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NONCATALYTIC AMMONIA INJECTION FOR NO_x REDUCTION ON A WASTE WOOD FIRED BOILER

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1.0 INTRODUCTION

In 1983 the Procter and Gamble Manufacturing Plant in Long Beach, California (P&G) installed and began to operate a boiler designed to burn industrial waste wood. This unit, designated #4 Boiler, is rated at 200x10^6 BTU per hour heat input. The boiler supplies the steam needs of the plant, including a 13.5MW generator which produces electricity for sale to the local utility. The boiler is designated a "resource recovery project" as defined in California Health & Safety Code Section 42314. At initial start-up, the boiler could not meet the permitted emission levels for NO_x or particulates.

This paper describes the successful application of Exxon Research & Engineering Co. (ER&E Co.) Noncatalytic Thermal DeNO$_x$ for control of NO_x (nitric oxides) and includes information on effects of Noncatalytic Ammonia Injection on particulate, carbon monoxide (CO), and system corrosion.

1.1 Background

After the boiler start-up, it became evident that the nitrogen content of the waste wood fuel was greater than what our earlier tests and technical literature indicated. The higher than expected nitrogen content in the waste wood fuel caused NO_x emissions to exceed the permit limit. (Reference 1)

A program to understand and control wood fuel properties and their effect on NO_x was initiated. The result of the combustion work and the fuel science work, defined operating conditions that reduced NO_x but was not sufficient to always insure that #4 boiler could operate below a 225 PPMv NO_x level (15 minute average).

Option studies provided a strong technical basis for installation of Noncatalytic Thermal DeNox, a wet electrostatic precipitator and continuous emission monitoring (CEM) for NO_x, CO, and O_2, to assure operation within permitted emission levels. This equipment was installed, and #4 boiler is now operating in full compliance with all permit conditions.

2.0 Present Wood Boiler System Design

Hogged wood is received by truck from several suppliers. It is dumped and the wood is conveyed to a classifier where the oversized pieces are rejected. The wood is then transferred to a large enclosed storage bin and then is conveyed to the boiler by an enclosed belt conveyor. The wood fuel is delivered into the boiler furnace via three wood screws. The boiler is a Foster Wheeler field erected unit with a fixed pinhole grate and spreader stoker.

The boiler has a grate heat release and a furnace heat release of 1,000,000 BTU/ft^2/hr. and 21,000 BTU/ft^3/hr. respectively. Extensive boiler combustion air flow modeling was conducted by Foster Wheeler, to insure that BACT design would be applied to this unit to minimize HC and CO emissions. The air flow modeling concentrated on the overfire air port locations and flows to promote complete combustion.

Flue gas leaves the furnace, passes through the superheater, generating bank, economizer and air heater. The post combustion treatment of the flue gas is comprised of a multiclone, prequench chamber, and a wet electrostatic precipitator. In addition to the particulate control equipment, ammonia is injected into the upper furnace to reduce the emissions of NO_x. Figure 2.1 illustrates the general arrangement of the wood burning process.

3.0 Control of Nitric Oxides

Initial technical review showed that Noncatalytic Thermal DeNO$_x$ offered the best value approach to NO_x control. Selective catalytic reduction was considered and ruled out for economic and operational reasons. The basic chemical reaction is $NO + NH_3 + O_2 + H_2O + (H_2) \quad N_2 + H_2O$.

3.1 Temperature Profiling

Noncatalytic Thermal DeNO$_x$ Ammonia Injection is only effective within a limited temperature range of 1600°F to 2000°F. Since the location of the required temperature window was unknown, a comprehensive temperature profiling of the boiler's furnace was undertaken. Most large, field erected steam boilers are mono tube wall construction, which is a continuous wall made up of water tubes joined by a membrane. This type of boiler wall construction encloses the furnace area where the temperature profiling activity would be conducted. The typical approach for penetrating a furnace of this design, to profile the flue gas temperatures, would be to use existing access ports and install bent tube openings in the mono tube wall such that acceptible volumetric coverage could be achieved.

The existing access ports were totally inadequate in number and location. Further, the installation of numerous bent tube openings would cost tens of thousands of dollars with no guarantee that these penetrations would later be utilized as NH_3 injection ports. At this point P&G and Sierra Environmental Engineering (Sierra) designed a unique watercooled, shielded, aspirated thermocouple probe. The probe can be inserted between the existing mono wall tubes after removing a small section of mono tube wall membrane where the tube to tube clearance is one inch. In essence, a thermal probe was designed for an inexpensive boiler wall penetration in lieu of using a standard, greater than 2" diameter, thermal probe where much larger penetrations are necessary. This unique probe allowed for low cost penetrations to be made at practically any location and easily welded up when that location was no longer needed.

Figure 3.1 is an excerpt from the boiler side elevation print and a typical temperature distribution. The figure presents the location and orientation of the boiler wall penetrations used to insert the probes into the furnace. Odd port numbers are on the east side of the boiler, and even port numbers are on the west side.

The effective length of the thermal probe was five feet; therefore, only half of the ten foot wide furnace could be profiled at one port location. It was found early in the testing that temperature symmetry existed at each port elevation.

Temperatures in the $DeNO_x$ requirement range of 1600°F to 2000°F were found in the upper furnace cavity. Depending on boiler operating conditions, the optimum temperature region varied in location from 6 ft to 8 ft below the plane of the boiler arch to 8 ft to 10 ft above the plane of the arch. A significant finding is that the measured temperature window was found in the furnace cavity region and not within the superheater tube section. The potential for improved mixing and sufficient reaction residence time is better in the furnace cavity.

3.2 Demonstration Ammonia Injection System

After temperature profiling, the next step undertaken was to design and construct a full scale experimental ammonia injection system. The experimental ammonia injection system provided the capability to inject up to 70 #/hr of NH_3 into the boiler furnace. Typically when working with ER&E Co., a test temperature profile is given to ER&E Co. who in turn models the unit and produces a design package for installation. P&G was under schedule pressures and used the experimental test data on the permanent ammonia injection system, such as the optimum number of nozzles, nozzle elevations, nozzle size, NH_3 flow(s), carrier fluid preference and carrier flow(s). P&G also purchased a design $DeNO_x$ package from ER&E Co. Predictions from this package on temperature distribution and injection configuration supported our empirical data gathered during temperature profiling and experimental NH_3 injection testing. Once the experimental phase was completed, nonapplicable hardware and piping was removed and replaced with a properly designed permanent system.

3.3 Effectiveness of NH_3 Injection on Reducing Nitric Oxide Emissions

The ammonia injection ($DeNO_x$) system is a success. The ammonia injection system on this boiler significantly reduces NO_x emissions. The testing demonstrated that front wall nozzles and the molar ratios presented on Table 3.1 can be utilized to reduce NO_x well below the Rule 475 prohibitory level of 225 PPMv at 3.0% O_2 at any tested operating condition of load, boiler outlet O_2, undergrate air ratio and during grate cleaning. The NH_3 injection effectiveness is not sensitive to wood fuel type.

Long term test run data was obtained by setting up four different molar ratios on the ammonia system and allowing the system to operate at this fixed molar ratio for several days. The purpose of the long term run was to evaluate the ability of the ammonia injection system to control NO_x emissions on a day-to-day basis during normal operating conditions.

The system was left unattended, except for safety checks and minor readjustments of the ammonia flow setpoint. During each run the following parameters were continually monitored and recorded: boiler steam load, ammonia flow, NH_3:NO_x molar ratio and NO_x concentration at the stack. The average boiler load over the test period was 140,000 #/hr. Data during upset conditions such as, the gas burner in service, or very low load due to a jammed wood feed screw, etc. were excluded from the analysis of the long term data.

The NO_x concentrations and NH_3:NO_x molar ratios reported in Figures 3.2 and 3.4 were measured on a continuous basis and represents the overall average of several hundred 15 minute running averages. They were recorded over a minimum of 153 hours of continuous operation at each molar ratio setting.

At a base line steam load of 140,000 #/hr, NH_3 injection through nozzles on the front wall can reduce NO_x emissions approximately 55% at a 2:1, NH_3:NO_x molar ratio, as presented in Figure 3.2. Figure 3.2 also shows that the change in efficiency of Thermal $DeNO_x$ is relatively strong at molar ratios up to 0.5. Above 0.5 molar ratio the change in NO_x reduction is not as dramatic. For example, at 0.4 molar ratio the NO_x reduction is 35%, while at 3.0 ratio the reduction is 70%. Figure 3.4 presents the average NO_x concentration in PPMv at 3.0% O2 (dry basis) versus NH_3:NO_x molar ratio that was measured during the continuous long term test run. The actual emission reduction of the NO_x was from 330 ppm to 200 ppm at an injection rate of 10 # NH3/hr. or 0.5 molar ratio. Ammonia injection of 40 # NH3/hr or 2.0 molar ratio, reduced the NO_x emission to 150 ppm.

At higher molar ratios greater NO_x reductions are achievable, but NH_3 slip (or carryover) increases, as presented in Figure 3.3. The ammonia slip at the boiler outlet is 10 ppm at molar ratios below 2.0. At higher ammonia injection rates, above 2.5 molar ratios, the measured ammonia slip exceeds 40 ppm at the boiler outlet. Ammonia has an extremely high affinity for moisture and very little free ammonia was detected for any injection rate downstream of the wet electrostatic precipitator (stack).

TABLE 3.1

Operational and NO_x Emission Data Summary

Summary of Operational Period

Run #	Operational Period, 1985	Number of 15 minute rolling Avg. Data points	Total Run Time in hours
1	Oct.4-6 & 14-18	711	178
2	Sept. 23-28	610	153
3	Sept. 16-23	784	196
4	Sept. 28-Oct. 4	678	170

Run #	Average NH_3:NO_x Molar Ratio	Average NO_x PPMv (Dry at 3.0% O2 Based on Rolling 15 Minute Averages)	Average Steam Load
1	0.46	210	139
2	1.03	182	140
3	2.12	134	140
4	3.11	103	139

3.4 General Description of Permanent Ammonia Injection Facilities

A 12,000 gallon horizontal vessel was installed for the storage of anhydrous ammonia. The vessel is installed to meet Zone 4 seismic design criteria. It is in a diked area providing 30,600 gallons of containment and protection from flying objects or projectiles. This tank and containment area has a deluge sprinkler system, leak detectors, safety shower and eyewashes to meet safety requirements.

Deliveries are received from an 8000 gallon tanker truck. At the normal expected ammonia usage rate, the truck will refill the tank approximately once per month. All valves on the truck and storage tank are excess flow shut off type to minimize the quantity of spill in the event of a piping or hose break. The ammonia is pumped through a hose into the storage tank with vapor being returned to the tanker truck. The hose couplings are break-away type to minimize the spill quantity. A vaporizer, approximately 15 KW, is included in the system with controls to maintain the storage tank evaporation rate when necessary.

Figure 3.5 presents a simplified flow sheet of the ammonia injection system. Saturated ammonia vapor leaves the 12,000 gallon storage tank at approximately 90 psig and is reduced in pressure across a pressure regulator valve to approximately 75 psig. This pressure regulation prevents condensation downstream and maintains constant pressure to the downstream ammonia flow control valve (FCV). The ammonia flow rate is controlled by a single control valve which follows a control curve based on previous empirical data on NO_x generation versus boiler load. The NH_3 is then mixed with superheated steam at approximately 425°F which is used as a carrier fluid. The steam flow is controlled by a flow control valve within a range of 400 to 1000 #/hr. The system includes a combustion control safety device system to shut off the flow of ammonia in the event the flow of steam (carrier fluid) is lost. Final introduction of ammonia is at one of the multiple levels of injectors on the boiler front wall. These levels provide NO_x control through a wide boiler load range.

3.5 Cost

Full Scale Demonstration System	$240,000
a) Temperature Profiling	
b) Temporary NH_3 storage tank	
c) Carrier fluid piping	
d) NH_3 piping	
e) Boiler modifications	
Permanent System	$560,000
a) 12,000 gallon NH_3 storage tank including 10 inch concrete encasement walls	
b) NH_3 unloading facility	
c) Automatic controls to regulate NH_3 and carrier	
d) Safety shutdown systems	
e) Engineering	
TOTAL INSTALLED COST	$800,000
Annual Operating Cost	
a) NH_3	$ 30,000
b) Steam	$ 20,000

Cost Effectiveness

This system reduces NO_x by approximately 86 tons/year. Using the above cost data, a 10% interest rate and a 15 year life results in an effectiveness of $1790/ton/year or $0.90/lb. of NO_x removed.

4.0 Byproducts and Related Effects Due to NH_3 Injection

4.1 Particulate Emissions

The decision to install the NH_3 injection systems impacted other environmental issues. The concurrent effort to reduce particulate emissions was affected by the NH_3 injection project. Figure 4.1 indicates the history of particulate emissions from the wood-fired boiler. It shows that shortly after the start-up, when the equipment was in its best operating condition and at the time we were able to buy the "best" waste wood available the particulate emission rates were at 13-14 #/hr.

With time, the supply of good construction lumber waste decreased and we started to find an increase in the quantity of processed wood, such as plywood and particle board. This type of waste wood impacted both the NO_x, due to higher nitrogen levels in the waste wood, and the particulate emissions due to increased Na, K, and Cl. By January 1985, it was obvious that the particulate emissions could no longer be controlled by the existing 18" H_2O venturi scrubber and a pilot demonstration of several other technologies was required.

The following were selected to pilot test on a boiler slip stream:

- high pressure drop venturi scrubber
- Hydrosonic scrubber
- baghouse
- wet electrostatic precipitator

The test results from the pilot demonstrations were as follows:

RESULTS OF THE PILOT TEST

Equipment	P (in. H2O)	Emissions (lbs./hr.)
Venturi Scrubber	60	8.0
Hydrosonic Scrubber	45	8.0
Baghouse	6	25.0
Wet ESP	4	8.0

The bag house was not selected owing to its slip stream test results and based on an economic analysis, the wet electrostatic precipitator was selected over the scrubbers. Total capital costs were near parity while the operating costs of the scrubbers were significantly higher than the wet electrostatic precipitator. The final compliance tests were conducted in December, 1986 and the results were as predicted by the pilot test at 8#/hour.

The poor performance from the baghouse was not due to the equipment itself. At the baghouse operating temperature, above 300°F ammonia slip from Thermal $DeNO_x$ and the chlorides present in the flue gas from wood burning pass uncollected through the filter. However, beginning at 250°F and ending at approximately 150°F, which is past the baghouse, the ammonia and the chlorides react and form ammonium chlorides. It was primarily the ammonium chloride which contributed to the large emission rate (25 #/hr) from the baghouse.

Preliminary calculations indicated that at moderate flue gas concentrations, 20-30 ppm HCl and 20 ppm NH_3, these components will be in the vapor phase at 300°F, and above. As the flue gas cools to 250°F, ammonia and chlorides begin to react and ammonium chloride (NH_4Cl) precipitates in a submicronic size white powder and severely affects the visible plume. The presence of an excess of either component will tend to increase the temperature at which the precipitation will begin but the change in temperature is minor (less than 20-30°F). As the temperature further decreases below 250°F, the precipitation continues until one or both of the components is exhausted. Below 180°F the incremental increase in NH_4Cl concentration becomes insignificant, therefore for all practical purposes the reaction is exhausted. Figure 4.3 shows the equilibrium calculations for the ammonia chlorides.

The kinetics of the ammonia and chloride reaction (Figure 4.2) based on actual concentrations in the flue gas from the boiler shows that theoretically ammonia is exhausted at 330°K (135°F). However, for practical purposes, at 360°K (190°F) NH_3 is less than 0.5 PPM; therefore, further precipitation of NH4Cl is not likely.

To avoid the formation of a detached opaque plume, as well as exceedance of the particulate emission limit, the exhaust gas must be cooled to a temperature below 180°F prior to entering the particulate abatement device. This way the precipitation of the ammonium chlorides becomes collectable in the control equipment. A baghouse is not recommended to operate at flue gas temperatures of 200°F and lower because of acidic and water dew-point conditions.

4.2 CO Emissions

A side effect of ammonia injection in this particular boiler was the influence of NH_3 on CO emissions. The CO/NH_3 relationship from Thermal $DeNO_x$ has been reported by Mr. Boyd Hurst ER&E Co., and Dr. R. K. Lyon (reference 2 & 3) and is believed to be due to competition for the OH radical from NH_3 and CO. It was found that when NH_3 was injected into the furnace CO would increase. The increase in CO appeared to be related to a number of variables including injection location, quantity of ammonia injected, excess combustion air, and underfire/overfire air ratio.

An experiment was designed to study the affects of these variables on NO_x and CO using Response Surface Methods and factorial testing. The experimental model consisted of 125 tests at specific operating conditions. In addition, 350 tests, previously conducted, were included in the evaluation.

It was found that each increase in the ammonia rate of 20#/hr. (one molar ratio) resulted in a 25ppm increase in the CO emissions. This relationship was brought to the attention of the SCAQMD and was an important consideration in establishing final NO_x and CO permit limits.

4.3 Metallurgical Considerations

The affect of ammonia injection on the materials of construction within the boiler and associated equipment in contact with flue gas was a concern.

We consulted with a specialist in the field of flue gas chemistry/high temperature corrosion: Mr. Honghi Tran, from Douglas Reeve & Associates. Mr. Tran felt that formation of corrosive ammonium compounds, such as ammonium chlorides, bisulfite, and nitrates, was unlikely based on our flue gas chemistry. The temperature range of concern was 300°F to 800°F, and a series of tests to determine the effects of ammonia injection on corrosion rates of boiler components were recommended.

Metal coupons made from carbon steel, T11, T22, and electrical resistance corrosion probes were installed in four areas: boiler outlet (650°F), economizer (525°F), air heater (400°F), and multiclone (350°F). Also 304SS and 316SS coupons were installed in the original venturi scrubber. The tests were conducted for operating conditions with and without ammonia injection. Results showed no significant difference in the corrosion rates of these metals in any of the above locations.

ACKNOWLEDGEMENT

It is with appreciation that we acknowledge the efforts of Mr. George W. Coates, Engineering Division of the Procter & Gamble Company. Mr. Coates developed and conducted the metallurgy test program in Section 4.3 of this paper.

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(2) Lyon, R. K.: Hardy, J. E. Ind. Eng. Chem. Fundam. 1986, 25, 19.

(3) Lyon, R. K.: Thermal DeNO$_x$, Environ. Sci. Technology, VOL. 21, NO. 3, 1987

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(1) Hurst, B. E. "THERMAL DeNO$_x$ Technology Update", 1985 Joint Symposium on Stationary Combustion NO$_x$ Control, Boston, May, 1985

(2) Hurst, B. E. & White, C. M. "Thermal DeNO$_x$: A Commercial Selective Non-catalytic NO$_x$ Reduction Process for Waste-to-Energy Applications", ASME 12th Biennial National Waste Processing Conference, Denver, June, 1986

FIGURE 2.1

RESOURCE RECOVERY SYSTEM

WOOD-FIRED BOILER

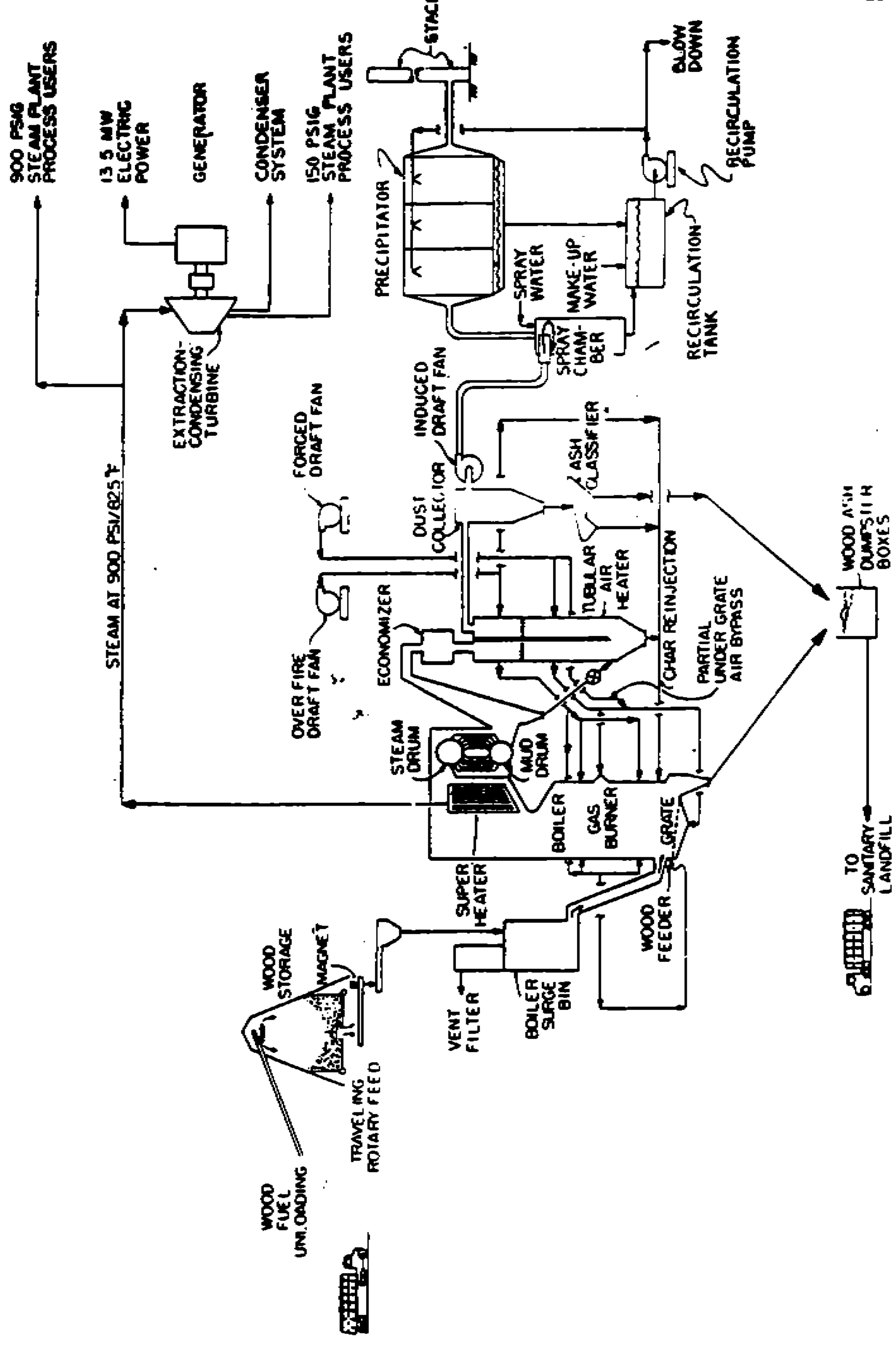


FIGURE 3.1

TYPICAL TEMPERATURE DISTRIBUTION UNDER
NORMAL OPERATING CONDITIONS

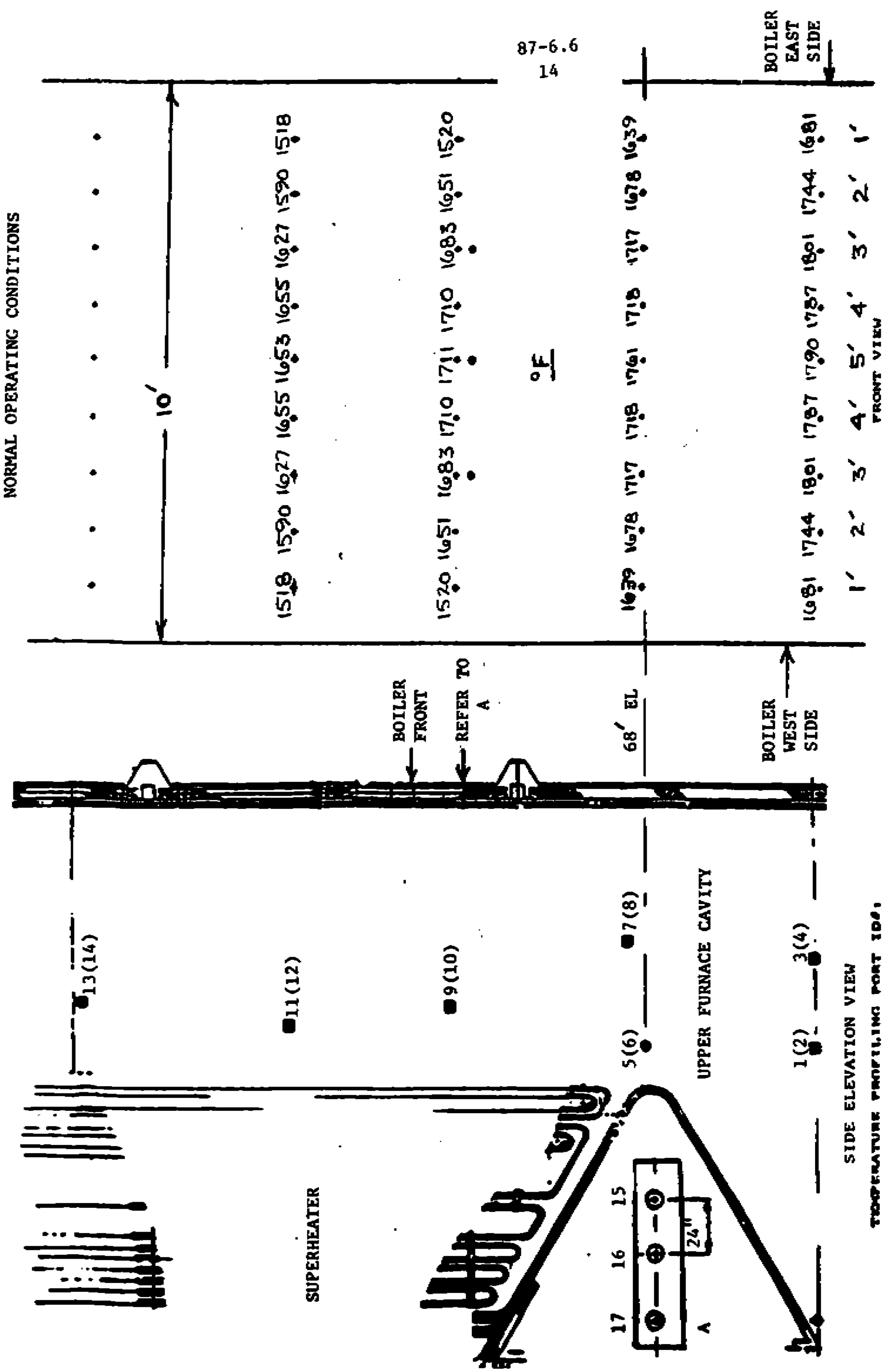
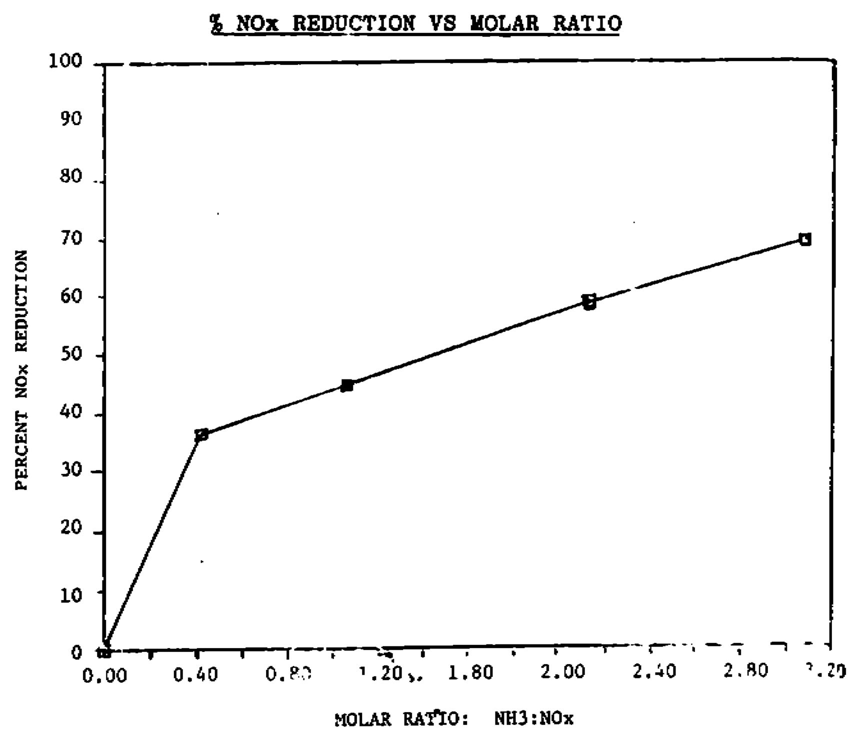


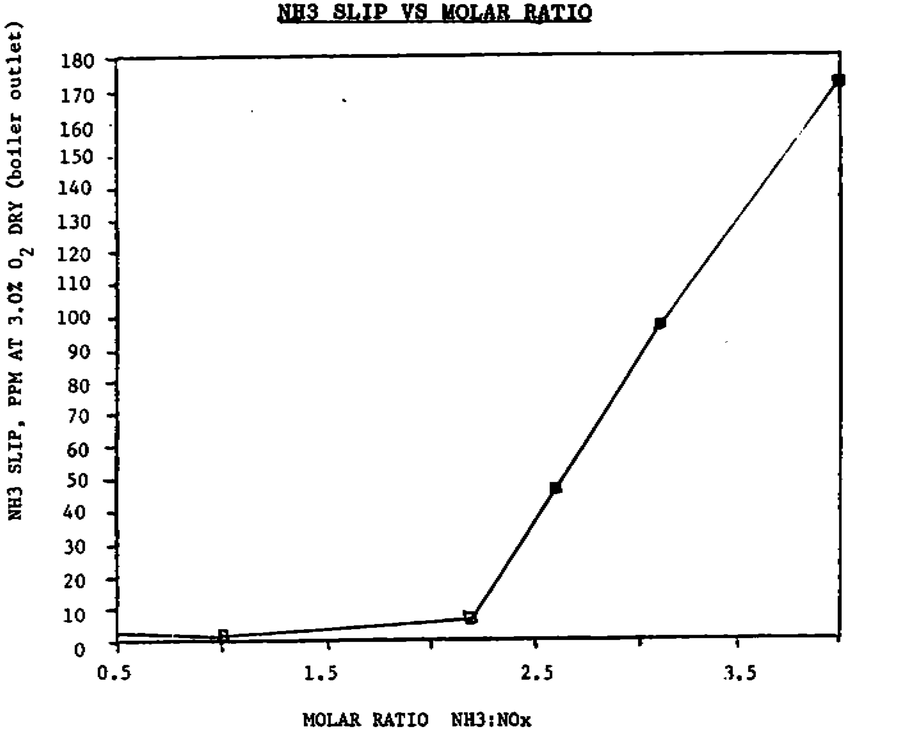
FIGURE 3.2



Percent NOx Reduction versus NH_3:NOx Molar Ratio

FIGURE 3.3

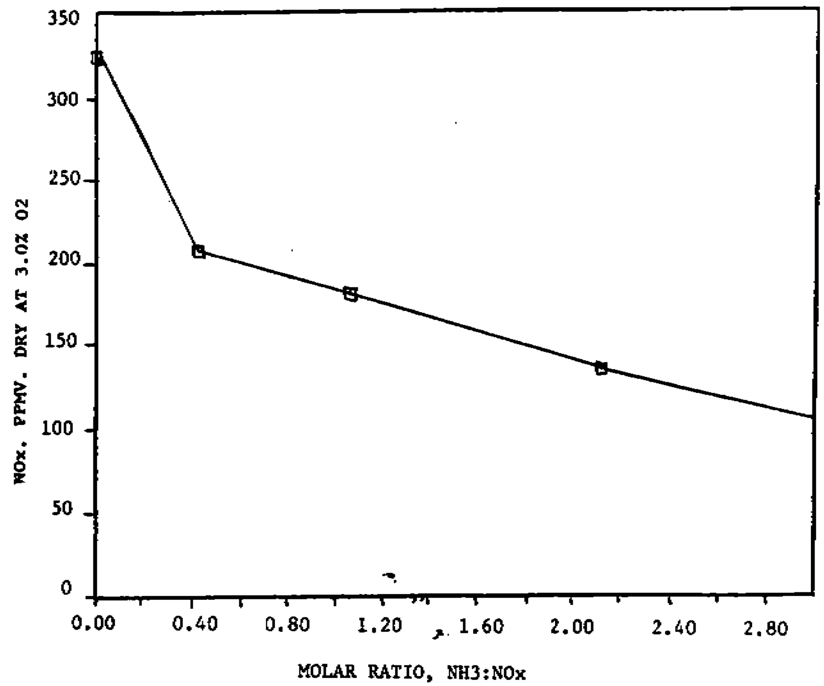
NH3 SLIP VS MOLAR RATIO



Ammonia Slip versus NH_3:NOx Molar Ratio

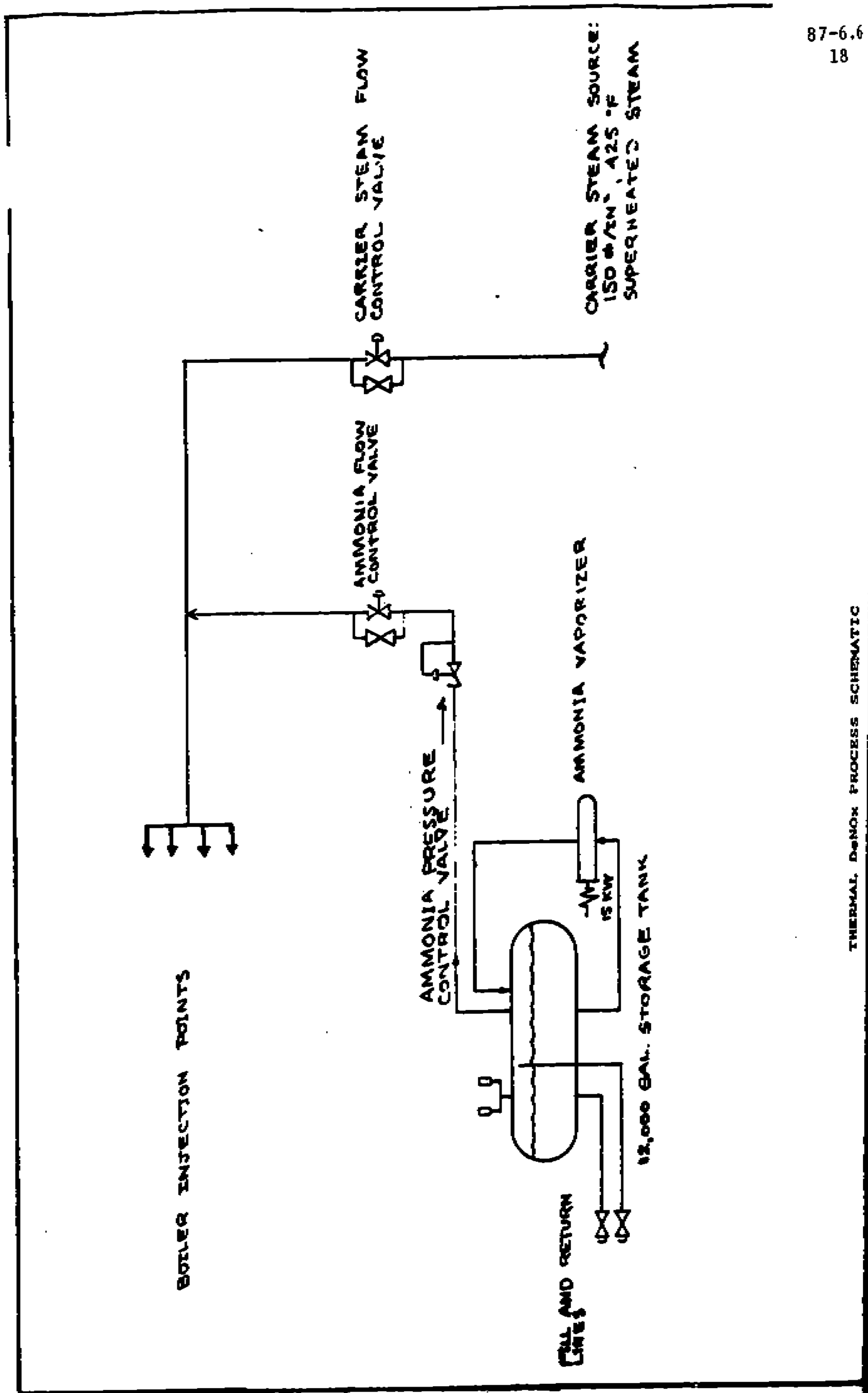
FIGURE 3.4

NOx VS MOLAR RATIO



Average NOx concentration at 3.0% O_2 versus NH_3:NOx Molar Ratio

FIGURE 3.5



THERMAL DeNOx PROCESS SCHEMATIC

FIGURE 4.1

PARTICULATE EMISSIONS - HISTORY

WOOD-FIRED BOILER

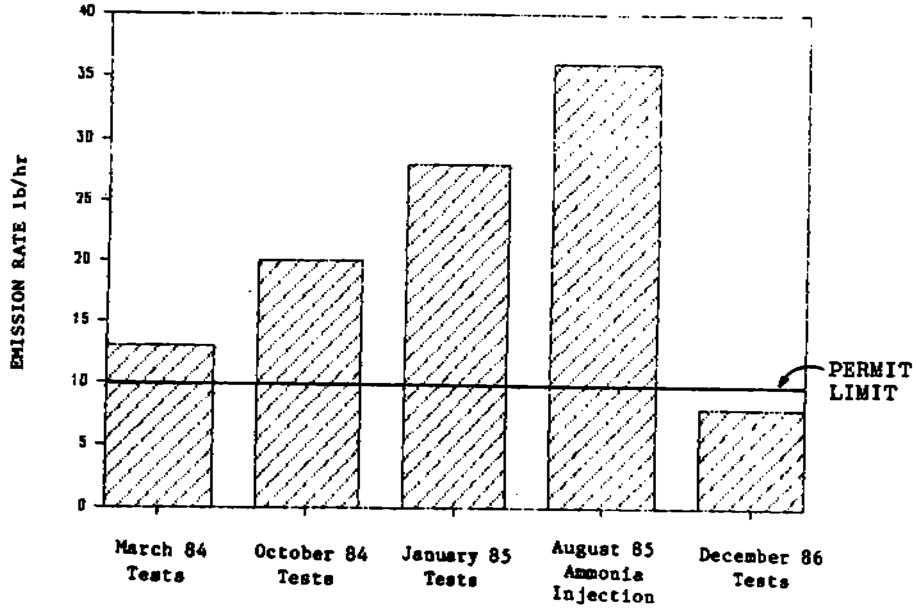


FIGURE 4.2

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FLUE GAS ANALYSIS

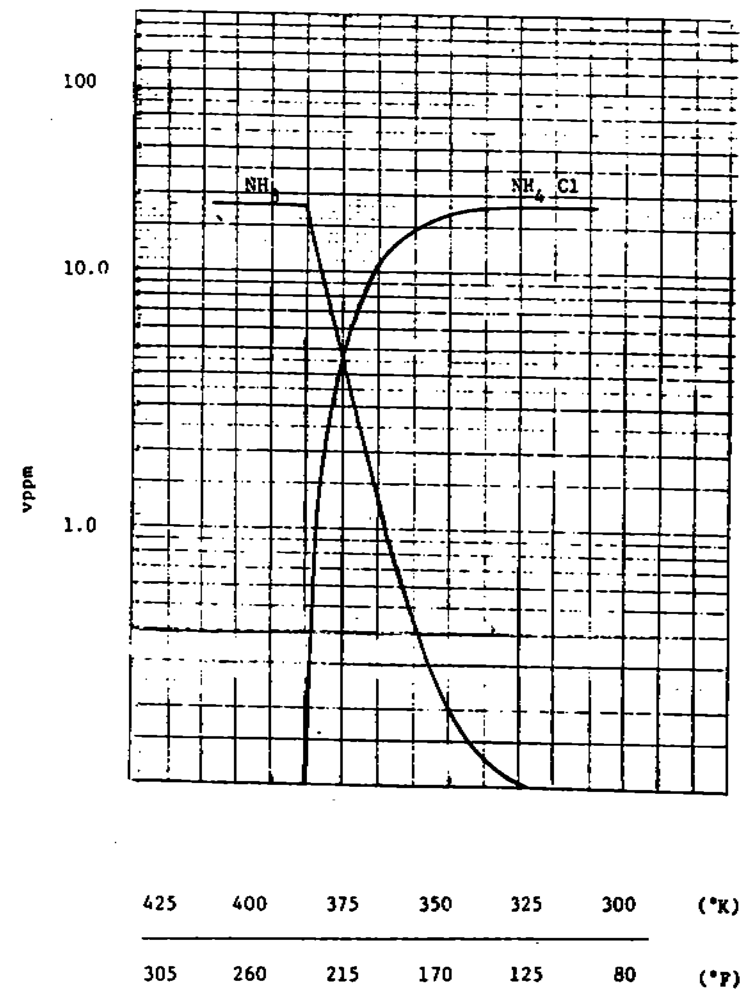

FIGURE 4.3

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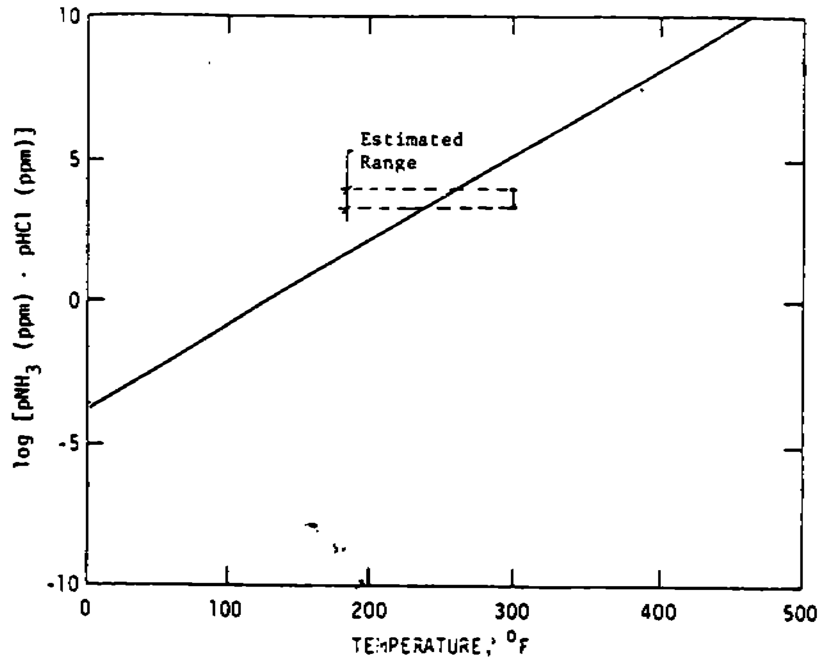

Ammonium chloride equilibrium calculation.

NOTE TO EDITORS