

FINAL TECHNICAL REPORT
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Project Title: **CATALYTIC OXIDATION OF NO IN FLUE GAS FOR CAPTURE IN WET SCRUBBERS**

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ABSTRACT

CONSOL R&D, the research arm of Consolidation Coal Company, which mines about 5 million tons of Illinois coal each year, began development of NO_x oxidation catalyst technology that was expected to result in cost-effective NO_x removal by wet flue gas desulfurization (FGD) scrubbers. Wet FGD is the preferred technology for removing sulfur dioxide generated during the combustion of high- and medium-sulfur Illinois coal in the production of electric power. In this work, catalysts were tested for the ability to oxidize NO to NO₂ for efficient capture of NO₂ in wet scrubbers. The concept of catalytic in situ oxidation of NO to NO₂ was demonstrated. Several catalysts were identified that oxidized about 50% of NO to NO₂ in the absence of SO₂. Unfortunately, some of these catalysts were unable to oxidize 50% of the NO when SO₂ is present in synthetic flue gas. The catalysts also oxidized a substantial amount of SO₂ to SO₃, which can raise the acid dew point and cause corrosion in power plant ducts and air heaters.

Project background and objectives are provided in the report. The report describes the design and construction of the catalyst test unit, the catalyst test runs, test unit operating difficulties, and suggestions for future development.

EXECUTIVE SUMMARY

Because selective catalytic reduction (SCR) NO_x control technology is costly, CONSOL R&D initiated laboratory development of a low-cost alternative NO_x control method. This technology was based on the use of existing or new wet flue gas desulfurization (FGD) scrubbers. The overall project goal was to commercialize, by the year 2003, a low-cost alternative NO_x control method suitable for use on coal-fired utility boilers that could achieve a 65 µg/MJ (0.15 lb/MMBtu) NO_x emission rate. In 2004, additional NO_x controls are expected when the recently revised NO_x SIP regulations set the framework for NO_x emissions limits. The novel NO_x control process is based on catalytic oxidation of NO to NO₂. At typical flue gas conditions downstream of the boiler economizer, most of the NO_x (>95%) is NO. The residual oxygen (3% to 6%) in the flue gas is the oxygen source. Based on bench-scale tests, (Shen and Rochelle, 1995; Zemansky et al., 1993), NO₂ is more soluble in aqueous solutions than NO. An existing flue gas desulfurization (FGD) wet scrubber can remove the NO₂. The catalyst can be placed upstream of the air heater section, downstream of the air heater but upstream of the particulate collector, or downstream of the particulate collector. A desirable characteristic of the catalyst is that it minimize the oxidation of SO₂ to SO₃. Based on equilibrium calculations, 60% to 95% removal of NO_x is possible, but laboratory evaluation is required to determine the actual NO_x removal efficiency. The process can be used in combination with combustion modification (i.e., low-NO_x burners) to control NO_x emissions. The process requires a relatively small capital investment to achieve high NO_x removal.

This technology will promote the use of wet FGD scrubbers for combined NO_x and SO_x control. This will benefit the use of medium- to high-sulfur coals, such as those produced by the Illinois coal industry, by preserving or expanding their markets.

The planned research activities included three tasks. However, because a suitable catalyst was not identified, Task 3 was not completed.

Task 1 - A catalyst screening program to identify a catalyst capable of oxidizing at least 50% of the NO to NO₂ while oxidizing less than 5% of the SO₂ to SO₃ under typical coal-fired flue gas conditions. A catalyst test unit was constructed that uses simulated flue gas. A major catalyst manufacturer provided ten candidate catalysts for evaluation in this program.

Task 2 - Extended catalyst testing to simulate boiler cycling and observe catalyst deactivation. Originally, boiler cycling was to be simulated by multiple start-up/shut-down cycles. However, at the suggestion of the catalyst manufacturer, these tests were performed by conducting a 4-hour lineout without SO₂, followed by an 8-hour lineout with 2000 ppm SO₂, prior to measuring NO and SO₂ conversion.

Task 3 - A process economic evaluation to estimate the process economics, identify significant cost areas for process improvements and cost reductions, and evaluate options for process scale-up. However, because none of the test catalysts satisfied the criteria of oxidizing at least 50% of the NO to NO₂ while oxidizing 5% or less of the SO₂ to SO₃, a process economic evaluation was not justified.

The catalyst test unit consists of a tubular quartz reactor that is wrapped with heating tape and temperature controlled. The honeycomb catalyst samples were 1" dia. x 4" long. The catalyst test unit design conditions were 300-600 °F, 10,000-60,000 hr⁻¹ space velocity (std L/hr gas flow per L catalyst bed volume) of simulated flue gas containing 100-1000 ppmv NO, 1000-3000 ppmv SO₂, 3-7 vol % O₂, 10-14 vol % CO₂, 4-8 vol % H₂O, and the balance N₂. For this range of space velocity, and the catalyst bed volume chosen, the combined flow

(including water vapor) of simulated flue gas will be 8.6-51.5 SLPM. Gas will be fed from the plant nitrogen supply and mass flow controllers were used to meter the flue gas component gases into the mixing and preheat zone prior to entering the catalyst reaction zone. Exit gas was analyzed using continuous NO/NO_x and SO₂ analyzers; SO₃ yield was calculated from changes in the SO₂ concentration. Catalyst test duration was defined by steady-state conditions, as determined by gas analyzer data. Several test runs were 24 hours in duration.

The test strategy was to screen all catalysts at one test condition, and select the best catalysts for more extensive testing. The conditions chosen for the screening test were 600 °F, 10,000 hr⁻¹ space velocity, 1000 ppmv NO, 2000 ppmv SO₂, 5 vol % O₂, 12 vol % CO₂, and 6 vol % H₂O. During the extensive test program, the space velocity and temperature was varied at several levels, two levels were used for the SO₂ and NO concentrations, and the concentrations of H₂O, O₂ and CO₂ were tested at only one level.

The catalyst test unit consists of five subsystems: (1) The gas supply and mixing subsystem provides inert gas (nitrogen from the plant supply) for reactor start-up and shutdown, inert gas (nitrogen from the plant supply) for the balance of the simulated flue gas, and CO₂, O₂, SO₂, and NO from cylinders to produce the simulated flue gas. Special features provide for safety of personnel and equipment. (2) The humidification/gas preheat system consists of metered water injection into the gas stream, followed by evaporation and preheating to approximately 230-260 °F with the gas flowing through a coil in an oil bath. (3) The reactor system consists of a custom-built three-sectioned tubular quartz reactor; two sections are heated and one is cooled. In the first section, the simulated flue gas is preheated to reaction temperature, 300-600 °F. The second section contains the catalyst, and the third section cools the gas to about 300 °F at the reactor outlet. (4) The flue gas conditioning and analysis system provides reactor effluent gas drying, pressure control, and gas analysis for NO/NO_x, SO₂, CO₂, and O₂. (5) The data recording system logs data, including mass flow rates of component gases, temperatures of the reactor zones, and the concentrations measured by the gas analyzers.

After construction of the catalyst test unit was completed, several equipment problems were identified and corrected during the integrated system start up. Failure and re-start modes of several components were evaluated as part of the safety considerations. Specific procedures were set up for area monitoring for NO and SO₂ using color indicator tubes. A unit operating and safety manual was written.

In the absence of SO₂, all of the catalysts tested exhibited some degree of activity for oxidation of NO to NO₂ over the temperature range 350-600 °F at the conditions tested (10,000 hr⁻¹ space velocity, 1000 ppmv NO, 2000 ppmv SO₂, 5 vol % O₂, 12 vol % CO₂, and 0-6 vol % H₂O). Several catalysts met the target of 50% or greater conversion of NO at these conditions. Performance with each catalyst depended on temperature.

Most of the catalysts showed moderate to substantial conversion of SO₂ to SO₃ at the test conditions. The SO₂ to SO₃ conversion was dependent on space velocity and temperature. In the absence of NO, oxidation of SO₂ to SO₃ still occurred. To be considered a suitable candidate for large-scale testing, a catalyst must oxidize at least 50% of the NO to NO₂ while oxidizing no more than 5% of the SO₂ to SO₃. None of the catalysts tested satisfied both criteria simultaneously.

Neither the NO oxidation nor the SO₂ oxidation reactions were dependent on the presence of water vapor in the gas stream. With 6% water vapor in the gas, the SO₃ formed was deposited on tubing surfaces downstream of the reactor as sulfuric acid condensation.

Without water vapor in the gas (and with NO in the feed gas), the SO₃ formed was deposited as a white, solid, sulfur-nitrogen compound that would eventually plug the system.

OBJECTIVES

The overall project goal is to commercialize, by the year 2003, a low-cost (\$20-40/kW capital cost) alternative NO_x control technology for coal-fired utility boilers. It should be efficient and economical to capture NO_x and mercury in an existing wet scrubber. A low-cost alternative NO_x control method, combined with FGD scrubbing, would benefit the utility, their customers, and producers of high-sulfur coal.

Four areas define the process development objectives. First, the availability and performance of catalysts to convert NO to NO₂ must be assessed; second, the capability of wet FGD scrubbers to capture NO₂ must be determined; third, the impact of captured NO₂ on the solid and liquid waste must be determined; and fourth, the overall process economics must be examined. Insufficient information in any of these areas has the potential to delay or prevent commercialization of the process. A fifth objective for a later phase of development is to examine the extent of mercury oxidation by the process catalyst. An advantage to catalytic oxidation of NO is the possibility that elemental mercury would also be oxidized. Current evidence indicates that oxidized mercury is captured in wet FGD scrubbers much more readily than elemental mercury. Although this is not necessary for the commercial success of the process, it can provide additional incentive for utilities to use the process.

This project specifically addresses the first process development areas. To assess the availability and performance of catalysts to convert NO to NO₂, NO oxidation tests were performed with simulated flue gas, and SO₂ oxidation was measured to ensure that less than 5% oxidation occurred at the same conditions. The viability of the process to enable NO capture depends on whether catalysts can be found that will effectively meet our goals. Another objective of this work was to evaluate the economic viability of this process (Task 3) at conditions established in the catalyst testing program (Tasks 1 and 2).

Specific objectives of this work are:

TASK 1

- Construct a catalyst test unit for screening catalysts to determine whether they can achieve high NO oxidation activity and low SO₂ oxidation activity at flue gas conditions.
- Conduct screening tests on 10-20 catalysts and select one or more catalysts that:
 - Achieve a minimum of 50% NO oxidation at flue gas conditions.
 - Achieve a maximum of 5% SO₂ oxidation at flue gas conditions.

TASK 2

- Conduct extended stability and performance tests on the catalysts selected in Task 1.
- Simulate boiler cycling tests on one or more catalysts.

TASK 3

- Evaluate the economic viability of this process for two generic, coal-fired, FGD-equipped boilers.

In Task 2, boiler cycling was to be simulated by multiple start-up/shut-down cycles. However, at the suggestion of the catalyst manufacturer, these tests were conducted using a 4-hr lineout without SO₂, followed by an 8-hr lineout with 2000 ppm SO₂, prior to measuring NO and SO₂ conversion.

INTRODUCTION AND BACKGROUND

CONSOL R&D, began development of technology that is expected to result in cost-effective capture of NO_x in wet flue gas desulfurization (FGD) scrubbers on coal-fired utility boilers. Wet FGD is the favored technology for removing sulfur dioxide from the emissions generated by the combustion of high- and medium-sulfur Illinois coal during the production of electric power. The existing FGD capacity in Illinois is limestone wet FGD processes. In addition to the units in Illinois, there are numerous scrubbed units in other states within the marketing area of Illinois coals.

A combined SO₂, NO_x and mercury control process would help preserve the use of domestic medium- to high-sulfur coal for the nation's energy needs. Furthermore, if the market for scrubber technology can be expanded, sales of high sulfur coal with scrubbing could replace business lost to low-sulfur western coal. A complete environmental control package based on the process under development and existing scrubber technology could be positioned to compete very well with the combined use of low sulfur coal and other NO_x and mercury control technologies. Because the Illinois coal industry produces principally medium- to high-sulfur coal, deployment of this technology should result in protecting and perhaps expanding market opportunities for those coals.

The overall project goal is to commercialize, by the year 2003, a low-cost alternative NO_x control method suitable for use on coal-fired utility power plants that can achieve a 65 µg/MJ (0.15 lb/MMBtu) NO_x emission rate and 80-90% mercury reduction. NO_x control processes will be needed in the year 2000, when Phase II of Title IV of the 1990 Clean Air Act Amendments (CAAA) goes into effect. Additional NO_x controls are expected when the recently enacted SIP NO_x regulations set the framework for NO_x emissions. The current state of the art for NO_x control is expensive and creates a market opportunity for PRB coal. The process being developed by CONSOL consists of catalytic oxidation of NO to NO₂ and possible oxidation of elemental mercury, followed by capture of NO₂ and oxidized Hg in a wet scrubber. At typical flue gas conditions downstream of the boiler economizer, most of the NO_x (>95%) is NO and about 10-20% of the mercury is elemental mercury. The residual oxygen (3% to 6%) in the flue gas is the oxygen source. NO₂ and oxidized mercury are more soluble in aqueous solutions than NO and elemental mercury. An existing FGD scrubber can remove the NO₂ and oxidized mercury. The catalyst can be placed upstream of the air heater section, downstream of the air heater but upstream of the particulate collector, or downstream of the particulate collector. A desirable characteristic of the catalyst is that it minimize the oxidation of SO₂ to SO₃. Based on equilibrium calculations, 60% to 95% removal of NO_x is possible. However, additional testing will be required to determine the actual NO_x removal efficiency. The process can be used in combination with combustion modification to control NO_x emissions. The process requires a relatively small capital investment to achieve high NO_x removal.

The catalytic oxidation-scrubber NO_x process is geared toward both the new and retrofit segments of the coal-fired utility industry. A catalytic system would be relatively easy to construct, install, operate, and maintain. This flexibility and versatility means that the catalytic oxidation process could be applied to a broad spectrum of user situations, including physical plant constraints, process requirements, and local environmental regulations.

In this process, reagents and reagent storage equipment are not needed. This reduces the capital and operating cost by about 50% relative to Selective Catalytic Reduction (SCR), the current technology option for post-combustion NO_x control. The catalytic oxidation process is especially attractive for plants with existing wet FGD scrubbers because it requires a relatively small capital investment to integrate the process with the existing equipment to achieve high NO_x removal.

EXPERIMENTAL PROCEDURES

CATALYST TEST UNIT

Test Unit Design Criteria

Catalyst samples were made from 1" diameter cores cut from 6" thick ceramic honeycomb substrate. The cores were cut to 4" length for testing. The catalyst manufacturer supplied 100 cell/in² (CPSI) honeycomb for the test catalysts.

A downflow reactor configuration was recommended by the catalyst manufacturer. Quartz construction was used for the high-temperature zones. Teflon FEP, FETFE, and borosilicate glass components were used in temperature regions of about 250-300 °F. Stainless steel construction was used below about 250 °F, where it exhibits no catalytic activity. Because of potential thermomechanical problems with quartz/metal seals, their use was avoided altogether. Although the catalyst manufacturer recommended minimum use of Teflon in the system, the use of Teflon was necessary in portions of the system. Tests with catalyst blanks (substrate only) characterized the system line-out behavior and degree of interferences in the absence of test catalysts.

The catalyst test unit design conditions are 300-600 °F, 10,000-60,000 hr⁻¹ space velocity, 100-1000 ppmv NO, 1000-3000 ppmv SO₂, 3-7 vol % O₂, 10-14 vol % CO₂, and 4-8 vol % H₂O. For those conditions, the combined flow (including water vapor) of simulated flue gas was 8.6-51.5 SLPM, giving a linear gas velocity through the catalyst bed of 0.93-5.55 ft/s (ignoring the honeycomb cell wall contribution to volume or area). Inert gas (nitrogen) flow was used for reactor start-up and shutdown. Design flow rates for the gas components are: 6.1-42.7 SLPM N₂; 0.9-7.2 SLPM CO₂; 0.3-3.6 SLPM O₂; 0.3-4.1 SLPM H₂O vapor (0.3-3.2 mL/min liquid H₂O); 9-154 SCCM SO₂; and 0.9-51.5 SCCM NO.

Catalyst Test Unit Description

The catalyst test unit consists of several subsystems that are described below. Figure 1 shows a diagram of the unit.

1. Gas Supply and Mixing System

The gas supply and mixing subsystem consists of gas cylinders, regulators, relief and purge systems (relief valves, tee purge assembly, vacuum pump), on-off valves, check valves, and mass flow controllers. This system provides inert gas (nitrogen from the plant supply) for reactor start-up and shutdown, inert gas (nitrogen) for the balance of the simulated flue gas, and the gases CO₂, O₂, SO₂, and NO from cylinders to produce the simulated flue gas. The relief and toxic gas purge systems provide for personnel safety and protect rotameters,

analyzers, the quartz reactor, and the mass flow controllers from damage due to excessive pressure in case of regulator diaphragm failure. Low-pressure (1/3 psi) check valves are used to avoid cross-contamination of gas lines.

Solenoid valves upstream of gas humidification/preheating and downstream of the gas dryer are used to select the gas flow through the reactor, either inert gas or simulated flue gas. When the inert gas is fed to the reactor, such as during start-up, the simulated flue gas is sent to the analyzers so that the feed gas component concentrations can be verified.

2. Humidification/Gas Preheat System

The water injection portion of the humidification system consists of a deionized water reservoir, digital solenoid diaphragm metering pump, back pressure control valve, gauge, manual bleed valve, and check valve. At a particular pump stroke length and fixed (i.e., regulated) outlet back pressure, the metering rate is controlled by setting the number of pump strokes per minute from 0 to 100. The target metering rate is 0.30-3.2 mL/min. The water is injected into the gas stream through the side connection of a union tee fitting. The gas and water then enter the remaining portion of the humidification/gas preheat system. This consists of the water/gas preheater coil, temperature-controlled circulating oil bath, and a heated transfer line from the coil outlet to the reactor inlet. The gas stream temperature at the coil outlet is about 113 °C (235 °F) with the bath set to 125 °C (257 °F). The heat-traced and insulated transfer line is self-regulated to maintain a temperature of approximately 127 °C (260 °F). Thus, the gas humidity should be maintained when it enters the reactor (integrated test not yet conducted). This is supported by the subjective observation that, on slight cooling of the gas preheated and humidified in this manner, the water did not readily condense from the gas. Should it be necessary to avoid condensation, quartz beads and a perforated quartz plate can be installed in the preheater section of the reactor.

3. Reactor System

The reactor system consists of a tubular quartz reactor (three sections connected by two standard taper ground joints; two sections are heated and one section is cooled) and associated fittings, heat tracing, thermocouples and thermocouple wells, blower and cooling shroud, and controllers for two heating sections and the cooling section. The first heated section (approximately 2 ft in length) is provided to preheat the gas to reaction temperature, 300-600 °F. A thermocouple at the bottom of this section, just upstream of the joint and the catalyst, is used as input for control of the temperature through a silicon controlled rectifier power output to the heating tape on the outside of this first quartz reactor section. The second heated section (about 1 ft in length) contains the catalyst, and is controlled at the catalyst operating temperature. A thermocouple placed just downstream of the catalyst section is used as input for control of the temperature through silicon controlled rectifier power output to the heating tape on the outside of this quartz reactor section. The third reactor section (about 2 ft in length) is for cooling the gas sufficiently (to about 300 °F).

The cool upstream and downstream ends of the reactor are straight tubing. Fittings at the ends of the reactor, and on sidearms extending from the main reactor tubing consist of appropriately-sized Ace-Thred threaded connectors, adapters, bushings, and O-rings. Connectors and adapters are borosilicate glass or Teflon FEP; bushings are of Teflon FEP, and O-rings are FETFE.

Reactor pressure relief is provided by a manometer filled with an inert fluorinated vacuum pump oil (the relief pressure is approximately 2 psi or less), or an adjustable low pressure check/relief valve (adjustable to 3-50 psi). The reactor effluent is vented through a low-pressure check valve; a sample is withdrawn at this point for the analysis system. A water-

cooled condenser removes condensable liquid (water and acid mist) prior to venting the remainder of the reactor effluent.

4. Flue Gas Conditioning and Analysis System

The flue gas conditioning and analysis system (Figure 2) consists of a refrigerated gas dryer, a vacuum/pressure sample pump, four analyzers with rotameters and associated equipment (two pumps, an accumulator, and an ozone scrubber are used with the NO_x analyzer), back pressure control valve, rotameter, and gauge used on the sample bypass line. The refrigerated dryer dries the gas sample by cooling it to a dew point of about 40 °F. The sample pump and back pressure control valve are used to maintain adequate pressure for proper operation of the analyzers.

5. Data Recording System

The data recording system (not shown in the diagram) records up to 18 channels of data. Trend graphs of key channels are plotted at frequent intervals, and digitized data points from all of the channels are printed in numeric form at less frequent intervals. Logged data include mass flow rates of individual component gases, temperatures of the reactor zones, and the gas component concentrations from the gas analyzers. Other temperatures, such as the humidification/gas preheater coil outlet temperature and the refrigerated gas dryer outlet temperature, were recorded manually.

EXPERIMENTAL PLAN

Task 1. Catalyst Screening Tests

Task 1 consisted of construction and start-up of a catalyst test unit, and acquiring and testing the catalysts. As described in the previous section, CONSOL constructed a catalyst test unit suitable for screening candidate catalysts for NO and SO₂ oxidation activities using a range of simulated flue gas composition representing wet-scrubbed Illinois combustors and wet-scrubbed combustors firing Illinois coal. Unit design and operating conditions will be finalized after consultation with the catalyst manufacturer. The catalyst manufacturer selected for screening ten candidate catalysts with potential for high NO oxidation activity and low SO₂ oxidation activity.

CONSOL conducted a catalyst screening program to identify a catalyst capable of oxidizing at least 50% of the NO to NO₂ while oxidizing 5% or less of the SO₂ to SO₃ (revised from 1% or less, based on catalyst manufacturer recommendations) under typical coal-fired flue gas conditions, with low-NO_x burners. The extents of NO oxidation and SO₂ oxidation were determined at a range of temperatures, space velocity, and flue gas composition. It is important that oxidation of SO₂ to SO₃ be minimized. Excessive SO₃ concentrations could result in formation of a corrosive sulfuric acid mist downstream of the catalyst in a boiler. SO₃ condensation could be alleviated by increasing the temperature in those sections of the boiler; however, this would result in loss of efficiency.

The laboratory catalyst test unit (Task 1) was sized to provide meaningful results from a large number of catalysts in a relatively short period of time based on catalyst manufacturer recommendations.

The reactivity and selectivity were determined at several NO and SO₂ concentrations, space velocities, and temperatures. The flue gas temperature was varied between 300 °F (to simulate catalyst installation between the air preheater and the scrubber) and 600 °F (to

simulate catalyst installation between the economizer exit and the air preheater inlet). All tests were performed at approximately atmospheric pressure.

Two catalysts were selected for long-term tests in Task 2 using the same test unit as that used in Task 1.

The original test strategy was to screen all catalysts at one test condition, and select the best ones for more extensive testing. However, initial tests showed that SO₂ oxidation was higher than expected. The testing strategy for screening the catalysts was modified for more efficient testing. The modified strategy included determining NO oxidation as a function of temperature in the absence of SO₂. The temperature then was held at the point of maximum NO conversion, and SO₂ was added to the flue gas. The NO oxidation in the presence of SO₂, and the SO₂ oxidation, were then measured. Also, during the initial tests sulfuric acid condensation was a major problem. The initial tests showed that water vapor was not important to the NO or SO₂ oxidation reactions, so humidification of the gas was discontinued to avoid acid condensation in the test unit.

Task 2. Catalyst Stability Tests

Originally, two to four catalysts were to be selected for 1-week stability (deactivation) tests to provide a more demanding test for the most promising catalysts. The effect of boiler cycling was to be simulated by three to five heat up/cool down cycles during the test. However, the catalyst manufacturer advised that not much would be learned about catalyst stability from 5 cycles. They suggested that a series of 24-hour tests be performed without SO₂ for the first 4 hours to condition the catalysts. Two catalysts were used in these long-term tests.

Based on the stability test results, one or more catalysts were to be recommended for testing at a larger scale to verify catalyst performance under actual coal-fired conditions. Coal flue gas contains particulate matter and trace elements that cannot be practically simulated in a laboratory unit. However, because none of the test catalysts satisfied the criteria of oxidizing at least 50% of the NO to NO₂ while oxidizing 5% or less of the SO₂ to SO₃, a large scale test is not justified until a suitable means of handling the high SO₃ production is found.

Task 3. Process Economic Evaluation

A process economic evaluation for a conceptual full-scale process is not justified until a suitable means of handling the high SO₃ production is found.

RESULTS AND DISCUSSION

CATALYST SCREENING TESTS

Summary

CONSOL conducted screening tests of ten catalysts supplied by a commercial catalyst manufacturer. A total of 33 test runs were performed, with test durations ranging from about 6 hours to more than 24 hours. The following table lists the manufacturer's designations for the catalysts tested:

<u>Catalyst</u>	<u>Manufacturer's Designation</u>
1	18,753-13-1
2	18,753-13-4
3	18,636-17-5
4	18,838-37-2
5	18,836-37-3
6	18,836-37-4
7	18,836-37-5
8	18,923-28-3
9	18,923-28-6
10	18,923-29-2

The catalysts are proprietary to the manufacturer.

In the absence of SO₂, all of the catalysts tested exhibited some degree of activity for oxidation of NO to NO₂ over the temperature range 350-600 °F at the conditions tested (10,000 hr⁻¹ space velocity, 1000 ppmv NO, 2000 ppmv SO₂, 5 vol % O₂, 12 vol % CO₂, and 0-6 vol % H₂O). Catalysts 1,2,3, and 4 met the target of 50% or greater conversion of NO without SO₂ in the gas. Performance with each catalyst depended on temperature; most catalysts gave the highest NO conversions in the 400-450 °F temperature range.

The presence of SO₂ inhibited catalytic NO oxidation by an unidentified mechanism. This occurred regardless of the catalyst's activity for SO₂ oxidation. Possible mechanisms for the observed results are: (1) competition of the two species for catalyst active sites, or (2) subsequent reduction of NO₂ by SO₂, either on the catalyst surface or in the gas phase. This latter reaction is thermodynamically favored at the temperatures used.

Most of the catalysts showed moderate to substantial conversion of SO₂ to SO₃ at the test conditions. This reaction was dependent on space velocity and temperature. In the absence of NO, oxidation of SO₂ to SO₃ still occurred

Neither the NO oxidation nor the SO₂ oxidation reactions were dependent on the presence of water vapor in the gas stream. With 6% water vapor in the gas, the SO₃ formed was deposited on tubing surfaces downstream of the reactor as sulfuric acid condensation. Without water vapor in the gas (and with NO in the feed gas), the SO₃ formed was deposited as a white, solid, sulfur-nitrogen compound that would eventually plug the system.

The catalyst tests are summarized in Table 1. A description of the tests follows.

Initial Catalyst Tests, CA-1 to CA-10

In initial tests with the first three catalysts, it became apparent that the oxidation of sulfur dioxide to sulfur trioxide could be extensive (up to 90%). With humidification of the gas stream to 6% water vapor, sulfuric acid condensation was a major problem. The oxidation of NO to NO₂ was low (25% or less) under these conditions. A variety of tests were completed to understand the observed phenomena. A test performed without NO (test CA-4) showed that SO₂ oxidation did not require the presence of NO in the feed gas. In the same test, decreasing the oxygen concentration to a low value (0.3%) decreased, but did not eliminate, the sulfur dioxide oxidation in the absence of NO. In the absence of SO₂, the oxidation of NO could be up to 60% (CA-3, CA-7 to 9). The oxidation of NO and SO₂ depended on temperature. In these tests, maximum NO oxidation occurred between 400 and 500 °F, while maximum SO₂ oxidation occurred above 550 °F. NO and SO₂ oxidation were not dependent on the water concentration in the gas.

Because the water vapor content was not important to either oxidation reaction, humidification of the gas was discontinued after run CA-7 to avoid acid condensation in the test unit. The testing strategy to screen catalysts was modified to increase test efficiency and to minimize the formation of sulfuric acid deposits in the test unit. The strategy was modified to determine the NO oxidation as a function of temperature and the absence of SO₂. The temperature then was held constant at maximum NO conversion, and the SO₂ was added to the flue gas. The NO oxidation in the presence of SO₂ and the SO₂ oxidation were measured.

After reviewing the results from tests CA-1 through CA-10, the catalyst manufacturer fabricated four new catalysts with formulations designed to reduce the SO₂ oxidation.

Improved Formulation Catalyst Tests, CA-11 to CA-20

Two of the new catalysts (4 and 5) gave results similar to the earlier catalysts, i.e., the SO₂ oxidation was substantial (20% to 80%, CA-11, 14, 15). However, the other two catalysts (6 and 7) showed substantially lower SO₂ conversions, about 10% (CA-12 and 13). All four catalysts showed good NO oxidation activity in the absence of SO₂, ranging from 35% to 54% oxidation at 450 °F. However, the presence of SO₂ reduced the NO oxidation to 15% to 45%. The two low-SO₂-oxidation catalysts, 6 and 7, showed NO oxidation activity of 37% and 17%, respectively, at 450 °F. An attempt to increase NO oxidation was made in CA-19 and CA-20 by using catalysts 6 and 7 in series in the reactor, thus decreasing the space velocity from 10,000 hr⁻¹ to 5,000 hr⁻¹. However, the decreased space velocity had the effect of increasing SO₂ oxidation to 20% to 55%.

Overnight Catalyst Tests, CA-21 to CA-26

Several catalyst tests of 20-24 hours duration were attempted based on the recommendation of the catalyst manufacturer, who indicated that additional time for catalyst conditioning would improve the catalyst performance. They recommended 4 hours without SO₂ followed by 8 or more hours with SO₂ in the feed gas. A number of operating difficulties were encountered, including the formation of an unidentified white solid that plugged the analyzer gas lines downstream of the reactor, and a broken thermocouple well that resulted in temporary loss of catalyst bed temperature control. The white solid is discussed in another section of this report; it appeared to be the product of reaction between NO_x and SO₂ or SO₃.

Although the catalysts were expected to perform better after conditioning, the opposite effect was observed. For example, in test CA-22 the NO oxidation was 31% after three hours, just prior to the introduction of SO₂. After 13 hours with SO₂ in the gas, the NO and SO₂ oxidations were 37% and 26%, respectively; 8 hours later, the NO oxidation had fallen to 8% while the SO₂ oxidation was essentially unchanged. This behavior was typical of the long-term tests.

Final Catalyst Tests, CA-27 to CA-33

Three more catalyst formulations were made by the catalyst manufacturer in an attempt to come up with a suitable catalyst. These catalysts were formulated for maximum NO conversion at a higher temperature than the previous catalysts. The hope was that oxidation would proceed faster at the higher temperature. The results for these catalysts, however, were similar to the earlier catalysts. The maximum NO conversion, occurring at 500 to 550 °F, was 34% to 39% without SO₂, but only 16% with SO₂. The SO₂ conversion was only 4% for two of these catalysts.

Blank Runs, CB-1 to CB-3

Three runs were made using catalyst substrate blanks to insure that the substrate was not interfering with the tests. For all three tests, NO and SO₂ oxidation were zero.

Problems Encountered

There were several start-up difficulties. The oil bath and NO mass flow controller and two gas-supply regulators failed. The oil bath was replaced with powerstat-controlled heating mantles, which generally simplifies the equipment. Spare regulators were used for the gas supplies. The mass flow controller was repaired under warranty. The manufacturer indicated that failure occurred because a plastic component was inadvertently used instead of a stainless steel one. It had failed after only about 4 days of use with NO. While the flow controller was being repaired, a rotameter and flow valve combination was substituted.

At low gas flow rates, there was insufficient pressure to push the condensate through the refrigerated gas dryer drain valve. An aspirator was added to the automated condensate drain to enable operation at low gas flow rates, and the drain valve was replaced with a valve with timed settings.

The blower and cooling shroud did not adequately regulate cooling on the lower part of the quartz reactor. Therefore, they were replaced by another system consisting of coiled Teflon tubing through which an adjustable flow of cooling water was circulated. The cooling water flow rate was controlled by an automatic valve with an adjustable timer.

An early hindrance to successful operation of the unit was the presence of an unidentified liquid that condensed in the system. The liquid seemed to originate in, or be associated with, the NO supply cylinder. A filter trap in the supply line resolved this problem.

Without water vapor in the flue gas, a reaction between NO_x, SO₂, and SO₃ caused the formation of a white, solid compound in the tubing downstream of the reactor. Eventually, the solid would plug the tubing and force the shutdown of the overnight tests prematurely. To combat the formation of the solid, dry nitrogen was added to the reactor effluent gas to dilute the reactants. The percent dilution was calculated and adjusted based on the oxygen and carbon dioxide concentrations in the flue gas stream. This method slowed down the rate of deposition enough to increase the operating time and enable the overnight tests to be completed.

Some attempt was made to identify the white solid compound. The material generates brown NO₂ gas upon contact with water. Analysis of the resulting solution using ion chromatography showed the presence of nitrate, nitrite, and sulfate, but no sulfite. An infrared spectroscopic analysis of the material was inconclusive. Because SO₃ has an affinity for electrons and NO and NO₂ can easily lose them, the material is probably a molecular Lewis acid/base complex, or an ionic complex of nitronium (NO₂⁺) and nitrosonium (NO⁺) ions and SO₃.

CONCLUSIONS AND RECOMMENDATIONS

The concept of catalytic in situ oxidation of NO to NO₂ was successfully demonstrated. Several catalysts achieved the target 50% of NO to NO₂, in the absence of SO₂. Unfortunately, some of these catalysts were unable to oxidize a sufficient percentage of the NO when SO₂ was present in the gas. The remaining catalysts also oxidized a substantial amount of SO₂ to SO₃, which can raise the acid dew point and cause corrosion in power plant ducts and air heaters.

The following are recommended:

- Since the concept of catalytic oxidation of NO was successful, catalyst development should be directed to suppressing SO₂ oxidation.
- Alternatively, a method of enabling power plants to cope with the high SO₃ concentration could be explored. For example, the cost of retrofitting duct work and air heaters for high corrosion resistance could be explored. Also, dry injection of an alkali metal oxide, carbonate, or hydroxide to react with the SO₃ might be investigated.
- The chemistry of NO_x and SO₂/SO₃ interactions could be explored to find out why SO₂ suppressed NO oxidation for some catalysts.

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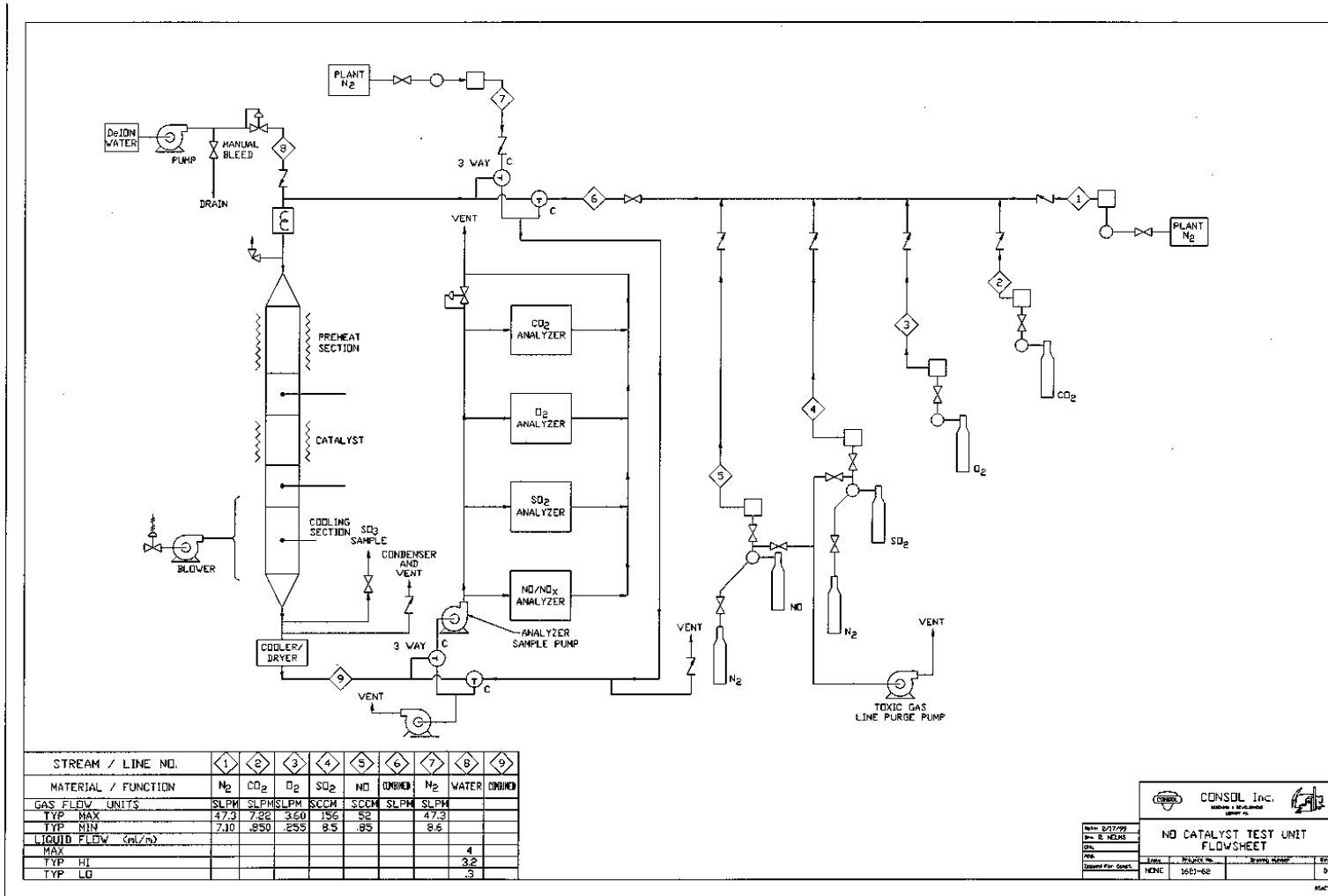
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			450							46	
			500							37	
			550							32	
			600							24	
			450	0	12	5	1000	2000	10	45	67
CA-15	4	01/03/00	450	0	12	5	1000	0	10	45	
			450	0	12	5	1000	2000	10	40	81
CA-16	3	01/05/00	350	0	12	5	1000	0	10	39	
			400							50	
			450							53	
			500							43	
			550							23	
			600							24	
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			600							16	72
CA-17	3	01/06/00	450	0	12	5	1000	0	10	50	
			600							31	
			450	0	12	5	1000	2000	10	24	51
CA-18	4	01/10/00	350	0	12	5	1000	0	10	34	
			400							50	
			450							54	
			500							50	
			550							41	
			600							12	
			450	0	12	5	1000	2000	10	45	60
			600							22	79
CA-19	6/7	01/28/00	350	0	12	5	1000	0	5	26	
			400							44	
			450							38	
			500							26	
			450	0	12	5	1000	2000	5	33	55
CA-20	6/7	02/01/00	450	0	12	5	1000	0	5	46	
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CA-21	6/7	02/03-04/00	450	0	12	5	1000	0	5	42	
			450	0	12	5	1000	2000	5	17	32
CA-22	6/7	02/07-08/00	450	0	12	5	1000	0	5	31	
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CA-23	6/7	02/09-10/00	450	0	12	5	1000	0	5	15	

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CA-24	4	02/10-11/00	450	0	12	5	1000	0	10	25	
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CA-24R	4	03/02-03/00	450	0	12	5	1000	0	10	22	
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CA-25	4	03/07-08/00	450	0	12	5	1000	0	10	23	
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CA-26		03/14-15/00		0					10		
CA-27		03/15/00		0					10		
CA-28	2	03/29/00	450	0	12	5	1000	2000	10		
CA-29	8	04/05/00	400	0	12	5	1000	0	10	21	
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CA-32	10	04/10/00	350	0	12	5	1000	0	10	13	
			400							15	
			450							23	
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			600							31	
CA-33	10	04/11/00	550	0	12	5	0	2000	10	4	
			550	0	12	5	1000	0	10	38	
CB-1	Blank Core	10/13/99	350-600	6	12	5	1000	0-2000	10-29	0	0
CB-2	Blank Core	01/04/00	350-600	0	12	5	1000	0-2000	10	0	0
CB-3	Blank Core	01/07/00	350-600	0	12	5	1000	0-2000	10	0	0



STREAM / LINE NO.	1	2	3	4	5	6	7	8	9
MATERIAL / FUNCTION	N ₂	CO ₂	O ₂	SO ₂	NO	COMB	N ₂	WATER	COMB
GAS FLOW UNITS	SLPM	SLPM	SLPM	SCGM	SCGM	SLPM	SLPM		
TYP MAX	47.3	7.22	3.60	156	52		47.3		
TYP MIN	7.10	.250	.255	8.5	.85		8.6		
LIQUID FLOW (mL/m)									
MAX							4		
TYP HI							3.2		
TYP LB							.5		

CONSOL Inc.		NO CATALYST TEST UNIT FLOWSHEET	
Rev: 2/17/99	Drawn: R. NEJRS	Checked: R. NEJRS	Scale: 1:1
Proj: 100000000	Sheet: 16	Scale: 1:1	Scale: 1:1
Design: R. NEJRS	Checked: R. NEJRS	Scale: 1:1	Scale: 1:1
Approved For: None	Scale: 16E1-ES	Scale: 1:1	Scale: 1:1

Free Flow et NO Oxidation Catalyst Test Unit.

figure 1.10 she for

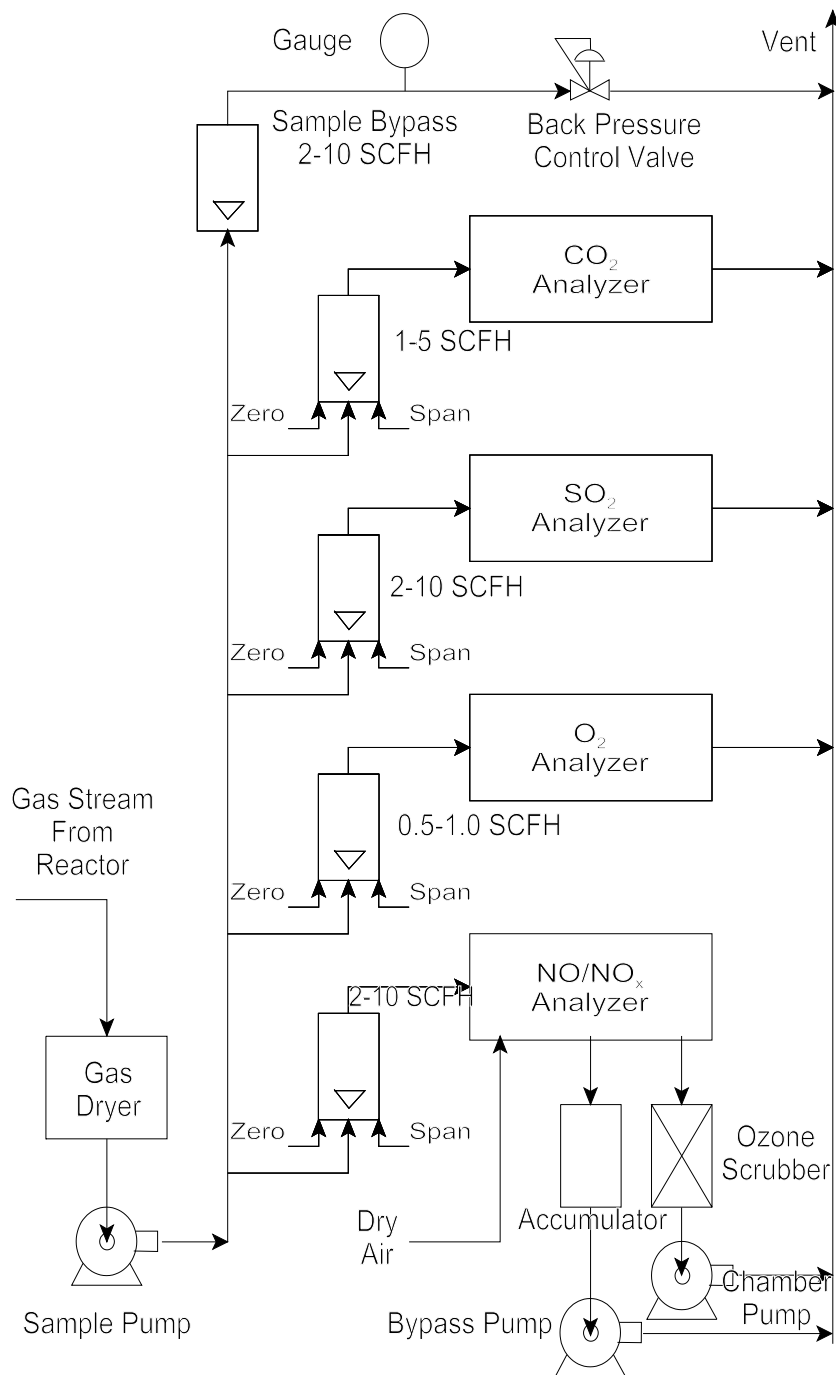


Figure 2. Diagram of Analyzer Subsystem.