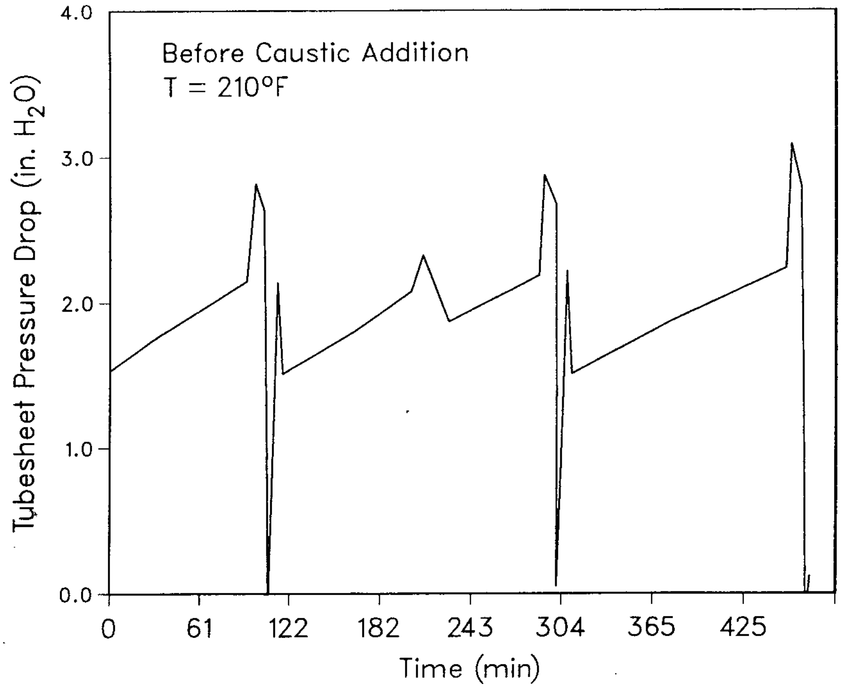

FIGURE 5.3 Pressure Drop vs. Time before Caustic Addition (Compartment B)

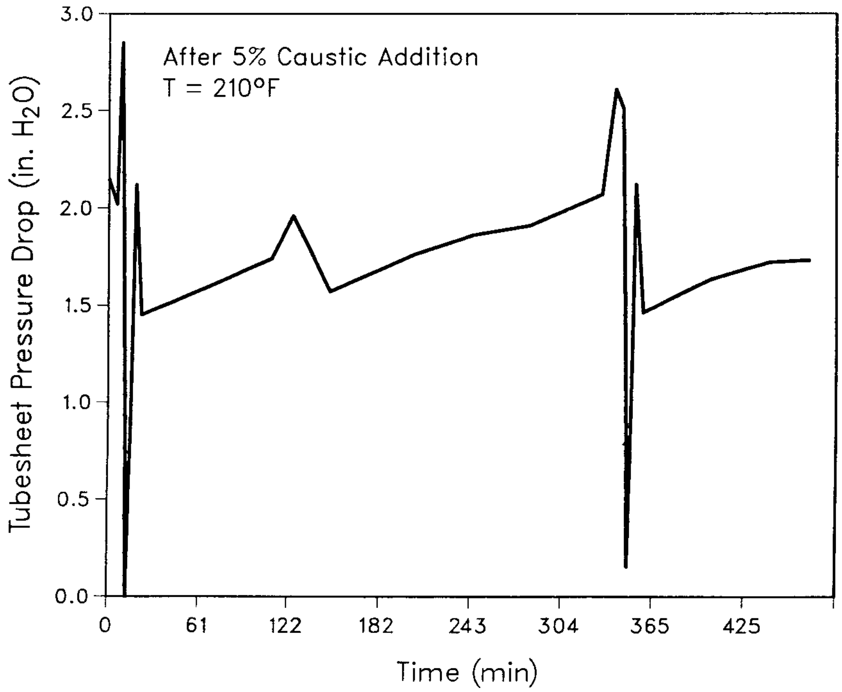

FIGURE 5.4 Pressure Drop vs. Time after Caustic Addition (Compartment B)

addition had a surface area of 20 m^2/g, whereas after 5 wt% caustic soda addition the surface area increased to 24 m^2/g. While the surface area increased, baghouse surface moisture (see Table 5.4) remained less than 1%.

5.3.3 Nitrogen Oxides Removal

With addition of caustic soda to the feed slurry (at 5 wt% caustic with respect to fresh lime), an increase in NO_x removal from the flue gas was observed. Readings from the NO_x analyzer (TECO Model 10) installed between the spray dryer and the fabric filter, when compared with the analysis of the flue gas entering the spray dryer and exiting the stack, indicated that the removal occurred predominantly within the fabric filter. Table 5.3 shows the NO levels at three critical points in the system (spray-dryer inlet, spray-dryer outlet, and stack). Table 5.4 shows, for the same period, the removal of NO between these points, the spray-dryer exit temperature, and whether caustic soda was added to the system.

TABLE 5.3 Nitric Oxide Levels in Argonne Spray-Dryer System (ppm, by volume)[a]

Date[b]	NO SDA, In	NO SDA, Out	NO Stack, Out
04	286	281	272
	292	285	282
05	274	253	259
	304	266	287
06	317	285	298
	306	282	285
07	297	272	281
	286	282	273
08	289	311	263
	326	283	266
09	280	286	220
	281	278	209
10	275	275	205
	278	291	213
11	277	293	195
	271	225	198
12	297	218	222
	293	301	224
13	280	273	188
	292	280	201
	299	295	218
14	280	281	206
	275	262	222
	281	278	207
15	287	295	221
	291	280	223
	290	268	220
16	293	304	226
	312	314	252
	313	324	262
17	356	355	319
	319	312	276
	307	303	272
18	325	325	294

[a] All NO levels are corrected for air inleakage and adjusted to 6% oxygen.

[b] All dates refer to August 1986.

TABLE 5.4 Nitric Oxide Removals by System Component

Date[a]	Spray-Dryer Outlet Temp. (°F)	Caustic Addition (wt%)	Coal Sulfur	Removal (%)			Moisture Content of Spent Sorbent (%)
				Across SDA	Across BH	Across System	
04	150	0	High	2	3	5	1.6
				2	1	3	
05	150	0	High	8	-2	5	1.5
				13	-8	6	
06	170	0	High	10	-4	6	1.9
				8	-1	7	
07	170	0	High	8	-3	5	1.7
				2	3	5	
08	190	0	High	-8	15	9	1.5
				13	6	18	
09	190	0	High	-2	23	21	1.4
				1	25	26	
10	210	0	High	0	25	25	1.4
				-5	27	23	
11	210	0	High	-6	33	29	1.2
				17	12	27	
12	210	5	High	27	-2	25	1.2
				-3	26	24	
13	210	5	High	2	31	33	1.2[b]
				4	28	31	
				1	26	27	
14	210	10	High	-0	27	27	1.2
				5	15	19	
				1	26	26	
15	210	10	High	-3	25	23	0.9
				4	20	24	
				8	18	24	
16	210	10	Medium	-4	26	23	1.4
				-1	20	19	
				-4	19	16	

TABLE 5.4 (Cont'd)

Date[a]	Spray-Dryer Outlet Temp. (°F)	Caustic Addition (wt%)	Coal Sulfur	Removal (%) Across SDA	Across BH	Across System	Moisture Content of Spent Sorbent (%)
17	210	10	Low	0	10	10	1.5
				2	11	13	
				1	10	11	
18	210	10	Low	0	9	9	1.6

[a] All dates refer to August 1986.

[b] The moisture content of materials from the baghouse was 0.5%.

5.4 EFFECTS OF RATIO OF SULFUR OXIDES TO NITROGEN OXIDES

On the basis of the ANL field tests, the relationship between successful NO_x removal from flue gas and the SO_x/NO_x ratio appears very strong. At the set operating temperature of 210°F, both with and without the addition of caustic soda to the lime, NO_x removals up to 47% and NO removals up to 54% were observed. These levels were attained with the combustion of a high-sulfur coal in the boiler and resultant SO_x/NO_x ratios of 5-6:1.

During the 10% caustic soda addition (Task III), it became necessary for the power-plant staff to switch over to the firing of a low-sulfur eastern coal in place of the high-sulfur Illinois Basin coal normally burned. Although this change appeared at first to be a serious deviation from the original test plan, it was eventually recognized as presenting a unique opportunity. This opportunity was the chance to study the performance of a combined NO_x/SO_x dry scrubbing system over SO_x/NO_x ratios ranging from 2 to 6:1. Figure 5.5 shows the effect of the SO_x/NO_x ratio on the removal of NO and NO_x. The NO_x removal is rather low (3-7%) at a SO_x/NO_x ratio of 2:1. As the SO_x/NO_x ratio increases, the removal follows the same trend, increasing to 15-20% at a SO_x/NO_x ratio of 6:1.

With the caustic addition continued and the spray-dryer outlet temperature maintained at 210°F, the dependence of NO_x removal on the SO_x/NO_x ratio was very strong. Toward the end of the field test, the inlet concentration of sulfur oxides decreased to 400 ppm, the inlet NO_x concentration being approximately 250-280 ppm (i.e., SO_x/NO_x = 1.4-1.6:1). Although the removal of SO_x was close to 100% (in order to minimize the number of variables during this part of the field test, no change was

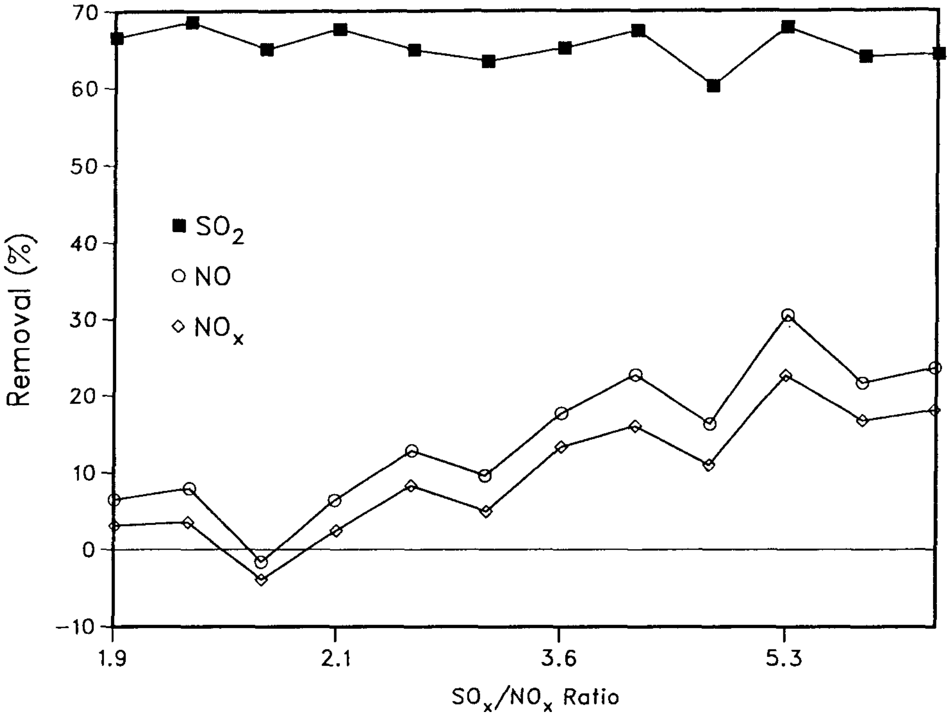

FIGURE 5.5 Removal of Nitric Oxide, Nitrogen Oxides, and Sulfur Dioxide at 205-210°F

made in the fresh lime flow rate), the NO_x removal decreased almost to zero. This situation persisted despite the continued high porosity of the filter cake (and hence, high cake thickness), which had been observed to have a significant effect on NO_x removal with high-sulfur coals.

5.5 EFFECTS OF FABRIC FILTRATION

5.5.1 Variation of Cake Porosity with Temperature and Caustic Soda Addition

Another phenomenon encountered as the temperature from the spray dryer was increased was an increase in cake porosity, which we believe is connected with the net production of NO_2. Under normal operating conditions, the baghouse at ANL goes through a cleaning cycle approximately every 1.5 h. At a spray-dryer outlet temperature of 210°F, the time between cleaning cycles prior to caustic addition was 3 h (Fig. 5.3) for the same pressure-drop setpoint . After caustic addition was started, the time between cleaning cycles increased to 6 h. Even discounting any decrease in cake density, it is clear that the cake thickness after caustic addition must have been at least four times as great as that under normal conditions.

5.5.2 Nitrogen Oxides Removal

During the 6-h period in which cake accumulated on the filter bags, we also observed increases in both NO and NO_2 removal (see Fig. 5.6). The removals ranged from 42 to 53% for NO and from 37 to 47% for NO_x, the difference between these values being the net production of NO_2. The build-up in filter-cake thickness is essentially an increase in the amount of available alkali that an NO_x "molecule" can contact and react with while it is in the baghouse; thus, any increase in this amount will produce an increase in NO_x removal, all other conditions being the same.

At this point, some explanation is needed for the differences in NO_x removal indicated in Figs. 5.5 and 5.6. The data in Fig. 5.5 represent the NO and NO_x removal on an 8-h-average basis, whereas the data in Fig. 5.6 represent a 10-min rolling average. The 8-h-average data include not only the period during which the filter cake was being built up on the filter, but also the periods before and after this build-up, which encompass the cleaning of the bags as well. We believe the thickness of the filter cake plays a key roll in the removal of NO_x from flue gases. Consequently, the removal of NO_x (and SO_x) is much lower when there is little or no filter cake on the bags.

During the cleaning cycle, the compartment being cleaned is isolated from the gas stream (off-line cleaning), so that the gas velocity through the remaining

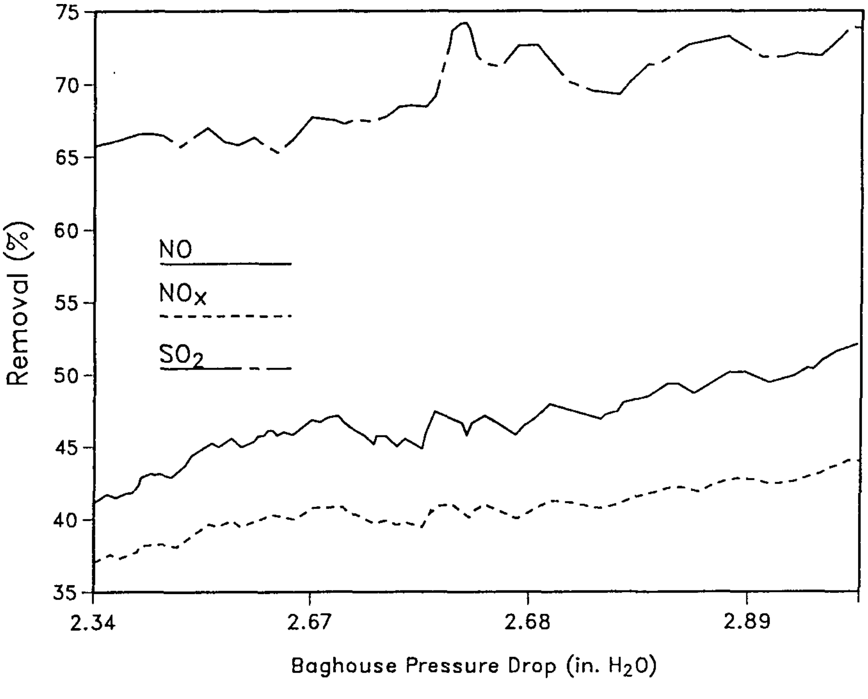

FIGURE 5.6 Removal of Nitric Oxide and Nitrogen Oxides vs. Baghouse Pressure Drop

compartments is increased by about 33%. This decreases the residence time of the flue gas through the remaining filter cake, further lessening NO_x removal.

In commercial practice, it would be necessary to operate the fabric filter with as thick a filter cake (as high a pressure drop) as possible in order to achieve significant NO_x removal. It will probably be necessary for fabric-filter manufacturers to redesign their equipment in order to maximize filter-cake retention.

5.5.3 Sulfur Dioxide Removal

During the extended (6-h) period between bag cleanings noted above, steadily increasing removal of SO_2 was also observed, as shown in Fig. 5.6. This increase was somewhat expected due to the increased availability of unused alkali in the filter cake to react with SO_2 as the thickness of the filter cake increased with time. Under normal operating conditions, it had been found that SO_2 removal across the baghouse filter was about 15 to 20% of the total SO_2 going into the system. The observed increase in SO_2 removal (about 8%) during cake build-up on the fabric filter is relatively substantial (40-50%), even though it is small compared with total SO_2 removal.

5.6 PROCESS STREAM COMPOSITIONS AND VARIATION WITH TEMPERATURE

5.6.1 Available Alkali

The performance of the spray-dryer/fabric-filter FGC system has been well established with respect to SO_2 removal. As the spray-dryer outlet temperature is raised (an increase of the approach to adiabatic saturation temperature), the performance at a given stoichiometry declines. This is caused primarily by the more rapid drying of the slurry droplets, resulting in the shorter duration of the gas-liquid interface. Accordingly, at a fixed emissions limit (which means, for steady-state operation, a relatively fixed level of removal), it would be expected that the internal stoichiometry would increase with increasing spray-dryer outlet temperature.

5.6.2 Sulfite-to-Sulfate Ratio

Under normal operating conditions, the ratio of sulfites to sulfates in the waste material (recycled powder) produced by the ANL high-sulfur dry-scrubbing system is approximately 6:1 (see Fig. 5.7). Sulfites predominate over sulfates because the droplets produced during the atomization process take an estimated 4-5 s to dry; during this drying period, some oxidation of sulfites to sulfates takes place, but not to the extent seen in wet scrubbing systems (where the particles are never really dry).

As the spray-dryer outlet temperature is raised, the drying time for the droplets decreases. It would be expected that the amount of sulfates produced by the system

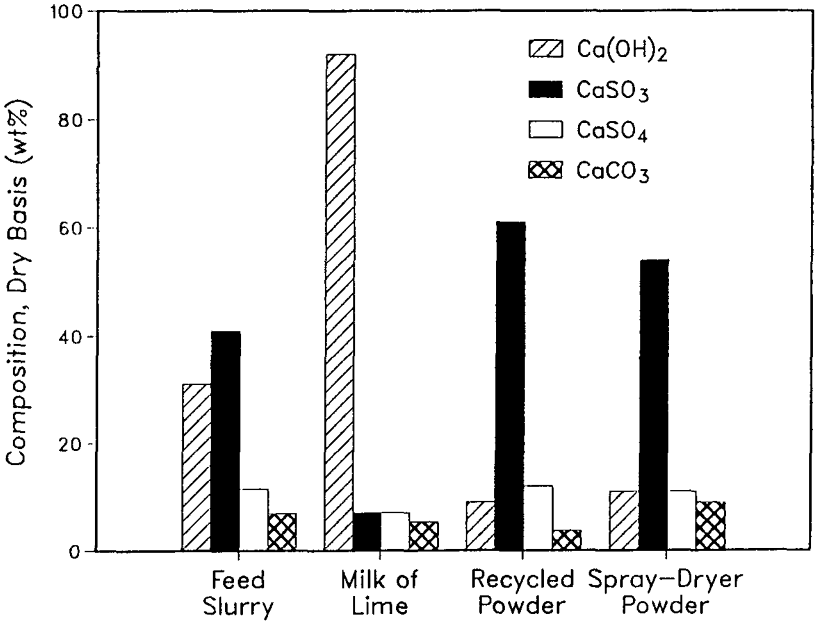

FIGURE 5.7 Composition of Process Streams at 150-170°F

would decrease with the drying time. The composition of the process streams at 190°F (see Fig. 5.8), however, showed evidence of increased oxidation of sulfites to sulfates. At this temperature, the ratio of sulfites to sulfates in the recycled powder decreased, from 6:1 down to about 5:1. Similarly, the sulfite-to-sulfate ratio of the powder produced in the spray dryer decreased from a ratio of 5:1 at 150°F down to 4:1 at 190°F.

The oxidation of sulfites to sulfates continued as the temperature from the spray dryer increased to 210°F (see Fig. 5.9). At this temperature, the ratio of sulfites to sulfates decreased in both the spray powder and the recycled powder (seemingly with no chemical relation to the addition of caustic soda) to a ratio of about 3:1. In addition to being unaffected (chemically) by the addition of caustic soda, the oxidation of sulfites to sulfates appears not to have been a function of the sulfur content of the inlet gas stream. This is indicated by the results of chemical analysis of process streams (see Fig. 5.10); at an average SO_2 inlet rate into the spray dryer of 400 ppm, the recycled powder had a sulfite-to-sulfate ratio of 1:1. Under these conditions, the powder produced in the spray dryer had a sulfite-to-sulfate ratio of about 1.1:1.

The analysis of a sample of powder obtained from the baghouse fabric filter showed that the effect of oxidation in the baghouse (at a spray-dryer outlet temperature of 210°F) was much greater than the average oxidation for the system (including that in the spray dryer). In the baghouse, the sulfates overtook the sulfites, resulting in a ratio of sulfates to sulfites in the powder of almost 9:1.

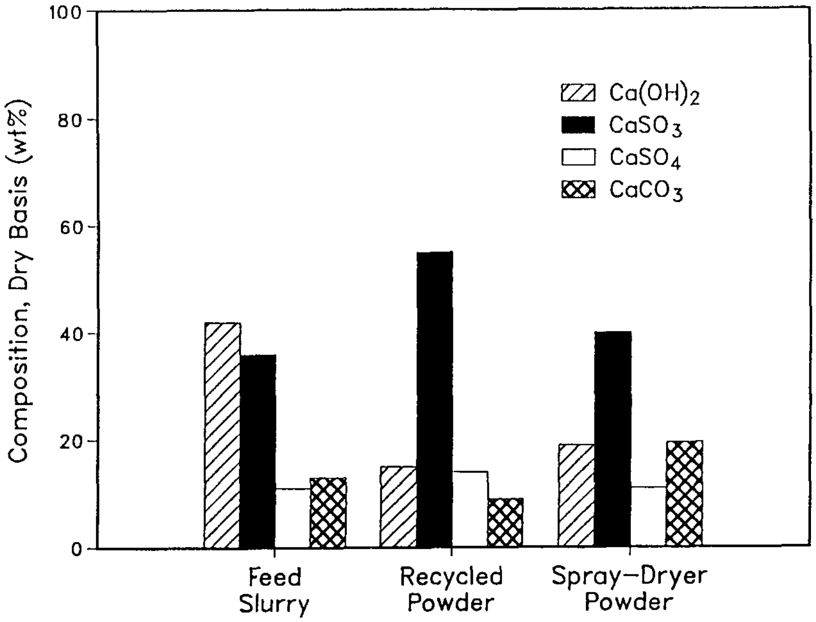

FIGURE 5.8 Composition of Process Streams at 190°F

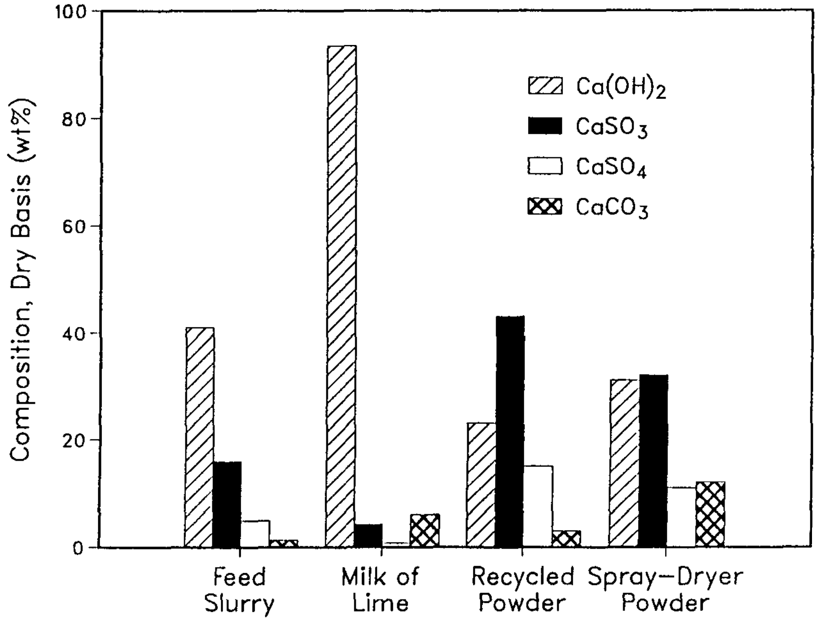

FIGURE 5.9 Composition of Process Streams at 210°F

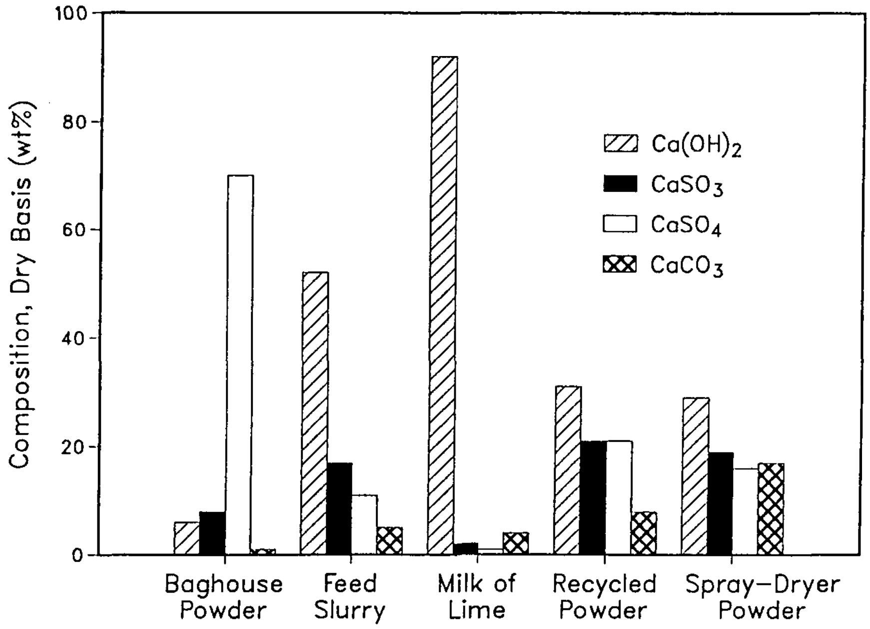

FIGURE 5.10 Composition of Process Streams, Low-Sulfur Coal

5.6.3 Nitrite and Nitrate Levels

Typical nitrite and nitrate levels in recycled powder samples collected during the field testing are shown in Fig. 5.1. At temperatures below 170°F, very low levels of nitrites and nitrates (less than 200 ppm) were detected in the samples, suggesting that only a minute amount of NO_x removal had been occurring under these conditions. As the spray-dryer temperature was increased to 190°F, the nitrate level in the recycled powder almost doubled, while the nitrite level remained about the same. In concert with the increase in gas-phase NO_x removal, the nitrate level in the powders also increased as the temperature was further increased to 210°F and with the addition of caustic soda. However, the nitrite levels in the recycled powders remained fairly constant when high-sulfur coal was burned. The nitrate-to-nitrite ratios ranged between about 10:1 and 20:1 with high-sulfur coal.

In contrast, the nitrite level in the recycled powder was substantially higher when low-sulfur coal was burned; the nitrate-to-nitrite ratio was about 3:1. This phenomenon suggests that the SO_2 concentration in the flue gas affects not only the level of NO_x removal, but also the form of the reaction product. This phenomenon remains to be further investigated in future experiments.

5.7 SPENT-SORBENT CHARACTERISTICS

5.7.1 Particle Size

Recycled and baghouse powder samples acquired during the field tests have been subjected to both visual (visible-light and scanning-electron microscopes) and analytical examination. The results are shown in Figs. 5.11-5.14 and in Table 5.5.

Figure 5.14 shows that the median volumetric (mass) particle diameter for all the powders produced was about 28 μm. This was to be expected, because the degree of atomization was not greatly affected by variations in the amount of slurry fed to the rotary atomizer. Other factors that would control the median droplet size produced by a rotary atomizer, such as the wheel's diameter (210 mm), the wheel's angular velocity (14,000 rpm), or the number and diameter of openings of the nozzles (six, each 1 cm in diameter) were not varied during the field test.

5.7.2 Surface Area and Pore Size

Table 5.5 indicates that an increase in the overall surface areas of the particles produced occurred both during the ramp-up of the spray-dryer outlet temperature and

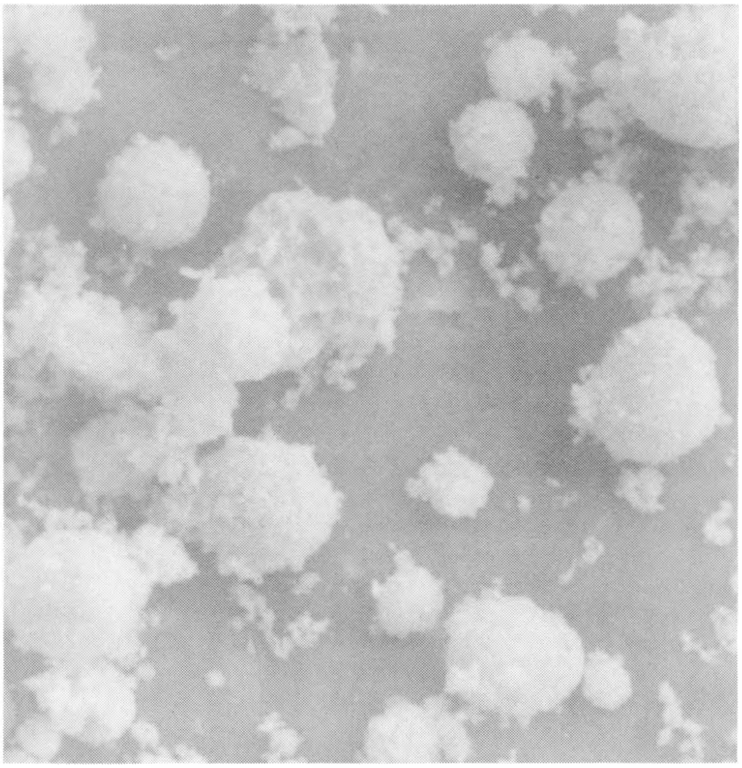

FIGURE 5.11 Scanning Electron Microscope Photograph of Recycled Powder Produced at 150°F (600X magnification)

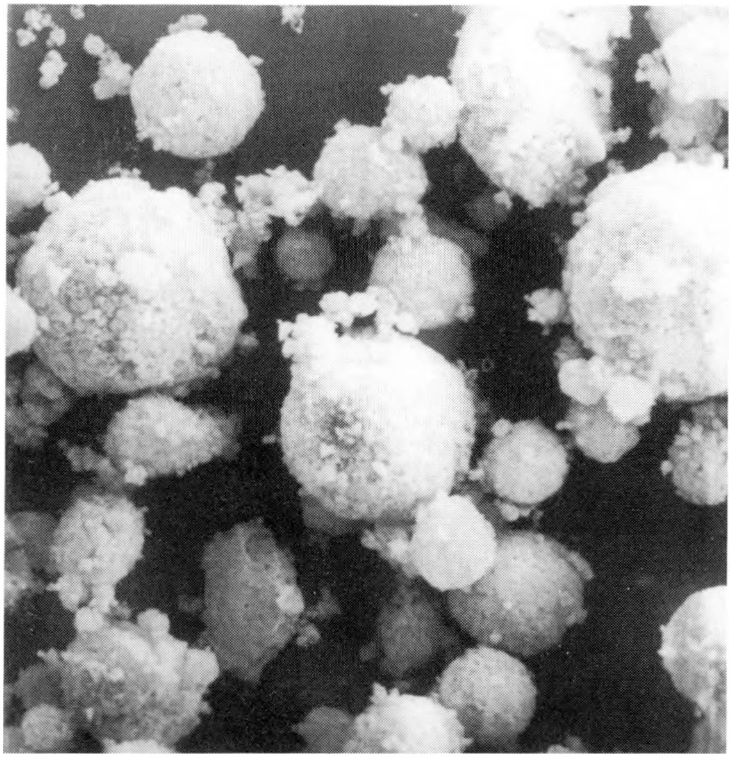

FIGURE 5.12 Scanning Electron Microscope Photograph of Recycled Powder Produced at 210°F (600X magnification)

during the caustic addition. One effect of a different type of particle being produced at the elevated temperatures, both with and without the addition of additives, was a much more porous filter cake. The increase in filter-cake porosity has been such that the times between fabric-filter cleanings increased by a factor of 4-5. Consequently, the mass of powder on the bags at the time of cleaning has been calculated to be three times that normally found at 150°F. Table 5.5 also indicates a decrease in the arithmetic median pore diameter, from 0.42 μm to approximately 0.05 μm. This change indicates the proliferation of a large number of "micropores," which is somewhat confirmed by the slight decrease in the volumetric median pore diameter.

A well-operated slaker produces lime particles that are 1-3 μm in diameter. These particles make up part of the slurry used in the spray-dryer/fabric-filter system, the remainder of the solids being some fly ash and a great deal of recycled powder produced in the spray dryer. Consequently, the 25-50 μm particles produced in the spray dryer are made up of many much smaller individual particles. We suggest that one reason for the increased surface area of the particles, as well as the large number of submicron-sized pores, is the rapid drying of the droplets in the spray dryer. In normal spray-dryer FGC operations, the outlet gas temperature of the spray dryer is 20-30°F above the adiabatic saturation temperature. At this temperature, the droplets take 4-6 s to dry to a fine powder. During this "slow" drying process, the lime in solution with the

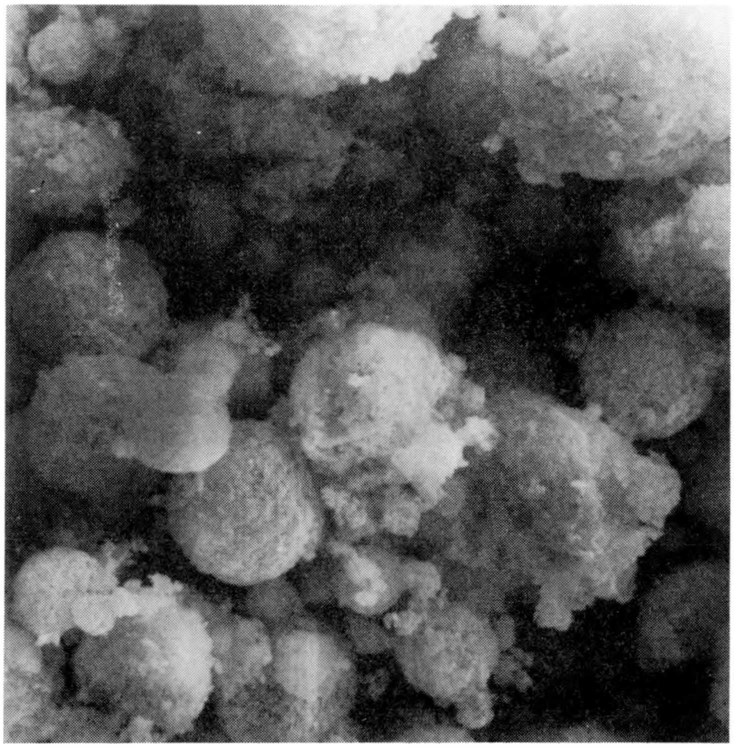

FIGURE 5.13 **Scanning Electron Microscope Photograph of Recycled Powder Produced at 210°F, 5% Caustic Soda Addition (600X magnification)**

droplet reacts with SO_2 to form calcium sulfite. As the calcium sulfite forms and precipitates out, more calcium hydroxide is forced out of the drying particle and into solution to maintain equilibrium. The slowly precipitating calcium sulfite gradually forms a shell around the small individual particles making up the solids in the droplet. As this shell is formed (in much the same way that a shell of calcium compounds is formed around a particle in a fluidized-bed combustor), it reduces the surface area of the final particle, "cementing over" many of the micropores in the individual lime particles and those formed between adjoining particles.

When the outlet temperature of the spray dryer is near the boiling point of water (190-210°F), the slurry droplets dry very rapidly. In this rapid drying mode, the calcium salts that are formed have no time to plate out over the individual small particles. Instead, cementatious actions tend to bind these small particles together into approximately the same particle size as before, although a small reduction in the mean particle size was measured (27.5 μm at 210°F vs. 28.5 μm at 150°F). This rapid drying and prevention of shell formation over the entire particle results in an increase in surface area, as well as a proliferation of the small micropores that had been previously covered over. This increased surface area of the individual particles, coupled with the lower drag of the particles (and, consequently, an ability to build up thicker filter cakes over the same pressure drop), is the main reason for the enhancement in NO_x removal.

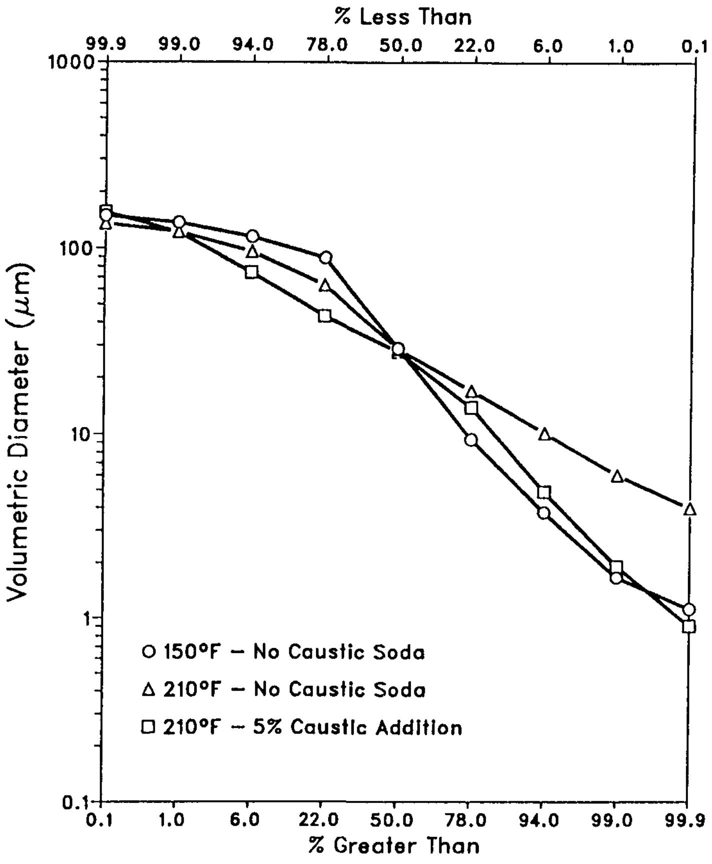

FIGURE 5.14 Particle Size Distributions of Recycled Powders Produced during Field Test with Caustic Soda Addition

TABLE 5.5 Characteristics of Recycled Powders Produced during Caustic Soda Addition in Field Tests

Sample No.	BET[a] Area (m^2/g)	Mercury Porosimeter (m^2/g)	Pore Diameter (μm)		
			Average	Volumetric Median	Arithmetic Median
RP-08056	14.6	15.9	0.32	3.44	0.42
RP-08116	13.0	20.2	0.24	4.47	0.04
RP-08136	20.2	24.4	0.24	4.13	0.06
BP-08136	16.5	26.5	0.20	7.83	0.03

[a] Brunauer, Emmett, and Teller equation of state for gas adsorption (Ref. 14).

Increased surface area also accounts for the increase in SO_2 removal reported by Niro Atomizer in some earlier caustic-addition tests. Niro reported a decrease in SO_2-removal performance as the spray-dryer outlet temperature was raised; this was followed by a sudden increase in removal as the spray dryer was operated at 210-220°F.[15] It is now clear that this increase in SO_2 removal was due almost entirely to the increase in surface area of the particles and the ability to develop relatively thick filter cakes.

5.8 POSSIBLE REACTION MECHANISMS FOR COMBINED NO_x/SO_x REMOVAL

5.8.1 Effects Observed

Many of the results from the data-acquisition effort and the chemical analysis of process streams point toward the development of potential reaction mechanisms. Some of the observations have been as follows:

- There was a net production of NO_2 during NO_x removal.
- The level of nitrates formed in the waste material increased, whereas the nitrite levels remained relatively constant.
- The balance of sulfur compounds in the waste material shifted from being predominantly calcium sulfite toward greater amounts of calcium sulfate.
- Increased removal of NO_x was proportional to the build-up of cake on the filter bags, with a subsequent loss of removal efficiency after the filters had been cleaned.
- The removal of nitrogen oxides declined (albeit with no net reduction in the production of NO_2) when flue gas with a low concentration of SO_2 was being treated by the system. This lack of NO_x removal was observed even though the concurrent SO_2 removal was well over 95%.

5.8.2 Material-Balance Results

Calculated material-balance results for the transfer of sulfur and nitrogen compounds from the gas phase to the solid phase are presented in Table 5.6. The calculations were based on information about flue-gas flow rates and SO_2, NO, and NO_x compositions in the flue gases at the system inlet and outlet; slurry feed rates; and sulfate, sulfite, total sulfur, nitrite, nitrate, and calcium contents in both the slurry feeds and the recycled powders collected during this period.

The flow rates of the solid materials from the spray-dryer bottom, the baghouse bottom (and hence, the total solid materials collected, both recycled powder and disposal

TABLE 5.6 Calculated Material-Balance Results

Date[a]	SO_2 Conc. (ppm)	SO_2 Removal (%)	Sulfur Balance[b]	NO_x Conc. (ppm)	NO_x Removal (%)	Nitrogen Balance[b]
10	1306	61	0.83	263	14	0.11
11	1251	58	0.98	227	16	0.32
12	1209	59	1.07	225	18	0.43
13	1218	66	0.83	234	15	0.54
14	1297	62	0.70	234	18	0.28
15	1327	62	0.71	247	15	0.22
16	1065	65	0.63	253	13	0.27
17	911	66	0.96	255	13	0.16

[a] All dates refer to August 1986.

[b] The ratio of sulfur and nitrogen gains in the solid phase to sulfur and nitrogen losses in the gas phase.

materials), and the fly-ash loadings in the flue gases entering the FGC system could not be monitored accurately and continuously. Therefore, the flow rates of the total solid materials collected were derived from the solids content in the slurry feeds and the calcium content in the two process streams, on the assumption that the fly ashes in the boiler flue gases contained no significant amount of calcium. In addition, due to occasionally erroneous readings of the magnetic flowmeter, the flow rates of the slurry feeds had to be checked and adjusted with respect to flow-rate readings for the milk-of-lime and water additions to the slurry mixing tank.

As shown in Table 5.6, the sulfur balance appears satisfactory at the beginning, but it is slightly too low later on. A second batch of coal, of lower sulfur content than the first batch, started to spread into the furnace on August 16th. The low sulfur balance calculated for this day suggests that the system was in a state of adjustment. The nitrogen balance over this period, however, was very low (15-55%). Unpublished results from the Niro researchers also indicated a low nitrogen balance (30-40%). The conversion of a significant amount of the NO_x in the gas phase to molecular nitrogen is believed to be at least partly responsible for these observations. The mechanisms for this complicated oxidation-reduction reaction are discussed in Sec. 5.8.3. Another possibility would be the production of nitrogen-sulfur compounds, which were not included in the analyses.

5.8.3 A Possible Set of Reactions

In evaluating the data from the field tests, we have developed a series of proposed reactions for the combined removal of NO_x and SO_x from flue gases with a spray dryer and fabric filter. These reactions are listed below:

a. $Ca(OH)_2 + SO_2 + H_2O \Rightarrow CaSO_3{*}2H_2O$

b. $2NO + O_2 \Rightarrow 2NO_2$

c. $Ca(OH)_2{+}CaSO_3{*}2H_2O{+}2NO{+}2NO_2 \Rightarrow CaSO_4{*}2H_2O{+}Ca(NO_3)_2{+}N_2{+}H_2O$

d. $Ca(OH)_2 + CO_2 \Rightarrow CaCO_3 + H_2O$

The pertinent thermochemical information is given in Table 5.7.

TABLE 5.7 Thermochemical Data

Compound	HF_{25}[a] (kCal/mol)	HF_{25}[a] (Cal/mol)	Specific Heat, C_p (Cal/mol·K)
$Ca(OH)_2$	-235.58	-235,580	20.91
SO_2	-70.94	-70,940	9.53
$CaSO_3{*}2H_2O$	-418.9	-418,900	42.7
H_2O	-57.8	57,800	8.025
NO	21.6	21,600	7.133
NO_2	7.93	7,930	8.89
O_2	0	0	7.016
$CaSO_4{*}2H_2O$	-483.42	-483,420	44.46
$Ca(NO_3)_2$	-224.05	-224,050	35.7
N_2	9	0	6.961
CO_2	94.05	94,050	8.87
$CaCO_3$	289.5	89,500	19.42

[a] HF_{25} = heat of formation at 25°C.

These chemical reactions (a-d) can account for phenomena observed during the field test, as well as trends noticed in the chemical analysis following the tests.

First, there is the temperature increase across the baghouse fabric filter, seen in some of our data and reported by Niro in their laboratory work.[15] The heats of reaction for reactions a-d are all exothermic (see Table 5.8). Initial calculations, based on 40-50% removal of NO (with appropriate allowance for heat loss to the atmosphere), predict a temperature increase of about 8-10°C. This increase is in the same range as that seen in the ANL field tests, as well as by Niro in their laboratory. If reactions a-d are correct, then approximately 75% of the heat release is a result of reaction c.

Second, the sulfate content of the "product" stream, as well as the amount of nitrates, increases without a similar degree of increase being seen in the amount of nitrites in the waste material. This would be predicted by reaction c, because the sulfites are part of the reaction that produces sulfites and nitrates (but not nitrites).

Finally, nitrogen is produced as an end product of the combined removal of nitrogen and sulfur oxides. A nitrogen balance determination performed on the field test data was able to close this balance only to the 40-60% level. Taking reaction c into account, the nitrogen balance was closed to the 80-100% level.

Some further analysis of the data is being performed to examine trends associated with increases in temperature from the spray dryer and the removal of NO_x as a function of the SO_x/NO_x ratio and the equivalence ratio. A table of most of the primary factors for NO and NO_x removal has been prepared and is being used for data reduction.

TABLE 5.8 Heats of Reaction[a]

	Heat of Reaction, by Temperature		
Reaction	363K	368K	373K
a	-54,304.725	-54,283.55	-54,262.375
b	-27,567.63	-27,585.14	-27,602.65
c	-169,883.15	-169,885.7	-169,888.25
d	-17,821.775	-17,833.45	-17,845.125

[a] All heats of reaction are expressed in calories per equivalent (taking into account different valence states) of reactant.

6 CONCLUSIONS

On the basis of field tests at ANL, the following conclusions have been formulated:

1. Significant removal of NO_x occurs when the outlet temperature from a lime-based spray dryer exceeds 190°F. The existence of a temperature "window" has not been confirmed, although the spray-dryer outlet temperature in Argonne's field tests did not exceed 215°F. In no case was an "optimal" temperature or a maximum temperature observed for simultaneous NO_x/SO_x removal.

2. The addition of caustic soda to a lime-based spray dryer at higher than normal operating temperatures tends to enhance NO_x removal. The main effect of caustic soda addition seems to be the creation of a much more porous cake than would otherwise be the case. This more porous cake appears to provide more active area for oxidation of NO to NO_2 and more contact of NO_x with available alkali, resulting in increased removal of the NO_x.

3. The high SO_x/NO_x ratios that result from the combustion of high-sulfur coal (as typically found in the midwestern United States) are necessary if there is to be any degree of simultaneous NO_x/SO_x removal. The ANL tests indicate that the low SO_x/NO_x ratios found in the combustion of low-sulfur coals result in little or no removal of NO_x (not greater than 10%) from a spray-dryer/fabric-filter system, under the same conditions at which good removal has been observed in gases from the combustion of high-sulfur coal. (In its wet scrubber research, Argonne has observed the same difference in removal of NO_x between high- and low-sulfur coals.)

4. The bulk of the oxidation of NO to NO_2, and consequently the removal of NO_x from the flue-gas stream, was observed to occur in the fabric filter rather than in the spray dryer. This removal tended to increase as the cake thickness on the fabric filter increased. After the filter had been cleaned and the cake layer removed, the level of removal of NO_x (and, to some extent, SO_x) decreased.

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APPENDIX A:

SAMPLE ANALYSIS PROCEDURES FOR ANL HIGH-SULFUR DRY SCRUBBER TEST, 1986

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SAMPLE ANALYSIS PROCEDURES FOR ANL HIGH-SULFUR DRY SCRUBBER TEST, 1986

1. Specific Gravity

Weigh approximately 30 mL of slurry in a tared 50-mL graduated cylinder (W_s). Add water to the 50-mL mark and reweigh (W_t). Record the temperature (T) of the water.

$$\text{Specific gravity} = \frac{W_s}{50 - \left(\dfrac{W_t - W_s}{\text{density } H_2O \text{ at } T}\right)}$$

2. Percent Moisture

Transfer solution from No. 1 to a tared polyethylene bottle. Dry at 95°C (overnight) and 110°C until weight is stable. Calculate moisture loss.

3. Weight Percent Solids

Weigh powder samples. Follow same drying and weighing schedule as in No. 2. Use glass containers.

4. Available Lime Index
and
5. Total Alkalinity

Take two weighed aliquots at the same time.

For No. 4 slurry sample in water, boil 1 min, cool, add sucrose solution, and allow reaction to proceed for 15 min. Titrate rapidly with HCl to pH 9.0. Calculate % CaO from meq HCl.

For No. 5 slurry sample in water, add a known acid excess of H^+-As^{+5} reagent and boil 2 min to remove CO_2. Back titrate with NaOH to pH 4.0. Sulfite is oxidized by As^{+5} and does not interfere. Calculate % CaO from net meq of H^+.

6. Sulfite

Add buffer to flask, weigh, add iodine solution, weigh, add slurry sample, weigh or add weighed powder sample. Let stand (in dark) for 5 min. Titrate excess iodine with arsenous reagent using an amperometric (dead stop) endpoint. Calculate % SO_3 from titer value of total iodine minus excess value.

7. Total Sulfur

Use a Leco semiautomatic titrator. Use an induction furnace to oxidize all S to SO_2. Titrate the SO_2, as it is generated, with iodine reagent. Take samples from the moisture-free residues.

8. Nitrate, Nitrite, and Chloride

Slurry the weighed sample in a known volume of water. Inject a portion of the filtered supernatant into the ion chromatograph. The anions are separated on an HPIC/anion column, detected by suppressed conductivity, and measured by recording peak heights.

9. Carbonate

Place the weighed sample in the apparatus. Add acid to generate CO_2. Pass the gases through a gas chromatograph, and measure the CO_2 by recording the peak height.

10. Calcium, Sodium, and Silica

Fuse the dried sample with lithium tetraborate and dissolve the melt in dilute HCl. The cations are determined by atomic absorption spectroscopy. The method is similar to the determination of major and minor elements in coal.

TABLE A.1 Summary of Chemical Analysis Procedures

	Measurement	Sample/Preparation	Methodology	Reaction/Measurement
1.	Specific gravity	Slurry	Gravimetric	Weight vs. water
2.	% moisture	Slurry	Gravimetric	Dry at 95°C
3.	Weight % solids	Powder	Gravimetric	Dry at 95°C
4.	Available lime index	Water slurry	Volumetric	Titrate soluble $(\mathrm{OH})^-$
5.	Total alkalinity	Water slurry	Volumetric	Oxidize sulfite and titrate soluble $(\mathrm{OH})^-$ and $(\mathrm{CO}_3)^=$
6.	Sulfite	Water slurry	Volumetric	Reduce excess iodine and back titrate
7.	Total sulfur	Powder or dried slurry	Leco semiautomatic titrator	Generate SO_2 and titrate with I_2
8.	Nitrate-nitrite (chloride)	Water-soluble portion of slurry	Ion chromatography Dionex Model 16	Separate anions and measure peak heights
9.	Carbonate	Powder	Gas chromatography	Generate CO_2 and measure peak height
10.	Calcium, sodium, silica	Dried powder	Atomic absorption	Fuse in lithium borate to dissolve

TABLE A.2 Data Quality of Chemical Analysis

Measurement/ASTM Method	Standards/SRM	Estimated Relative Accuracy (%)
1. Specific gravity	Relative to water at measured temperature	±10
2. % moisture	Dry to a constant weight	±10
3. Weight % solids	Dry to a constant weight	±5
4. Available lime index/C25	Std. HCl	Powder ±5, slurry ±10
5. Total alkalinity	Std. NaOH, SRM 1b	Powder ±5, slurry ±10
6. Sulfite/EPA-650/2-74-024	SRM 83 As_2O_3 Reagent $NaHSO_3$	Powder ±5, slurry ±10
7. Total sulfur	Reagent $CaSO_4$	±5
8. Nitrate-nitrite (chloride)	Reagent-grade chemicals	±5
9. Carbonate	Reagent $CaCO_3$	±5
10. Calcium, sodium, silica/D3174 D3682	Commercial stds.	±1-3 for Na ±1-5 for Ca, Si (when >1.0 wt%)

TABLE A.3 Chemical Analysis of Coal: Proximate and Ultimate

Measurement	ASTM Method	SRM/Instrument	Estimated Accuracy (%)[a]
Moisture	D3173	Gravimetric	0.2-0.3 r A
Ash	D3174	Gravimetric	0.2-0.3 r A
Volatile matter	D3175	Gravimetric	
Gross calorific value	D2015	SRM 1632B/Parr calorimeter	Note b
Carbon	D3178	SRM 141/PE 240x	±2 R
Hydrogen, nitrogen	D3178	SRM 141/PE 240x	±0.3 A
Sulfur	D4239	SRM 2684, 2683/ Leco 501-01/ Leco SC132	Note c
Major and minor elements	D3682	Commercial Stds./ PE5000	0.1-2 r

[a] R = relative, A = absolute, r = repeatability.

[b] 100 Btu/lb A, 0.50 Btu/lb r.

[c] $r = 0.03 \pm 0.04\,\bar{x}$, where $\bar{x}$ is the average value.

APPENDIX B:

REPORT ON CONTINUOUS EMISSION MONITOR CERTIFICATION TESTING

APPENDIX B:

REPORT ON CONTINUOUS EMISSION MONITOR CERTIFICATION TESTING

The following pages constitute portions of a report prepared by Clean Air Engineering, Inc., under Argonne National Laboratory Purchase Order 60240056. The purpose of the study was to determine the relative accuracy of continuous emission monitoring at ANL.

Note: The person listed first under "Objective" is Paul Farber (not "Farbor").

SUMMARY

OBJECTIVE

Clean Air Engineering, Inc was contracted by Argonne National Laboratory to determine continuous emission monitor (CEM) relative accuracy at Argonne, IL.

Testing took place at the Steam Plant Unit #5 on Aug 8, 1986. Coordinating the field testing were: Paul Farbor, Argonne National Laboratory and Peter Kaufmann, Clean Air Engineering, Inc.

CONCLUSIONS

Based on our review of the monitor and reference method data, the relative accuracies of the SO_2 monitor and NOx monitor were 5.3% and 2.8% respectively.

To the best of our knowledge, the information presented in this report is accurate and complete.

Respectfully submitted,

CLEAN AIR ENGINEERING, INC

Peter W. Kaufmann
Manager Monitor Services

DESCRIPTION OF INSTALLATION

Unit #5 at the Argonne National Laboratory Steam Plant is a coal fired boiler. A spray dryer controls sulfur dioxide emissions, and a baghouse controls particulate emissions.

The CEM system employed on Unit #5 is an extractive type system utilizing a dilution probe. The system is manufactured by Thermo Electron Corp (Model 200) and monitors both the stack and the boiler outlet.

All testing reported in this document was conducted at the stack.

SUMMARY OF PROCEDURES

SAMPLING PROCEDURES

The monitor certification was performed according to procedures outlined in U.S. Environmental Protection Agency (EPA) Performance Specification 2 titled: "Specifications and Test Procedures for SO_2 and NOx Continuous Emission Monitoring Systems in Stationary Sources" [Revised by 48 FR 23610, May 25, 1983].

Referenced with the above specification were U.S. EPA Methods 3, 4, 6, and 7. These methods are titled:

Method 3--"Gas Analysis for Carbon Dioxide, Oxygen, Excess Air and Dry Molecular Weight;"
Method 4--"Determination of Moisture Content in Stack Gases;"
Method 6--"Determination of Sulfur Dioxide Emissions from Stationary Sources;"
Method 7--"Determination of Nitrogen Oxide Emissions from Stationary Sources."

These specifications and methods appear in Title 40 of the Code of Federal Regulations (CFR), Appendix B and Part 60, Subpart A. The sampling apparatus for Methods 6 and 7 are shown in Figs 1 and 2 on pages 6-1 and 6-2.

Sampling Location

At the stack, three points located at 16.7, 50.0 and 83.3 percent of the stack diameter were sampled for a period of 7 minutes each during a single sulfur dioxide run. For nitrogen oxide sampling, one flask was sampled at each point, then all points were averaged to constitute one run.

ANALYTICAL PROCEDURES

Carbon Dioxide

The carbon dioxide content was measured with an Orsat apparatus as outlined in Method 3.

Sulfur Dioxide

The sulfur dioxide content was measured following the titrimetric procedure outlined in Method 6. In this procedure, barium-thorin titration measures the sulfur dioxide fraction.

Nitrogen Oxide

Nitrogen oxide content was measured colorimetrically using the phenoldisulfonic acid (PDS) procedure outlined in Method 7.

QUALITY CONTROL PROCEDURES

Quality control procedures were followed for all aspects of field sampling including sample preservation and holding time; reagent quality; analytical method; analyst training and safety; and instrument cleaning, calibration and safety. These procedures are consistent with EPA guidelines documented in "Quality Assurance Manuals for Air Pollution Measurement Systems," Vol 3, "Stationary Source Specific Methods" (EPA-600/4-77-027b).

RESULTS

The results of the relative accuracy testing of the SO_2 monitor are presented in Table 1. The results of the NOx relative accuracy testing are presented in Table 2.

A more complete breakdown of the SO_2 test runs are presented in Tables 3 and 4. The results of the individual NOx flasks are presented in Tables 5 and 6.

Test parameters, calibration data, laboratory data and field data are provided in the Appendix.

Table 1
SO_2 Relative Accuracy

Run #	SO2 ppm w		%CO2 w		SO2 lb/MBtu		
	RM	M	RM	M	RM	M	Diff
1	538	582	9.1	9.2	1.58	1.76	-0.18
2	620	585	8.8	9.1	1.89	1.79	0.10
3	521	554	8.1	9.1	1.72	1.70	0.02
4	520	536	8.4	9.0	1.66	1.65	0.01
5	553	563	8.6	9.0	1.72	1.74	-0.02
6	389	439	8.7	8.9	1.20	1.38	-0.18
7	536	509	8.7	9.1	1.65	1.56	0.09
8	545	563	8.9	9.0	1.64	1.74	-0.10
9	579	540	8.8	9.0	1.77	1.67	0.10
10	517	524	8.7	9.1	1.60	1.61	-0.01
11	507	509	8.8	9.0	1.54	1.58	-0.04
12	477	499	8.6	8.9	1.48	1.56	-0.08
Avg					1.62		-0.024

Confidence Coefficient 0.0620

Relative Accuracy 5.3 %

Table 2
NOx Relative Accuracy

Run #	NOx ppm w		%CO2 w		NOx lb/MBtu		
	RM	M	RM	M	RM	M	Diff
1	203	193	9.1	9.2	0.427	0.420	0.007
2	198	195	8.8	9.1	0.434	0.429	0.005
3	194	196	8.1	9.1	0.459	0.433	0.026
4	193	195	8.4	9.0	0.441	0.433	0.008
5	201	197	8.6	9.0	0.450	0.436	0.014
6	201	195	8.7	8.9	0.446	0.440	0.006
7	197	199	8.7	9.1	0.436	0.438	-0.002
8	199	197	8.9	9.0	0.432	0.437	-0.005
9	195	208	8.8	9.0	0.428	0.463	-0.035
10	200	199	8.7	9.1	0.442	0.441	0.001
11	182	192	8.8	9.0	0.397	0.428	-0.031
12	191	192	8.6	8.9	0.425	0.433	-0.008
Avg					0.435		-0.0012

Confidence Coefficient	0.0110
Relative Accuracy	2.8%

Table 3
SO_2 Results Dry

Run#	Start Time	Vmstd	%CO2	Sulfur Dioxide lb*10-5 dscf	ppm, dry	lb/MBtu*
1	10:35	0.912	10.3	10.103	608	1.58
2	11:02	0.978	9.9	11.652	701	1.89
3	11:35	0.979	9.3	9.915	596	1.72
4	12:00	1.003	9.6	9.883	594	1.66
5	12:30	0.980	9.8	10.479	630	1.72
6	13:00	0.954	9.9	7.373	443	1.20
7	13:30	0.989	9.8	10.031	603	1.65
8	14:00	0.985	10.0	10.212	614	1.64
9	14:30	0.954	9.8	10.761	647	1.77
10	15:00	0.988	9.7	9.613	578	1.60
11	15:30	0.982	9.8	9.380	564	1.54
12	16:00	0.941	9.6	8.815	530	1.48

* By "Fc" factor method

Table 4
SO_2 Results Wet

Run#	Start Time	Bwo	%CO2w	Sulfur Dioxide lb*10-5 scf	ppm, wet	lb/MBtu*
1	10:35	0.1151	9.1	8.940	538	1.58
2	11:02	0.1151	8.8	10.311	620	1.89
3	11:35	0.1258	8.1	8.668	521	1.72
4	12:00	0.1258	8.4	8.640	520	1.66
5	12:30	0.1224	8.6	9.196	553	1.72
6	13:00	0.1224	8.7	6.470	389	1.20
7	13:30	0.1124	8.7	8.904	536	1.65
8	14:00	0.1124	8.9	9.064	545	1.64
9	14:30	0.1054	8.8	9.627	579	1.77
10	15:00	0.1054	8.7	8.600	517	1.60
11	15:30	0.1012	8.8	8.431	507	1.54
12	16:00	0.1012	8.6	7.923	477	1.48

* By "Fc" factor method

Table 5
NOx Results Dry

Run #	Time	lbx10-5 dscf	ppm dry	%CO2	lb/MBtu*	Sdev ppm
1A	10:30	2.6548	222			
B	10:40	2.9258	245			
C	10:49	2.6161	219			
avg		2.7322	229	10.3	0.427	11.5
2A	11:03	2.5505	214			
B	11:13	2.6583	223			
C	11:25	2.7923	234			
avg		2.6670	223	9.9	0.434	8.3
3A	11:35	2.6605	223			
B	11:45	2.5887	217			
C	11:59	2.7118	227			
avg		2.6537	222	9.3	0.459	4.2
4A	12:05	2.6823	225			
B	12:15	2.5056	210			
C	12:25	2.7033	226			
avg		2.6304	220	9.6	0.441	7.4
5A	12:35	2.8171	236			
B	12:45	2.6510	222			
C	12:55	2.7504	230			
avg		2.7395	229	9.8	0.450	5.7
6A	13:05	2.7710	232			
B	13:15	2.6496	222			
C	13:29	2.7979	234			
avg		2.7395	229	9.9	0.446	5.4
7A	13:35	2.7270	228			
B	13:46	2.6492	222			
C	13:56	2.5769	216			
avg		2.6510	222	9.8	0.436	5.1
8A	14:06	2.7043	227			
B	14:18	2.6452	222			
C	14:29	2.6918	225			
avg		2.6804	225	10.0	0.432	2.1
9A	14:35	2.7154	227			
B	14:45	2.5880	217			
C	14:58	2.5183	211			
avg		2.6072	218	9.8	0.428	6.8
10A	15:01	2.7454	230			
B	15:10	2.5524	214			
C	15:20	2.6899	225			
avg		2.6626	223	9.7	0.442	6.8
11A	15:37	2.2635	190			
B	15:47	2.3301	195			
C	15:59	2.6552	222			
avg		2.4163	202	9.8	0.397	14.3
12A	16:05	2.4630	206			
B	16:12	2.6218	220			
C	16:19	2.5111	210			
avg		2.5320	212	9.6	0.425	5.6

* - By "Fc" factor method

Table 6
NOx Results Wet

Run #	Time	lbx10-5 vscf	ppm wet	%CO2w	lb/MBtu*	Sdev ppm
1A	10:30	2.3492	197			
B	10:40	2.5890	217			
C	10:49	2.3150	194			
avg		2.4178	203	9.1	0.427	10.2
2A	11:03	2.2569	189			
B	11:13	2.3523	197			
C	11:25	2.4709	207			
avg		2.3601	198	8.8	0.434	7.3
3A	11:35	2.3258	195			
B	11:45	2.2630	190			
C	11:59	2.3707	199			
avg		2.3198	194	8.1	0.459	3.7
4A	12:05	2.3449	196			
B	12:15	2.1904	183			
C	12:25	2.3632	198			
avg		2.2995	193	8.4	0.441	6.5
5A	12:35	2.4723	207			
B	12:45	2.3265	195			
C	12:55	2.4138	202			
avg		2.4042	201	8.6	0.450	5.0
6A	13:05	2.4318	204			
B	13:15	2.3253	195			
C	13:29	2.4554	206			
avg		2.4042	201	8.7	0.446	4.7
7A	13:35	2.4194	203			
B	13:46	2.3504	197			
C	13:56	2.2862	191			
avg		2.3520	197	8.7	0.436	4.6
8A	14:06	2.3993	201			
B	14:18	2.3468	197			
C	14:29	2.3882	200			
avg		2.3781	199	8.9	0.432	1.9
9A	14:35	2.4292	203			
B	14:45	2.3152	194			
C	14:58	2.2529	189			
avg		2.3324	195	8.8	0.428	6.1
10A	15:01	2.4560	206			
B	15:10	2.2834	191			
C	15:20	2.4064	202			
avg		2.3819	200	8.7	0.442	6.1
11A	15:37	2.0344	170			
B	15:47	2.0943	175			
C	15:59	2.3865	200			
avg		2.1717	182	8.8	0.397	12.9
12A	16:05	2.2137	185			
B	16:12	2.3565	197			
C	16:19	2.2570	189			
avg		2.2757	191	8.6	0.425	5.0

* - By "Fc" factor method

DISCUSSION

The first test run began at 10:30 AM. One test run was completed each half hour until 12 runs were completed. Results were calculated using the "Fc" factor method. An "Fc" factor of 1610, supplied by Argonne National Laboratory was used in all calculations.

No deviations from standard U.S. EPA Procedures were noted.

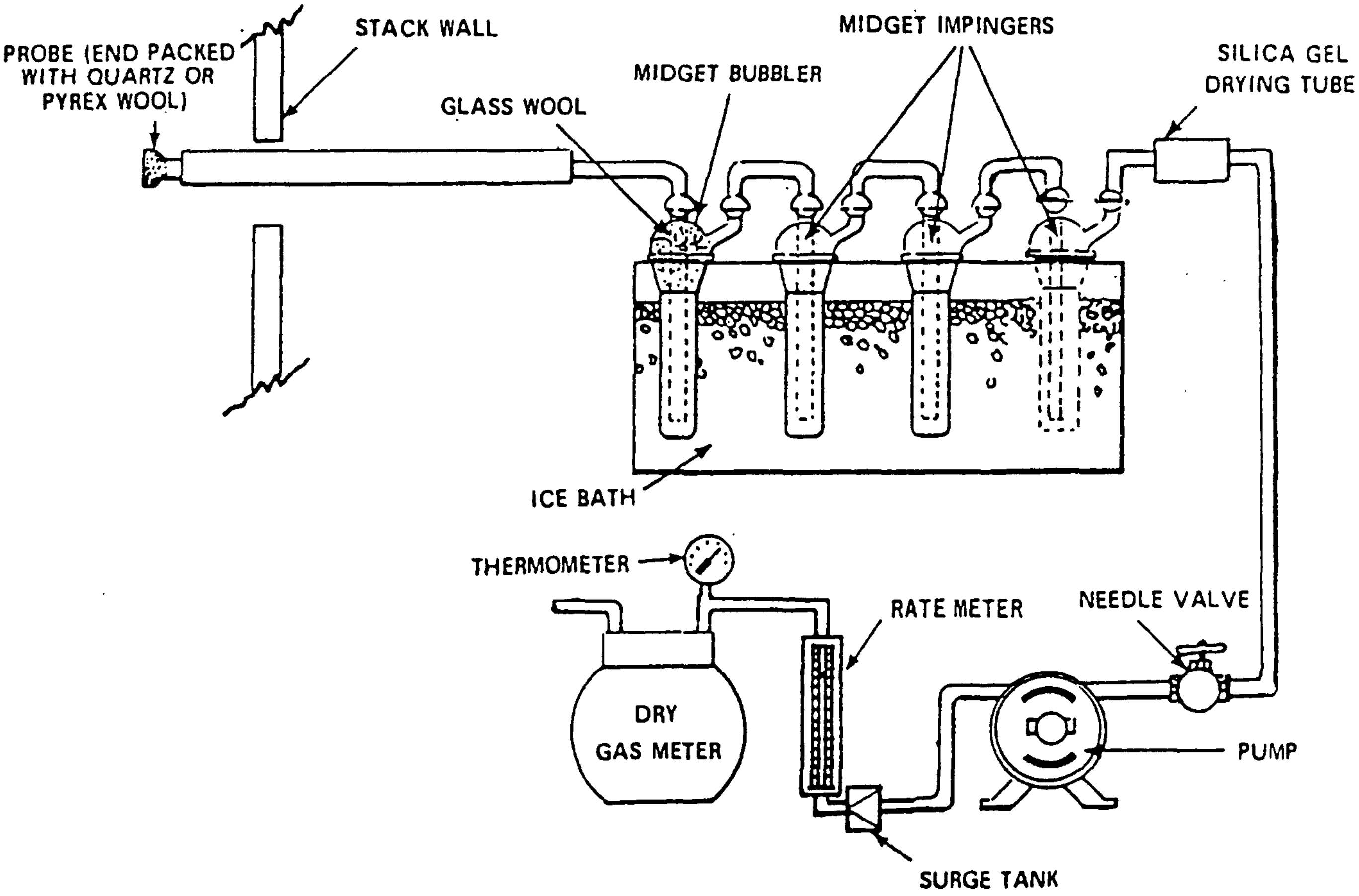

Fig 1. The Method 6 sampling apparatus is shown.

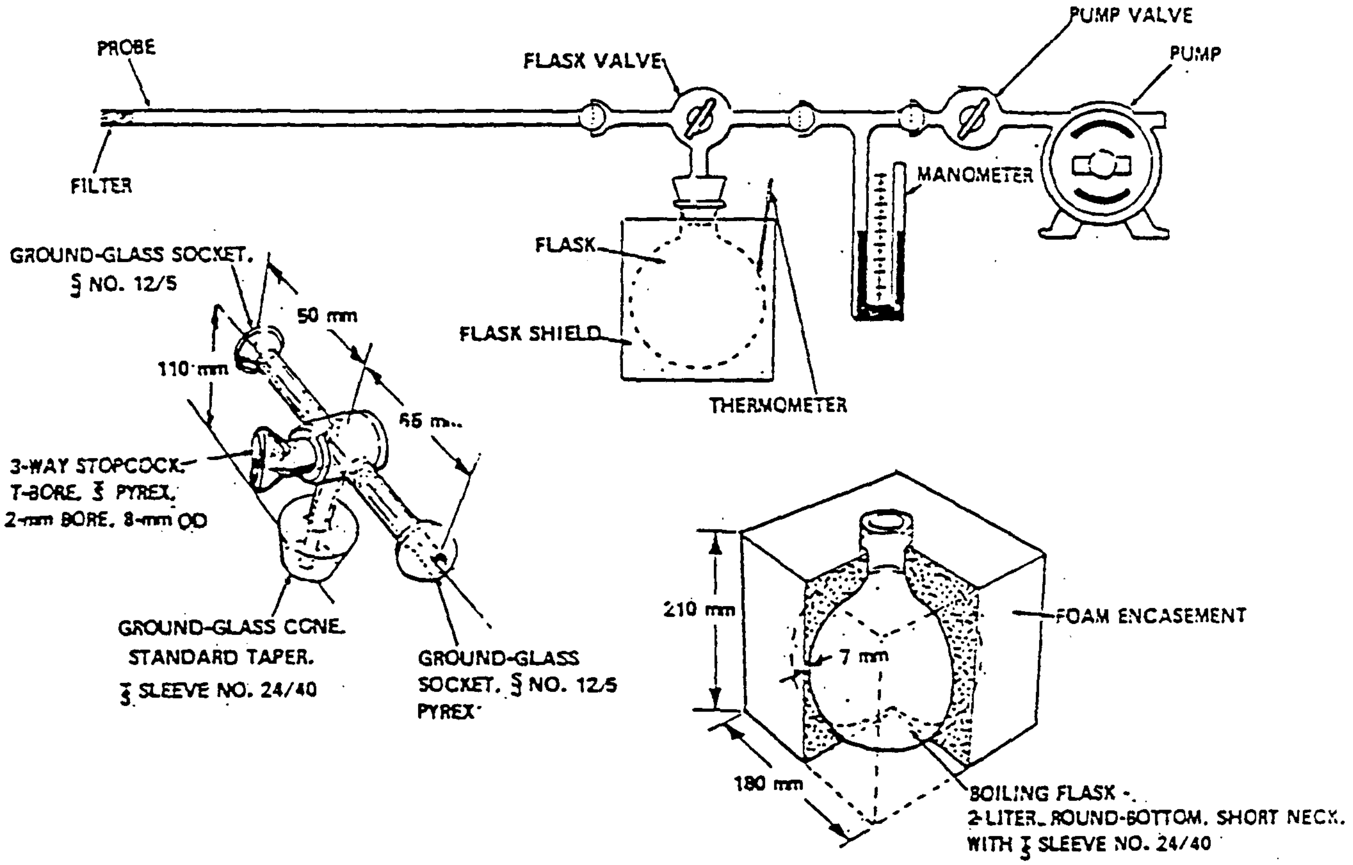

Fig 2. The Method 7 sampling apparatus is shown.

APPENDIX C:
CONVERSION FACTORS

APPENDIX C: CONVERSION FACTORS

Area:	$1\ \text{ft}^2 = 9.3 \times 10^{-2}\ \text{m}^2$
Heating value:	$1\ \text{Btu/lb} = 2.324 \times 10^{3}\ \text{J/kg}$
Length:	$1\ \text{ft} = 3.05 \times 10^{-1}\ \text{m}$
Mass:	1 oz (avoirdupois) = 28.4 g
Mass flow rate:	1 lb/h = 2.20 kg/h
Power per unit length:	$1\ \text{Btu/h} \cdot \text{ft} = 9.61 \times 10^{-1}\ \text{W/m}$
Pressure:	$1\ \text{psig} = 1.45 \times 10^{-1}\ \text{kPa}$
Temperature:	°F = 1.8 °C + 32, °C = (°F - 32)/1.8
Temperature difference:	°F = 1.8 °C, °C = 0.55 °F
Volume:	$1\ \text{in.}^3 = 16.4\ \text{cm}^3$ 1 gal = 3.78 L

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