Demonstration of Continuous Monitoring of Ammonia Slip in an SCR System

Technical Report

Demonstration of Continuous Monitoring of Ammonia Slip in an SCR System

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REPORT SUMMARY

The accurate measurement of unreacted ammonia (NH_3), or ammonia slip, is of interest to utilities employing urea- or ammonia-based selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) processes for NO_x control. However, ammonia measurement in utility boiler systems is difficult due to the reactive nature of NH_3, the presence of potential interferences, and the loss of gas phase NH_3 from reactions with ash, chlorides, or SO_3 in the flue gases. Practical and reliable methods to overcome these measurement difficulties have been evolving and only recently appear to have been incorporated into continuous NH_3 analysis. This report documents a continuous ammonia analyzer demonstration project conducted at Orlando Utilities Commission's Stanton Energy Center.

Background

NH_3 slip has important impacts on deposition, plugging and potential corrosion of cold-end equipment located downstream of the SCR or SNCR system. Excessive NH_3 slip can also impact ammonia adsorption by fly ash and can contribute to stack plume and visibility problems. NH_3 slip levels indicate the proper operation of the SCR/SNCR systems and the NO_x reduction process. As a result of these important NH_3 slip effects and the potential application of ammonia-based, post combustion NO_x controls, instrument manufacturers have attempted to provide a continuous analyzer for ammonia in the flue gas stream during the past 20 years. Initial systems were based upon fully extractive sample systems and NH_3 detection using NH_3 and NO_x converters as well as conventional NO_x analyzers. Since that time, modified extractive and in situ analyzers have been developed. EPRI and the Orlando Utilities Commission (OUC) cosponsored a continuous ammonia analyzer demonstration program to assess the current status of analyzer development and applicability to utility boiler systems.

Objectives

- To perform a long-term operating assessment under typical utility boiler conditions in order to determine expected O&M requirements of NH_3 slip monitoring instruments.
- To perform a measurement accuracy assessment comparing the monitor measurements to wet chemical flue gas sampling and analysis techniques.

Approach

OUC's Stanton Energy Center Unit 2—a 450 MWe coal-fired boiler unit equipped with an SCR system for NO_X control—served as the test site. Over the duration of the program from January 1998 to July 2000, investigators, working with the instrument suppliers, installed four analyzer (monitor) systems at the SCR exit or air heater gas inlet test locations and conducted continuous monitoring tests. They installed two analyzers at the beginning of the test program, and two more analyzers following a boiler outage in the spring of 1999. During that outage, an additional layer of catalyst was added to the SCR reactor to compensate for premature catalyst deactivation. Prior to the outage, analyzers operated with relatively high (6-9 ppm) ammonia levels. After the catalyst installation, the analyzers saw normal (1-2 ppm) ammonia levels. Investigators used two criteria in evaluating the ammonia slip monitors—the equipment's long-term reliability under daily operation and its measurement accuracy. Additional research on the wet chemical sampling methods and NH_3 calibration gas issues was also conducted.

Results

Tests of two of the in-situ, tunable, infrared laser-based ammonia analyzers have demonstrated good reliability and accuracy over a long operating period. Both instruments followed the expected trends, given varying SCR operating parameters. At relatively low NH_3 slip levels—1.6 ppm as determined by wet chemical measurements—the measurements from both instruments were within 0.6 ppm. In general, lower NH_3 slip levels posed a greater challenge for the monitors, since the levels became closer to zero and were thus more difficult to distinguish from normal background interferences. This report provides in-depth monitoring results along with a discussion of additional measurement accuracy considerations involving NH_3 calibration gases and the wet chemical sampling methods.

EPRI Perspective

Long-term NH_3 monitoring can be invaluable for evaluating SCR or SNCR system trends on a daily, monthly, or yearly time frame. For example, at Stanton Unit 2, the NH_3 analyzer could be used to evaluate long-term catalyst life and/or overall SCR system operation. Initial NH_3 analyzer operation during this demonstration program showed unexpectedly high NH_3 slip levels. Thereafter, more frequent air heater water washes and confirmation with wet chemical NH_3 measurements indicated premature catalyst deactivation. The degradation in catalyst activity required early addition of another layer of catalyst. An NH_3 analyzer installed at the startup of the SCR would have shown the increase of NH_3 slip, well in advance of the high NH_3 slip effects encountered later. This knowledge would have provided the opportunity to implement countermeasures, such as limestone injection or a change in coal supply, in order to avoid premature deactivation.

In the 1980's, German utilities began to install SCR systems for NO_x control on all of their coal-fired power plants. At that time, reliable and accurate ammonia monitors were not commercially available, so plant operators adopted the practice of measuring ammonia adsorption by fly ash, trending this data over time, and using it as an indirect indicator of NH_3 slip. A recent EPRI study of a range of coals has shown that ammonia adsorption by Powder River Basin (PRB) fly ash is not a good indicator of NH_3 slip. For PRB-fired units, in particular, the continuous ammonia monitor is likely to prove an invaluable tool for SCR operation in the United States.

Keywords

Ammonia
Monitoring
Selective catalytic reduction

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ABSTRACT

A continuous ammonia analyzer demonstration project was conducted at Orlando Utilities Commission's Stanton Energy Center. Unit 2 served as the test site. It is a 450 MWe coal-fired unit equipped with a selective catalytic reduction (SCR) system for NO_x control. During the test program, both relatively high and normal ammonia (NH_3) slip levels were obtained from the SCR exit location. Initial analyzer operation was conducted with relatively high (6 to 9 ppm) ammonia levels, followed by a more recent period of lower or normal (1 to 2 ppm) NH_3 slip SCR operation. Addition of another layer of catalyst in the SCR was responsible for the change in NH_3 slip levels during the program.

A number of analyzer manufacturers were invited to participate in the program. Four analyzer systems were installed at the SCR exit or air heater gas inlet test locations. This report describes the results for two of these analyzers that were operating under relatively high slip levels and for three of the analyzers that were operating with low NH_3 slip levels.

The monitors were evaluated by two criteria: the analyzers' long-term reliability and daily operation, and the analyzers' measurement accuracy. The long-term operating assessment was intended to demonstrate acceptable operation and maintenance requirements of the instruments, while operating under typical utility boiler conditions. The measurement accuracy assessment compared the analyzers' measurements to wet chemical flue gas sampling and analysis techniques for both higher and lower NH_3 slip level test periods.

Two *in situ* analyzers that utilize tunable infrared lasers demonstrated good reliability and accuracy. Both instruments followed the expected trends of the SCR process. At NH_3 levels of 1.6 ppm (wet chemical determination), the instrument readings were within ±0.6 ppm.

Additional measurement accuracy considerations involving NH_3 calibration gases and the wet chemical sampling methods are also discussed in the report.

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INTRODUCTION

The accurate measurement of unreacted ammonia (NH_3), or ammonia slip, is of interest to utilities employing urea- or ammonia-based selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) processes for NO_x control. NH_3 slip has important impacts upon deposition, plugging and potential corrosion of cold-end equipment located downstream of the SCR or SNCR system. Excessive NH_3 slip can also impact ammonia adsorption in the fly ash and can contribute to stack plume and visibility problems. The levels of NH_3 slip also indicate the proper operation of the SCR/SNCR systems and the NO_x reduction process.

As a result of these important NH_3 slip effects and potential application of ammonia-based, post combustion NO_x controls, means to provide a continuous analyzer for ammonia in the flue gas stream have been attempted during the past 20 years. Initial systems were based upon fully extractive sample systems and NH_3 detection with NH_3 and NO_x converters and conventional NO_x analyzers. Since that time, modified extractive and *in situ* analyzers have been developed.

Ammonia measurement in utility boiler systems is difficult due to the reactive nature of NH_3, the presence of potential interferences, such as SO_2 or H_2O, and the loss of gas phase NH_3 from reactions with ash, chlorides or SO_3 in the flue gases. Practical and reliable means to overcome these measurement difficulties have been evolving and only recently appear to have been dealt with in the continuous analysis of NH_3.

The Electric Power Research Institute (EPRI) sponsored a continuous ammonia analyzer demonstration program that sought to assess the current status of analyzer development and applicability for utility boiler systems. A number of analyzer vendors were invited to participate in an NH_3 demonstration program conducted at a typical coal-fired boiler system.

The test program evaluated the analyzers with two different criteria: long-term operation and reliability of the monitor, and the measurement accuracy of the flue gas NH_3 concentrations. After the initial installation of the analyzers and demonstration of acceptable operation, long-term and measurement accuracy tests were conducted. Additional investigations of the wet chemical and NH_3 calibration gas issues were also conducted.

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TEST SITE AND ANALYZERS

OUC Stanton Unit 2

The test site for the NH_3 analyzer demonstration project was the Orlando Utilities Commission's, Stanton Energy Center Unit 2. Stanton Unit 2 is a 450 MWe coal-fired boiler that employs low NO_x burners and a selective catalytic NO_x reduction system (SCR) to meet its current emission limits. The unit also employs an electrostatic precipitator and wet scrubber, both located downstream of the SCR. The boiler burns an eastern bituminous coal containing 1% sulfur and 10% ash. Typical SCR outlet flue gas concentrations include approximately 110 ppm NO_x, 750 ppm SO_2 and 5gr/scf ash. Flue gas measurements of SO_3 and chlorides were found to be 5 ppm and 95 ppm, respectively.

Figure 2-1 shows a side view of the SCR reactor, relative to the boiler and air heater. Flue gases from the boiler economizer exit flow into the SCR reactor system on the right side of the figure. Ammonia (NH_3) is injected and mixed with the gas as it enters the reactor system and flows upward. The injected NH_3 is reacted with the NO_x emissions on the catalyst layers on the downward pass through the reactor. A flue gas bypass duct is installed between the economizer exit and SCR exit ducts, but is closed in normal operation. The air heater is located below the SCR reactor; further downstream in the gas flow path. A series of ports at the SCR exit/air heater inlet duct served as the primary installation site for the NH_3 monitors.

The presence of the SCR reactor provides a coal-fired flue gas stream that has a trace amount of unreacted ammonia, or NH_3 slip, in the vicinity of the SCR exit and air heater inlet locations. This region was used as the test site for the analyzer installations. The initial configuration of the SCR reactor included only two layers of catalyst. Three layers of catalyst are shown in the figure, which was the final configuration of the SCR reactor at the completion of the program. During an outage in the spring of 1999, the third catalyst layer was added to deal with relatively high levels of NH_3 slip, and lower slip levels resulted for the remainder of the test program.

NH_3 measurements at the air heater gas inlet are of the greatest concern for utility boiler systems that employ post-combustion ammonia or urea based NO_x controls. NH_3 slip levels at this location reflect the potential for adverse effects in the air heater or in the fly ash. Potential problems or primary concerns with NH_3 slip include: formation of NH_3 compounds or by products within the air heater; air heater deposition; or NH_3 absorption into the fly ash. These effects can occur within the flue gas temperature range of the air heater; therefore, NH_3 slip measurements downstream of the air heater are generally not of great concern. Due to deposition and/or ash absorption mechanisms, the NH_3 slip levels downstream of the air heater will be typically lower than at the air heater inlet.

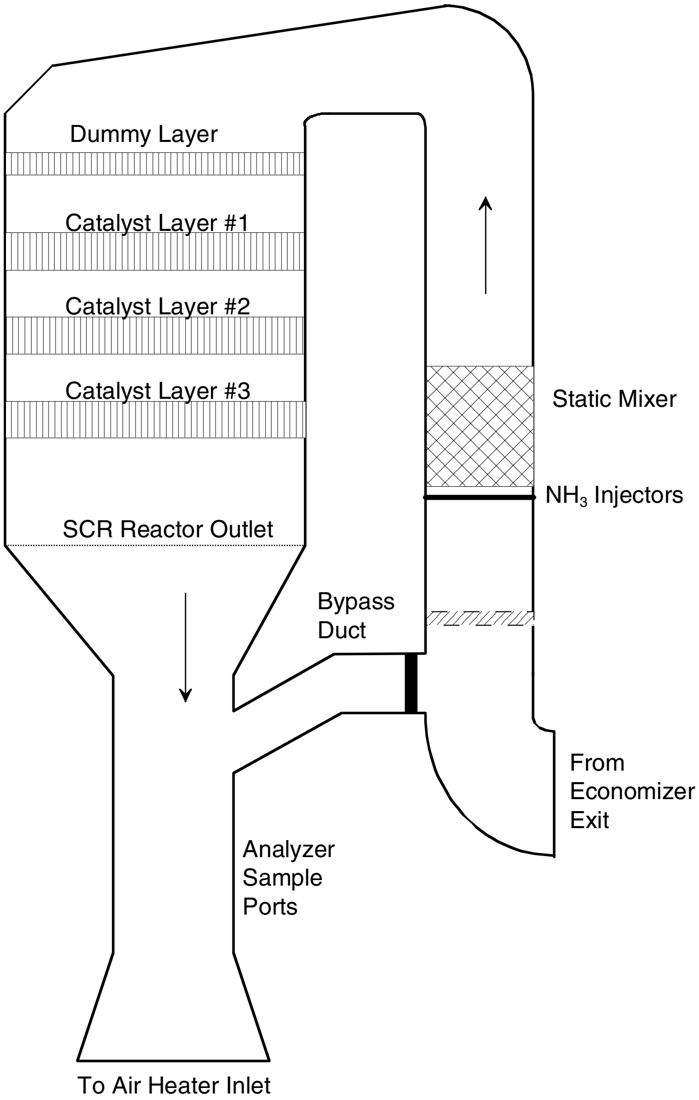

Figure 2-1
OUC Stanton Unit 2 SCR Layout

Continuous NH_3 Analyzers

Two main classes for NH_3 analyzers exist, extractive and *in situ* systems. Extractive systems use a sample probe and transport the flue gases to a remotely located analyzer for NH_3 measurement. *In situ* instruments mount the analyzer components directly to duct ports and generally do not withdraw gas samples from the duct.

Extractive systems may employ fully extractive samples or the dilution probe principles that are commonly utilized in many stack-located, continuous emissions monitoring (CEM) systems. Generally, extractive systems must deal with ash removal and preventing the NH_3 from reacting with ash, SO_2/SO_3 and chlorides. The sample systems must also deal with the adsorption of NH_3 on the walls or other losses of the measurement species.

Analyzer Participants

A number of analyzer vendors were invited to participate in the program. A wide range of NH_3 monitors was desirable because of the number of different sampling configurations and analysis techniques that currently exist. Table 2-1 lists the vendors that expressed initial interest in participating in the program, the basis of the instrument sampling and analysis technique and their final status in terms of the of the test program. A number of vendors declined to participate for a variety of reasons. The reasons included: determination that the flue gas conditions were too difficult for their current analysis systems, lack of analyzer availability, and the costs and support required for participating in the program.

Table 2-1
Vendor Participants and Status

Vendor	Analyzer Principle	Instrument Status
AltOptronic AB	*In situ* tunable IR laser, across duct	Installed during low NH_3 level operation
Norsk Electro Optikk (NEO)	*In situ* tunable IR laser, across duct	Installed during high and low NH_3 level operation
Monitor Labs	*In situ* tunable IR laser, single probe (prototype)	Installed during high NH_3 level operation, prototype instrument currently not operational
Spectrum Systems	Heated extractive dilution system, chemiluminescent NO_x difference measurement (prototype)	Installed during low NH_3 level operation, prototype instrument not operational. High NO_x background judged to be too difficult for low NH_3 levels
California Analytical Instruments	Extractive dilution photo acoustic IR with a prototype sample system	Pilot tests at FERCo showed SO_3 and HCl issues with prototype extractive sample system
Applied Analytics	Extractive UV, physical SO_2 separation	Declined to participate
Aldora (formerly US Filter/Altech)	Broadband multigas IR, heated extractive	Declined to participate (analyzer unavailable)
Sick Optical	*In situ* UV	Declined to participate, excessive SO_2 levels
Opsis	*In situ*, UV or IR	Declined to participate

Over the duration of the test program, four analyzers were installed at OUC Stanton Unit 2. Two analyzers were installed at the beginning of the test program, when relatively high levels of NH_3 were present. Subsequently, two more analyzers were installed, although, these instrument installations were completed after the boiler outage that included catalyst addition. These two analyzers saw only lower levels of NH_3 present during their demonstrations.

The first two analyzers (Monitor Labs and NEO, both *in situ* systems) have been installed at Unit 2's SCR outlet or the air heater gas inlet duct since late 1997 and early 1998, at the start of the test program. Both of these *in situ* analyzers employ infrared laser-based analysis. Although similar in concept, the two analyzers use different port and sampling configurations. The NEO LaserGas analyzer is an across the duct system and requires the installation of a laser transmitter and receiver on opposite sides of the duct. Purge air is required to keep the ports and optical windows clean and free of fly ash. The Monitor Labs prototype instrument utilizes a single probe mounted to one duct wall. The laser and detection systems are housed in a module attached to the end of the probe. Mirrors are used to fold the optical path within the probe and return the signal to the detector.

The NEO instrument operated throughout the duration of the demonstration program, which included approximately 30 total months of operation. The Monitor Labs instrument also was operational at the start of the demonstration program, but was withdrawn from further evaluation after approximately nine months of operation.

The third analyzer was a Spectrum Systems instrument, which employed a dilution probe and extractive sample system. This was the only extractive-based system tested at the demonstration site. A heated dilution probe and a sample line were used to transport the diluted gas sample to the analyzer system. NH_3 analysis was accomplished by an NO analyzer and sample converters, whereby the NH_3 is oxidized to NO and the NH_3 level determined by a differential chemiluminescent NO analysis. This analyzer was operated for five months with low NH_3 levels, before being withdrawn from the test program.

The fourth analyzer, an AltOptronic instrument (also an across the duct, *in situ* system), was the last analyzer installed during October 1999. Therefore, this instrument had less operational time than the other *in situ* instruments and only with the presence of lower NH_3 levels. The AltOptronic instrument operates with a configuration very similar to the NEO, although there were differences in actual physical construction. After installation, the instrument was operated for approximately ten months, until the completion of the test program.

Additional details concerning the configuration and operation of each analyzer are described in the following subsections in the order that each instrument was installed at the test site.

The NEO LaserGas Monitor

The NEO NH_3 instrument is an *in situ* infrared laser-based analyzer. Figure 2-2 shows the general instrument configuration on the duct. The analyzer optical system was mounted on four-inch flanged ports installed on the air heater gas inlet duct. The transmitter and receiver were located on opposite sides of the measurement duct and the analyzer operates with a single pass of the infrared laser through the flue gases. There is no preconditioning of the flue gases prior to passing into the NEO instrument laser path; therefore, the instrument must be able to handle an ash laden gas stream at duct operating conditions.

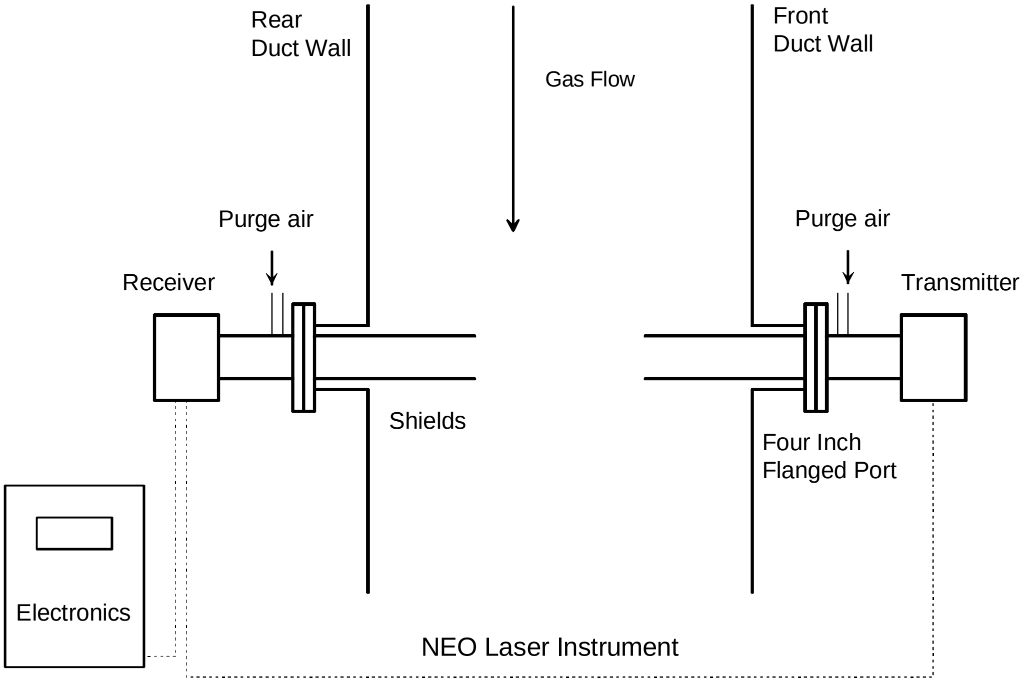

Figure 2-2
Across the Duct Type of *In Situ* Ammonia Monitor Configuration

The NEO Laser instrument was installed on the left side of the SCR outlet and air heater gas inlet duct. This duct is 14.5 feet deep at this location and was downstream of the SCR bypass duct. A set of four inch, flanged sample ports had been previously installed across the width and on the front side of this duct. Since the NEO instrument requires access across the sample duct, another four-inch flanged port was required on the rear side of the duct, opposite one of the existing ports.

The depth of the duct is sufficiently long that shields were required to limit the exposed path length of the infrared laser beam. Without the shields, the transmittance of the laser signal was not sufficient for proper instrument operation. The shields that were installed at both front and rear ports limited the effective optical path length to approximately 93 inches in the center of the duct. These shields were threaded to the inside of the instrument mounting flanges on both the transmitter and receiver ports. Alignment of the transmitter and receiver was accomplished with the adjustment of a series of four setscrews and the four mounting bolts that attached the instrument transmitter or receiver mounting flanges. A large elastomer O ring between the port and mounting flanges provided the sealing and a range of adjustment for the setscrews. A visible laser tool was supplied to aid in initial alignment of the mounting flanges.

Initial installation of the instrument showed a problem in obtaining instrument alignment. The receiver and transmitter must be aligned with one another to provide an acceptable signal across the duct. In addition, the shields must remain reasonably concentric with the aligned laser beam or interference with the beam may occur. The instrument alignment problems were also probably related to less than ideal installation of the rear port and its resulting physical alignment to the front port and to the duct.

Purge air was required to keep the optical windows and shields free from dust accumulation. A clean, dry compressed air supply was plumbed to the system. Initial operation of the air purge did not include flow measurement and valves were cracked open slightly to control airflow rates. However, air rotameters were eventually added to monitor and limit the purge airflow rates for both the transmitter and receiver sides.

A shielded cable connected the transmitter to the receiver, while another shielded cable attached the electronic control box to the receiver. All power to the receiver and transmitter was supplied through these cables from the control box. The cables were sufficiently long so that the control box was remotely located at a more accessible and cooler location than the elevated sample ports. The control box includes an LCD display that shows NH_3 concentration and other critical information. This instrument was set up for a 20-ppm full-scale indication.

Under normal conditions, the control box, receiver, and transmitter were sufficient for proper instrument operation. However, initial set up of the instrument required the use of a PC computer and operating software to modify the control box programming. Once the proper values were input, an EPROM was reset, and the control box did not require further use of the PC for operation. The PC and operating software also offered additional monitoring and data collection capabilities that could be used for trouble shooting or more detailed monitoring of the instrument. Other operations, such as resetting the instrument calibration, also required the use of the software and PC. An optional modem could also be used to access or monitor the control box, again with the instrument software.

Instrument calibration or checking the instrument response to calibration gases could not be performed with the instrument installed on the duct. This may be considered typical of an across-the-duct instrument application. However, a supplied calibration tube was used to mount the receiver and transmitter and allowed the gases to be “sampled”. Control box parameters pertaining to the calibration tube needed to be reset from the duct sample conditions.

NEO indicated that the current recommended user price ranges from US$ 30,000 to 35,000 depending on specific configuration and accessories. Assistance with installation by local representatives would incur additional costs.

The Monitor Labs Instrument

The Monitor Labs prototype NH_3 analyzer was also an *in situ,* infrared laser based instrument. However, the physical characteristics were significantly different from the across-the-duct instruments. Figure 2-3 shows the general instrument and sampling probe configuration as installed on the duct. The analyzer was composed of a probe that was mounted onto a single four-inch flanged port on the duct wall. Its sample probe contains a mirror and lens system that folds the laser path within a relatively short length. The laser and detector were located in a single enclosure mounted on the rear of the probe, outside of the mounting port flange and outside of the duct. A remotely located PC computer controlled and monitored the probe outputs.

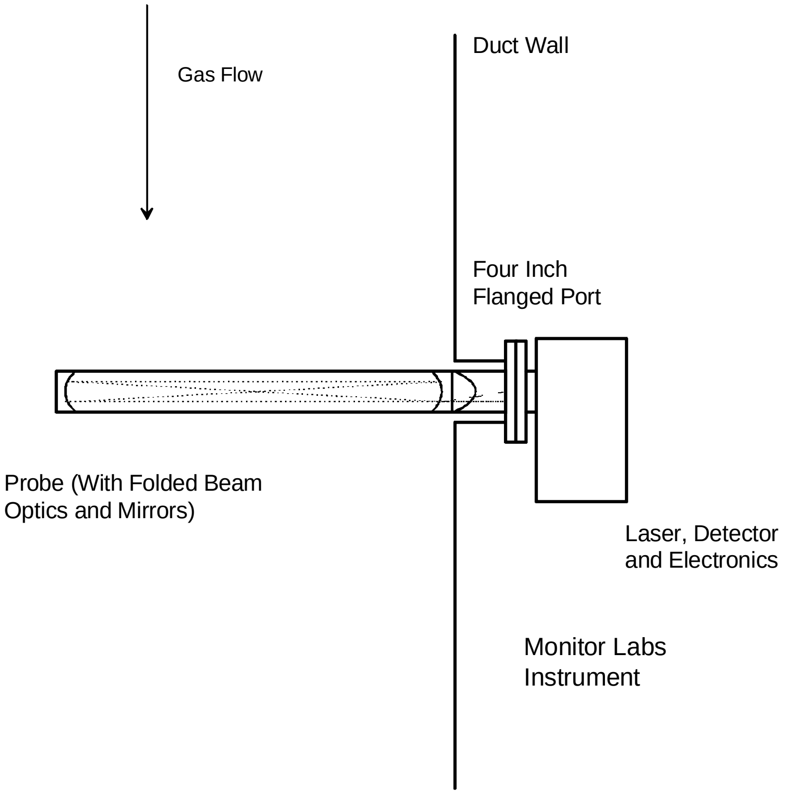

Figure 2-3
Probe Type *In Situ* Ammonia Monitor Configuration

Flue gas passed through sintered metal panels that are located on the probe length contained within the duct. Therefore, for access into the probe, ash was removed from the sample gas prior to entering the probe's measurement chamber. Calibration gases could also be introduced into the probe by flooding the sample chamber with a zero or span gas and displacing the flue gas through the sintered metal panels.

The potential advantages of the single probe design include the elimination of the across the duct alignment requirements and the relative ease of introducing calibration gases into sample zone.

The Monitor Labs analyzer was a prototype instrument that had been installed at the SCR reactor outlet. This port location was above the SCR outlet/air heater gas inlet duct where the other analyzers were located. This location was selected because of its proximity to an environmentally controlled shelter that housed other Monitor Labs analyzers (unrelated to the NH_3 demonstration program). The analyzer probe was installed on a single, four-inch flanged port, that was located just left of center and on the front wall of the SCR reactor exit region. The instrument sample probe extended approximately five feet into the reactor wall. Since the SCR reactor was approximately 35 feet deep at this location, the Monitor Labs instrument was sampling from the front area of the gas flow cross section.

Although the Monitor Labs instrument and wet chemical sampling ports were located at the SCR reactor exit and upstream of the air heater gas inlet location of the other instruments, similar NH_3 concentrations would be expected if the reactor exit NH_3 concentrations were fairly uniform.

However, gas flow rates would be much lower in the SCR reactor, relative to the SCR outlet duct. The only other potential difference was the location of the SCR bypass duct, which was located between the SCR reactor outlet and the air heater gas inlet sampling location.

Spectrum Systems

The Spectrum Systems NH_3 analyzer was a prototype instrument. The instrument consisted of a heated dilution probe that was installed in a four inch flanged port, on the front side of the reactor inlet and air heater gas inlet duct. The probe was connected to an analyzer and control system that was located approximately 25 feet from the probe. The analyzer and control system was located at an elevation lower than the sample port and probe, since the unit could not be located on the relatively small sample platform. The general system configuration is shown in Figure 2-4.

The Spectrum Systems analyzer differs from the *in situ* instruments by requiring a sample to be extracted from the flue gas duct, transported to the analyzers and subsequently measured by NH_3 analysis instrumentation. This requires that the NH_3 specie be withdrawn and transported to a remotely located analyzer system without degradation. To minimize sampling and conditioning requirements, a heated dilution probe system was utilized for sampling. A short, heated sample line transports the diluted sample to the analyzer cabinet. The sample and analysis system was considered a prototype system for the relatively low NH_3 levels that were expected.

The analysis principle used was a NO_x difference technique, whereby the NH_3 is converted to NO_x and the NH_3 signal obtained by difference from a separate total NO_x measurement. NH_3 is converted to NO gas species in a manner similar to that by which NO_2 is converted to NO in a conventional chemiluminescent NO_x analyzer. The technique requires that the NH_3 to NO and the NO_2 to NO converters be carefully chosen to provide the selective conversions. NH_3 levels are determined by comparing the $NH_3 + NO_x$ measurement with the total NO_x measurement conducted in parallel and subtracting to determine the NH_3 by difference. Conventional chemiluminescent NO_x measurement technology was utilized for the NO analysis. This NH_3 measurement methodology was one of the first techniques devised for NH_3 measurements in conventional combustion systems. However, this system utilized a dilution probe system, similar to typical CEM installations.

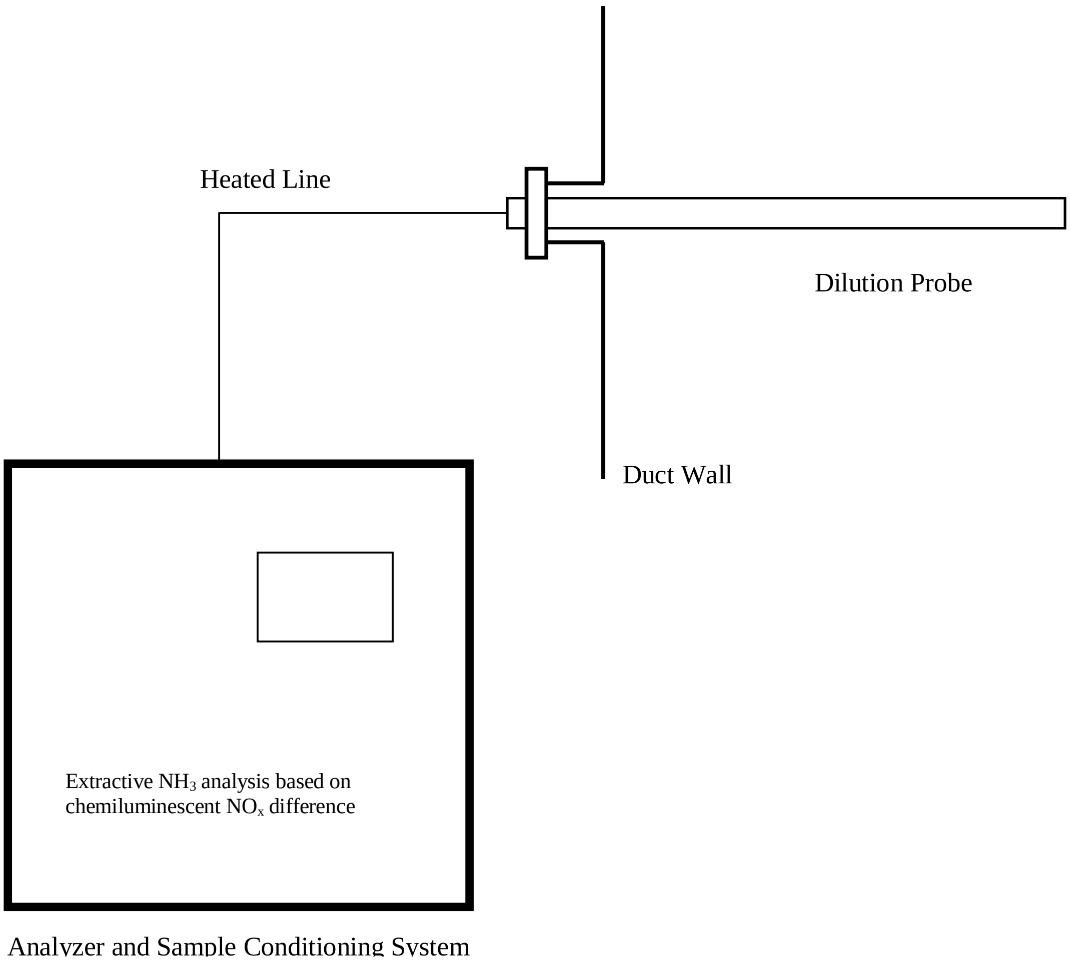

Figure 2-4
Extractive Ammonia Monitor Configuration

Since this was not an *in situ*-based system, there were no special probe or port alignment problems and installation was similar to conventional CEM techniques. However, the sample lines in this particular application were relatively short compared to CEM installations. The enclosure for the instrument and controls was environmentally controlled.

The Spectrum Systems analyzer was initially installed during the boiler outage, after the additional catalyst layer was installed into the SCR. The instrument was operational in late April 1999. As a result, all operating experience with the instrument was with the relatively low NH_3 slip levels. Operating experience with the higher NH_3 levels was not available for this instrument.

AltOptronic LDS 3000 NH_3 Analyzer

The AltOptronic instrument was installed late in the test program and became operational in October 1999. The AltOptronic configuration and general operating principle is also a diode laser-based, across the duct, *in situ* system, similar to the NEO instrument. Referring back to

Figure 2-2, the general configuration appears the same as the NEO, with the laser transmitter and receiver optics located on opposite sides of the duct and a remotely located control box. Purge air and shields are also utilized on the AltOptronic instrument. A second port was located across from one existing sample port on the air heater inlet duct. This was roughly four feet from the NEO installation.

Although conceptually similar, the AltOptronic instrument differs in the specific application of the measurement technology. The diode laser source was not located within the transmitter housing mounted on the duct. Instead, the laser was housed within the remotely located, control box and fiber optics transferred the laser signal in the cables connecting the control box and transmitter. The receiver detector was remotely located on the duct, but its output was converted to optical signal and transferred by fiber optics, as well. Low voltage power was also supplied to the remote units on the duct.

The control box (called the central unit) also differs by including an industrial 486 PC computer, display and keypad. The PC computer provided control, analysis and data acquisition capabilities of the instrument. The control box can also be remotely controlled and accessed by serial cable or modem, to another PC computer. Optional software installed on the remote computer is required for remote operation.

The control box also has the capability of a total of three simultaneous NH_3 measurement locations. Extra I/O boards, remotely located transmitter and receiver sensors, and cabling would be required for each additional channel. The unit tested at Stanton Unit 2 was a single measurement location system. This instrument was also set up for a 20 ppm full scale indication.

The central unit was housed in a slightly larger, environmentally controlled enclosure. Instrument start up showed that the unit was overly cooled and could not adequately cope with the high humidity at the test site, due to condensation problems. It appeared that the existing equipment provided could not be adequately sealed to eliminate the condensation problem, so the central unit was moved to the environmentally controlled shelter of the plant's Monitor Labs instrumentation. This control box location was approximately four floors above the sample port locations.

The size of the shields on transmitter and receiver were shorter than the mounting ports for the original installation. In effect, the AltOptronic instrument measured across the full duct width at OUC Stanton Unit 2 (approximately 14.5 feet). Purge air was also required for the transmitter and receiver units, to keep the optics and shields clean. Initial installation also showed difficulty in obtaining adequate alignment. Again, a non-optimum installation of the rear port's alignment and relative location to the front port contributed to these initial problems. Later in the program, longer shields were installed in the transmitter and receiver, in order to address some monitoring problems that occurred at low load or with boiler sootblowing.

A means to calibrate the instrument involves the use of a calibration cell located in the receiver unit. Recalibration of the instrument tested at Stanton was not performed during the test program.

Additional Instruments

Sick Optical is planning to offer an *in situ* diode laser based instrument in the near future. The manufacturer declined to participate in the demonstration program, due to the SO_2 interference problems of the UV based system that was then available. The new instrument utilizes a different measurement technology from their analyzer listed in Table 2-1; therefore, the interference problem would not be applicable.

The Sick Optical instrument will be a tunable diode laser based analyzer, similar to the NEO and AltOptronic instruments. Unlike these across the duct systems, this instrument will be housed in a single probe configuration similar to other analyzers currently offered by the manufacturer and somewhat similar to the single probe configuration shown in Figure 2-3. Installation requirements appear to be typical of instruments to be installed at the air heater inlet conditions.

Full-scale NH_3 measurement ranges from 10 ppm up to 200 ppm for the new analyzer. The instrument is expected to be available in April 2001 and estimated cost ranges from $40,000 to $50,000.

Although the manufacturer did not participate in the demonstration program with this instrument and no operating data is available, it may be an additional consideration for users interested in the tunable diode laser based NH_3 measurement systems.

3

TEST METHODS

The test program evaluated the analyzers with two different criteria: long-term operation and reliability of the monitor, and the measurement accuracy of the flue gas NH_3 concentrations. After the initial installation of the analyzers, a shakedown test period was conducted to determine if the analyzers would be able to function in a coal-fired boiler environment. After demonstration of acceptable operation, long-term and measurement accuracy tests were conducted.

Long Term Operation and Reliability

During the months of operating time with normal boiler and SCR operation, observation of the analyzers' reliability and data output were conducted on a qualitative basis. This long-term operating period was intended to demonstrate acceptable long-term operation and to determine the maintenance requirements of the instruments. Key factors of concern included: demonstrating acceptable operation in a typical utility boiler environment, the need for excessive maintenance (cleaning, alignment, replacement of consumable items, etc.), instrument breakdowns, or other reliability problems, and the qualitative assessment of the instruments' ability to follow the expected trends for the boiler and SCR operation.

The instrument outputs were connected to a data logger that allowed remote data collection and monitoring of the instrument operation. The data logger was configured to provide either 5- or 15-minute data averages. In order to evaluate the operation of the boiler and SCR system, periodic boiler and SCR data were provided by the plant. The spreadsheets were downloaded from the plant data logging system and contained hourly data of key boiler and SCR operating points. The boiler and SCR data were used to evaluate the operating conditions of these systems and help determine if the instruments tracked the expected trends of NH_3 slip.

Plant personnel performed the on-site, periodic observation of the instrument's operating conditions. If necessary, routine maintenance, repairs or other required instrument operations were also performed.

NH_3 Measurement Accuracy

The measurement accuracy of the analyzers was assessed during specific test periods where the instruments were compared with wet chemical sampling and analysis for NH_3 in the flue gases. These measurements were obtained from separate sampling ports that were located adjacent to the instrument sample probes. Initial wet chemical NH_3 measurements were conducted to compare with the relatively high NH_3 levels indicated by the analyzers. Subsequent to a boiler outage in spring 1999, where additional catalyst was added to the SCR reactor, the NH_3 slip levels were significantly reduced. Similar wet chemical comparisons were then conducted with these lower or normal NH_3 levels in November 1999 and February 2000.

The reference methodology used to verify the accuracy of the NH_3 analyzers was based on a wet chemical, gas washing technique and analysis with an NH_3 specific ion electrode. The flue gas NH_3 was captured into a solution and later analyzed for the solution NH_4^+ ion concentration. This methodology is generally considered to be one of the most accurate available for boiler flue gas samples. The sample methodology, and therefore the measurement accuracy, can be adjusted for the expected NH_3 levels by adjusting the sample volumes, etc., to suit the process. The ion electrode measurement method is generally highly specific for NH_3 and has few interfering species.

Wet Chemical NH_3 Measurement Method

Accuracy testing of the instruments was performed by comparing instrument output with the results from wet chemical, flue gas samples that were analyzed for NH_3 concentration. The flue gas NH_3 measurement and analysis was based upon a wet chemical absorption of the NH_3 into a slightly acidic solution. Subsequently, the solution and probe wash was analyzed for the total concentration of ammonium ion (NH_4^+) by use of the specific ion electrode and an electrode meter.

Figure 3-1 shows the wet chemical NH_3 sample train. The sample was withdrawn from the duct with a stainless steel, glass or quartz probe fitted with a quartz or glass wool plug to remove particulates. The sample gas was transported from the probe to an ice bath with flexible Teflon tubing. The sample gases were then passed through a series of gas washing bottles or impingers containing a dilute sulfuric acid solution (0.02 Normal H_2SO_4). The gas washing bottles were placed into an ice bath to cool the solution and flue gases. The ice bath also condensed all of the moisture from the flue gases and helped to protect the sample system located downstream. The NH_3 gas species was scrubbed out of the gas sample and collected into the sulfuric acid and condensate solution.

A leak free pump pulled the sample gases from the duct, while a dry gas meter accurately measured the gas sample volume passing through the system. Since the ice bath removed the moisture prior to gas meter measurement, the flue gas sample volume was a dry gas volumetric basis. Therefore, the wet chemical NH_3 measurements were based on a dry gas concentration basis (i.e., ppm, dry).

To retrieve the NH_3 sample, the solution from the three gas washing bottles was collected into a sample bottle. The entire sample train from the probe tip to the final gas washing bottle was rinsed with the sulfuric acid solution to capture all of the NH_3 species, which was also added to the sample bottle.

The NH_3 specific ion electrode technique was used to measure NH_3 solution concentrations of the samples, relative to known standard concentrations. The ion electrode senses the gas phase NH_3 from the solutions that pass through a gas permeable membrane. The NH_3 electrode is generally considered highly specific for ammonia and has very few cross species interferences because of the detection of gas phase NH_3 from the solution. The specific ion electrode is monitored by an ion electrode/pH meter, which gives a millivolt output corresponding to the ion concentration. Gas phase NH_3 in the solution was obtained by turning the calibration standards or the slightly acidic flue gas samples into a basic solution with the addition of a pH adjusting ISA (ionic strength adjusting) solution.

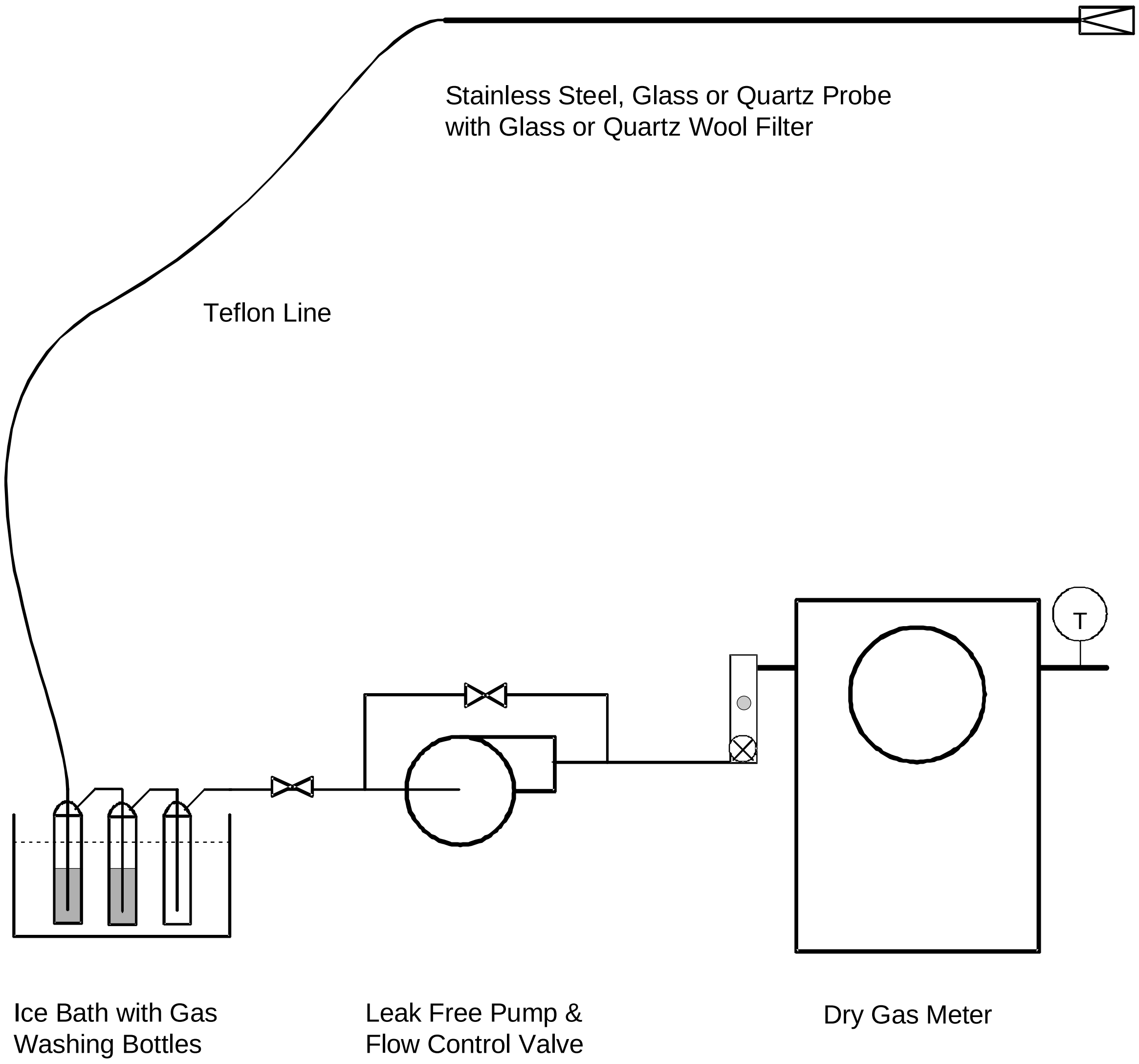

Figure 3-1
Wet Chemical Ammonia Sampling Train

A range of ammonia standards was prepared by serial dilution from a known concentration, ammonia standard solution. These standard solutions were then measured with the specific ion electrode technique and a calibration curve was made. The wet chemical test solutions were then compared with the standards and calibration curves to determine the molar concentration of the solutions. Sample solutions with 10^{-1} to 10^{-6} molar NH_3 concentrations can be generally measured with this technique. The accuracy of the measurement will be dependent upon the amount of flue gas sample volume, flue gas NH_3 concentration, and other specific sampling variables.

Wet chemical sampling with NH_3 specific ion electrode analysis, particularly with low NH_3 levels, did reveal potential interferences. These interferences were investigated and a cause was determined. Subsequently, additional samples were obtained and were reanalyzed with more accurate results. Additional details of these results are discussed in a later section.

4

LONG TERM MONITORING RESULTS

At the start of the program, the SCR contained two layers of catalyst. Approximately 13 months into the program, an additional layer of catalyst was added to the SCR reactor. The additional catalyst significantly reduced NH_3 slip. This change divided the long term monitoring program into two phases, a high NH_3 test period and a lower, normal NH_3 test period. Each will be discussed separately, for the monitors that were installed at the time. In general, the lower NH_3 slip levels pose a greater challenge for an NH_3 monitor, since the levels become closer to zero and become more difficult to distinguish from normal background interferences. The following summarizes the long-term monitoring program:

- Higher NH_3 Slip Monitoring Period
  - January 1998 to March 1999
  - Full Load NH_3 Slip, 6 - 9 ppm Typical
  - Instrument Under Evaluation
    - NEO LaserGas
    - Monitor Labs

- Lower NH_3 Slip Monitoring Period
  - April 1999 to July 2000
  - Full Load NH_3 Slip, ~1-2 ppm Typical
  - Instruments Under Evaluation
    - NEO LaserGas
    - Spectrum System
    - AltOptronics

Long-term Instrument Operation with Higher NH_3 Slip

Long term monitoring with relatively high levels of NH_3 slip ran from January 1998 through a spring outage in March 1999. Two analyzers were installed and evaluated during this time period: the NEO LaserGas and the Monitor Labs *in situ* monitors.

NEO LaserGas

The subjective, day-to-day evaluation of the NEO analyzer's data logger output during the shakedown period and long term monitoring indicated that the analyzer was responding to the

NH_3 levels in the duct. During this time, it appeared that the NEO analyzer output was reflecting the expected trends of an SCR and NH_3 slip. In general, higher NH_3 slip was shown under higher load conditions (i.e., higher gas flow rates, possibly higher NO_x input, and higher NH_3 injection rates). Conversely, very low NH_3 slip operation were shown under low boiler load conditions, when the NH_3 flow had been cut back and flow through the SCR was reduced (i.e., increased residence time in the reactor).

Figure 4-1 shows a typical cross plot of boiler load (MWe), SCR NH_3 injection rate (lb/hr or pph) and corrected NEO LaserGas instrument output (ppm, wet) with time. This data represents a one-week period of boiler and NEO operation that occurred near the time frame of the wet chemical measurements. The trends from the NEO instrument appeared to follow the trends expected for NH_3 slip from a SCR system and indicated the instrument appeared to be monitoring the process. This was also later confirmed by the wet chemical tests. The NH_3 slip levels appeared to drop very close to zero during the early morning low load hours and rise to consistent 6 to 8 ppm wet levels during steady state full load operation.

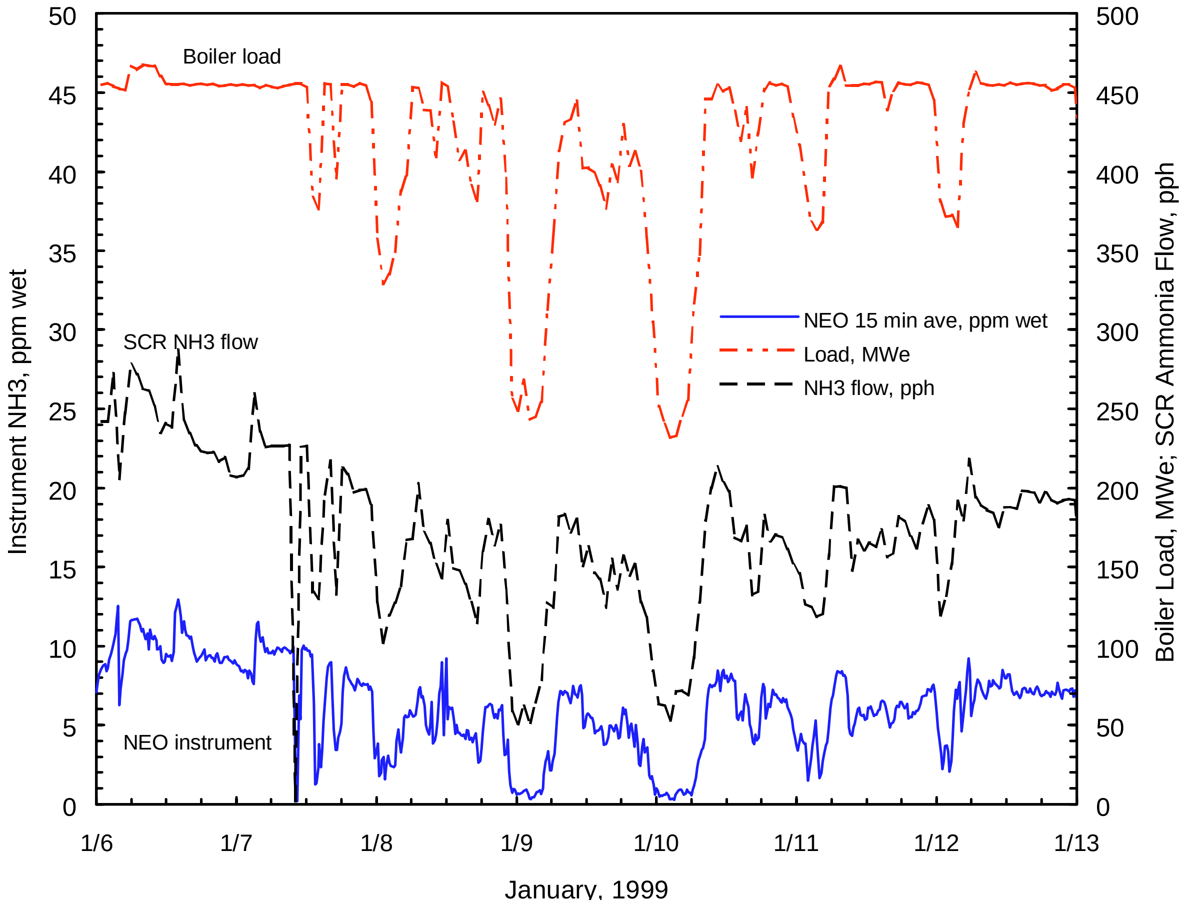

Figure 4-1
Early (Higher NH_3) NEO and SCR Operation for One Week

The NEO output and the SCR NH_3 injection rate showed a very close relationship, and very similar trends. Except for the magnitude difference, the NEO appeared to follow the NH_3

injection rate with very fine detail; again giving confidence that the NEO analyzer was operating correctly and accurately monitored the trends for the actual NH_3 slip in the duct.

Some of the minor differences observed in the data trends may be due to the differences in the data gathering processes. The boiler load and SCR NH_3 flow rate data were obtained from the OUC Stanton Unit 2 data logging system. The boiler data was acquired in approximately one-hour intervals and was a single point record, or snapshot, of the boiler operating conditions at the time. The NH_3 data logger was set up for 15-minute averages, yielding four points per hour that reflected the average NH_3 concentration during the interval. The differences of data averaging and frequency of collection may affect trends and their appearance.

During the long term monitoring period, approximately 13 months of operating time had been accumulated for the NEO with higher NH_3 levels. During this time, the NEO instrument had been initially calibrated to an NH_3 span gas, but no other re-calibrations performed. Checking the instrument calibration with gases required that the transmitter and receiver be removed and installed on a calibration test tube. At the end of the 12 month time period, the zero and span was rechecked (with acceptable results), but no adjustments to the instrument calibration settings were performed.

During the test period, one instance of component failure required the replacement of an electronic circuit board in the electronics module. The circuit board may have overheated and failed, possibly caused, in part, by high ambient temperatures from the plant and the room where the electronics were housed. Air circulation within the room was improved, and no further electronics problems were noted.

A few instances of re-alignment were periodically required, whenever the transmitter to receiver laser alignment caused insufficient transmittance of the laser signal. When the transmittance signal was insufficient, the instrument would hold the last valid reading. This inoperative instrument condition could be easily detected by the appearance of flat line data trends. During the long-term monitoring with higher NH_3 slip, approximately four to six instances of instrument realignment were required.

Low transmittance appeared to have been caused by a buildup of ash deposits on the end of one shield or from the loss of alignment caused by movement of the port mounts. The shield deposition problem may have been aggravated by non-concentric alignment of the shield with the laser, so that a relatively small ash deposit began to cut into the beam. The relatively long shield may also have played a factor in the concentricity of the shield. Misalignment caused by movement of the transmitter or receiver mounts may have been a consequence of normal boiler vibrations or transmitter to receiver duct movements. The stability of the ports and mounts and the accuracy of the port installation may have been a factor here. Obscuration caused by deposition on the optical windows was not a problem and did not appear to be cause of low laser transmittance. While the windows were cleaned whenever the instrument was removed, this was rarely, if ever, required.

The only other modification was the installation of flow rotameters on the purge air and the subsequent reduction of the air flowrates. It was determined from early wet chemical tests that excessive purge air flowrate was reducing the NEO NH_3 signal by impeding flue gas flow into the measurement zone (i.e., reducing the optical path length). Measuring and reducing the purge air eliminated this problem.

Monitor Labs

The subjective, day-to-day evaluation of the Monitor Labs analyzer's output during long term monitoring, indicated that the Monitor Labs output was not reflecting the expected trends of a SCR and NH_3 slip. In general, higher NH_3 slip would be expected under higher load conditions of an SCR (i.e., higher gas flow rates, possibly higher NO_x input, and higher NH_3 injection rates). Conversely, low NH_3 slip operation would be expected under low boiler load conditions.

However, the Monitor Labs instrument output did not appear to follow the trends expected for NH_3 slip from a SCR system. Overall, the instrument NH_3 signal appeared to be largely unaffected by large changes in boiler load and NH_3 flow rate. These trends indicated that the NH_3 output was not accurate and that there may have been a measurement problem with the Monitor Labs instrument. It appeared that the SCR system operation was not being accurately reflected by the long-term instrument data, particularly when compared with another instrument output. These early trends were also confirmed by some preliminary wet chemical NH_3 tests.

On several occasions during the long-term monitoring period, Monitor Labs personnel performed adjustments to the analyzer; however, significant operating improvement was not achieved. The Monitor Labs analyzer performance continued to degrade with time, and during October 1998, the instrument became inoperative. The instrument had failed to a constant 50 ppm output that was not affected by operation of the boiler and SCR. Additional adjustments or modifications were planned by the manufacturer, but were not implemented. The prototype instrument was eventually withdrawn from further evaluation in the test program.

Long-term Instrument Operation with Low NH_3 Slip

The following discussion pertains to the analyzers that were in operation subsequent to the installation of an additional catalyst layer into the Stanton Unit 2 SCR. Additional catalyst significantly reduced the SCR outlet NH_3 levels to concentrations that were expected at the beginning of the test program. Instrument operation with nominally 2 ppm and lower levels was continued after the spring 1999 outage. With the reduced NH_3 slip levels, it was more difficult to assess the operation of the instruments, due to the relatively low levels of NH_3 that were present.

During this time period, two additional vendors expressed interest in participating in the program and subsequently installed their instruments. Since these analyzers were being installed late in the long-term monitoring program and more experience with lower NH_3 levels was desirable, the long term monitoring program was extended.

The following discussion describes the long term, low NH_3 experience with the analyzers, in order of their installation at OUC Stanton Unit 2.

NEO LaserGas

In general, the NEO NH_3 analyzer showed reasonably good monitoring trends during the early testing with elevated NH_3 levels. This operation continued with the lower NH_3 levels. Again, the subjective, day-to-day evaluation of the NEO analyzer's output during the long-term monitoring indicated that the NEO analyzer output was reflecting the expected trends of SCR and NH_3 slip. In general, higher NH_3 slip corresponded to higher load conditions and visa versa. However, the magnitude of the changes was generally limited to a total range of 2 ppm NH_3, which made it more difficult to monitor changes.

Figure 4-2 shows the typical output of the NEO analyzer with low levels of NH_3 slip. The NEO output and the NH_3 injection rate generally showed good correspondence, despite the lower NH_3 levels. In general, the same trends with NH_3 injection rate remained. Except for the magnitude difference, the NEO appeared to closely follow the NH_3 injection rate; again giving confidence that the NEO analyzer accurately monitored the trends of NH_3 slip in the duct. The highest NH_3 indications were limited to 2 ppm, while early morning lowest levels approach zero ppm.

As with previous data, all NH_3 instrument outputs are 15-minute data averages, while the boiler and SCR data are once per hour snapshots of boiler operation. Note the low scale range for the NH_3 slip data.

During the combined long-term monitoring periods with high and low NH_3, a total of 30 months of operating time was accumulated with the NEO instrument. As mentioned previously, the NEO instrument had been initially calibrated to a span gas, but no other re-calibrations were performed throughout the operating periods. Rechecking the instrument installed on a calibration test tube was again verified with zero and span gases during the low NH_3 long term monitoring period. Again, the instrument appeared to be operating satisfactorily and the calibration gas comparisons were good. Since the zero and span were acceptable, no adjustments to the instrument calibration settings were performed.

No further instrument component failures were encountered during low level NH_3 operation.

Periodic re-alignment of the transmitter or the receiver laser was required. Misalignment reduced the transmittance to the point that the measurements could be compromised. The low transmittance problems were due to slight shifting of the transmitter or receiver. During periods of continuous low transmittance, the instrument would lock onto the last valid data point and the instrument problem could be detected by a flat line output. Error messages on the NEO electronics module would also note the problem. Realigning the transmitter was accomplished by adjusting the locking and position adjusting screws while checking the transmittance with a local voltage output. Again, the installation of the transmitter and receiver ports and the alignment of the two shields may be a critical factor in ease and stability of alignment. Approximately four realignments were required during the low NH_3 monitoring period.

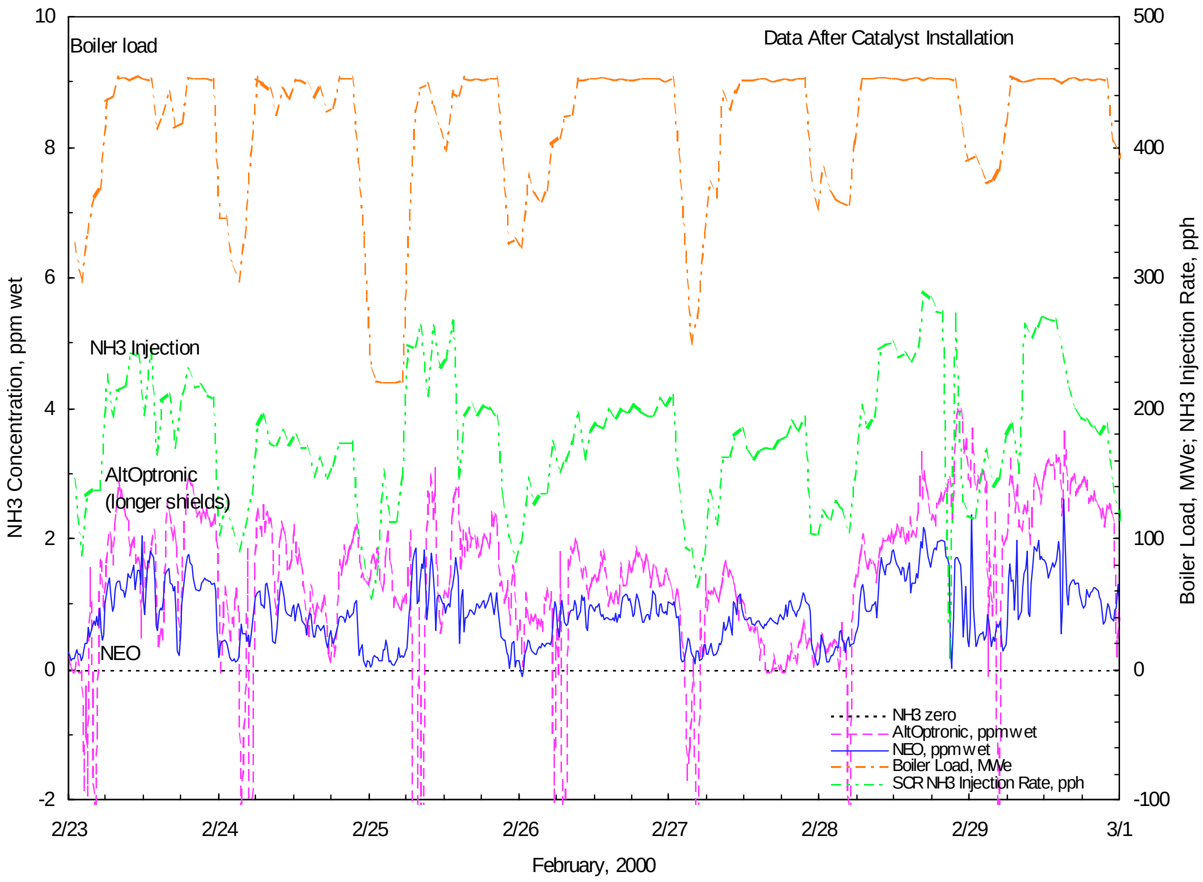

Figure 4-2
NEO and AltOptronic Instrument Operation at Low NH_3 Slip

The reduction of laser transmittance was not affected by obscuration by fly ash on the optical windows, similar to the early experience. The relatively long tubes that served as shields and sufficient purge air prevented ash from migrating towards the optical windows.

A small amount of fly ash deposition on the end of a shield continued to affect the transmittance problem; however, this ash was easily removed during a calibration check or removal of the optical unit. The effect of deposition may also have been influenced by the initial port and shield alignment. These ash deposits were occasionally removed during the infrequent inspections, but this was not a labor-intensive operation.

Spectrum Systems

The Spectrum Systems prototype NH_3 analyzer was initially installed during the boiler outage, when the additional catalyst layer was being installed into the SCR. The instrument was operational in late April 1999. As a result, all operating experience with the instrument was with the relatively low NH_3 slip levels. Experience with the high NH_3 level operation was not available for this instrument.

The Spectrum Systems instrument was operational during the monitoring period that extended into early September 1999. During this operating time, the instrument output was subjectively monitored and compared with the boiler and SCR operating parameters, as well as with other operating analyzers.

During this monitoring period, it appeared that the Spectrum output was not reflecting the trends of boiler/SCR operation and expected NH_3 slip. In general, the instrument output appeared to be somewhat erratic and appeared to be either high or low, relative to the expected NH_3 slip levels. The instrument NH_3 output did not always appear to follow large changes in load and NH_3 flow rate.

Initial operation indicated very high NH_3 levels that were not expected for the SCR after the addition of another layer of catalyst. Spectrum personnel returned to the test site and made modifications to the sample and analysis systems to improve performance. Instrument operation (with additional modifications) later showed lower NH_3 levels that were at times consistently less than zero.

On several occasions during the monitoring period, Spectrum Systems personnel performed adjustments and/or modifications to the analyzer. Modifications to the sample probe were also performed. The main objective was to improve sensitivity for NH_3, despite the presence of relatively high levels of NO_x. However, significant operating improvement was not achieved. At the SCR exit, the typical NO_x emissions were approximately 110 ppm at full load operation. This required the system to detect 1 or 2 ppm NH_3 levels (by NO_x difference) from a baseline NO_x level of 110 ppm. The analysis technique required that NH_3 be determined by difference from two large values (NH_3+NO_x versus total NO_x).

The NO_x difference technique suffers with either high NO_x levels or low NH_3 levels. Spectrum determined that these levels of NH_3 were too low for accurate measurements with the prototype instrument, given these relatively high, background NO_x levels. Spectrum also determined that acceptable performance was not to be expected with the current configuration of the analyzer system and withdrew the instrument from further evaluation.

Wet chemical comparisons were not performed with the Spectrum instrument.

AltOptronics

The AltOptronic instrument was the last analyzer installed (in October 1999) and operated for approximately 10 months, until the monitoring program was ended. All operating experience was with low NH_3 levels. The subjective observation of the long term monitoring of the instrument output was similar to the NEO analyzer. An example of the AltOptronic instrument output was included with the data presented in Figure 4-2.

Observation of the long-term operation of the analyzer showed that the instrument appeared to generally follow boiler and SCR trends expected for NH_3 slip. During high NH_3 flow situations, the instrument output increased, as would be expected. It is more difficult to determine if the instrument responds to low NH_3 slip conditions at reduced load, because of the low transmittance problems. During low transmittance, the instrument was designed to give zero output, which the data logger interpreted as –5 ppm NH_3 (0 mA for a 4 to 20 mA signal loop). The data logger would average the –5 ppm output signal with any other valid data, into the 15 minute data averages (see the negative AltOptronic output during early morning hours). As a result, erratic and negative spikes in the data indicated low transmittance conditions. However, this characteristic allowed these non-functioning analyzer incidents to be detected.

As shown in Figure 4-2, the AltOptronic instrument suffered from a nightly alignment or obscuration problem that caused the periodic negative data spikes. The low transmittance typically occurred during early morning hours, which could have been the result of either the low boiler load or the daily sootblowing schedule (boiler sootblowing frequently occurred during the early morning hours). Sootblowing may have caused low transmittance by the large amount of ash carried by the flue gas. If sootblowing was the cause, it may have been a consequence of the long path length of the AltOptronic instrument, which may cause excessive obscuration of the laser signal. Low load may have caused the low transmittance by physical duct variations (lower gas temperature or changing duct pressure) that caused the optics to become misaligned.

The exact cause of the low transmittance is not certain, but in any case, daily problems have been observed. It is also not certain if the problem lies with the specific operating conditions of Stanton Unit 2 or a characteristic of the analyzer. Subsequent to the initial operation, longer shields were installed on the instrument. This reduced the path length from 4.8 meters (18.8 feet), longer than the duct, to 3.6 meters (14.1 feet), slightly shorter than the duct. This modification appeared to have reduced, but have not entirely eliminated, the low transmittance periods. The data included in Figure 4-2 was subsequent to the installation of the longer shields. As a result, the low load or sootblowing transmittance problems noted previously have been reduced from initial results. Spikes of negative NH_3 value remained, indicating that the instrument continued to have low transmittance problems at these boiler conditions.

No major problems or failures of the instrument have been encountered. Misalignment of the analyzer has required at least two instances adjustment of the transmitter or receiver alignment to provide optimum operation. Similar to the NEO experience, alignment problems may be at least partially affected by the accuracy and stability of the port installation and the duct.

Comparison of the Low NH_3 Slip Results

At the end of the demonstration program, two *in situ* instruments, the NEO Laser and the AltOptronic, were in operation and appeared to be responding to NH_3 slip trends. Figure 4-2 compared 15-minute data for the two instruments for the same boiler operating conditions. Corresponding boiler load and NH_3 injection rates were also included in the graph for comparison.

Both instruments appeared to follow the NH_3 flow rate trends and indicated lower NH_3 slip levels with low flow and low boiler loads. Low NH_3 slips were expected because of the higher residence times within the fixed catalyst bed. During high load operation, the AltOptronic instrument had a higher output relative to the NEO analyzer. These relative analyzer characteristics were typical for normal, full load operation. This relative result also corresponds to the data presented for the wet chemical comparisons.

At low load operation during the early morning hours, the NEO output typically fell to zero NH_3 (typically ranging ±0.2 ppm levels at minimum loads). Operation of the AltOptronic instrument is more difficult to interpret due to the low transmittance problems and its negative default output, as noted previously.

The operation and accuracy comparisons for the NEO and AltOptronic instruments will be further discussed in the following measurement accuracy section.

5

MEASUREMENT ACCURACY RESULTS

On-site, wet chemical samples were periodically collected and analyzed to determine the instrument's measurement accuracy. Those instruments demonstrating reasonable, long-term operation would be tested by obtaining flue gas NH_3 samples in the vicinity of each instrument's measurement zone. Wet chemical NH_3 sample ports were located adjacent to the instrument installations. Measurements were typically obtained during steady, full load boiler and SCR operation. This allowed the NH_3 slip levels to be as consistent as possible, for the most accurate comparison between the instruments and wet chemical samples.

A long, stainless steel probe, sufficient to reach the centerline of the duct depth, or a glass/quartz probe was used to obtain flue gas sample in the central vicinity of the analyzer sample area. The wet chemical technique involved scrubbing the gas sample through impingers containing dilute sulfuric acid, washing the probe and sample line into the impingers, and analyzing the impinger solutions for NH_3 with a specific ion electrode.

Since the NEO and AltOptronic instruments are *in situ* monitors, they measure the NH_3 concentration on a wet gas basis. Therefore, a wet-to-dry gas concentration correction factor was made to the *in situ* analyzers to allow comparison, on the same basis, to the wet chemical analysis. The moisture content of the flue gases and wet to dry correction factor was estimated and was based upon the boiler, ambient air, and the duct flue gas operating conditions that existed at the time of the tests. A coal sample analysis and measurement of the ambient air humidity were also utilized in the estimation of the correction factor. Generally, the wet to dry correction factor was on the order of 10 percent or less.

NEO LaserGas Wet Chemical Comparison Results

The wet chemical NH_3 sample port was located adjacent to the NEO installation. Early tests with relatively high NH_3 levels utilized a long, stainless steel probe sufficient to reach the centerline of the duct depth. The long probe was also angled toward the NEO instrument to obtain flue gas near the center of the instrument sample zone.

Higher Level NH_3

The first wet chemical measurements from the NEO indicated there was a fairly good agreement between the wet chemical and corrected NEO NH_3 data. However, a correction factor was required to compensate for an excessive purge flow condition that existed at the time of these tests. It was later determined that the purge airflows were excessively high and had the effect of pushing the flue gas out of the measurement path. A series of purge airflow tests were conducted and the effect of the measurement on the NEO output was estimated. This purge airflow rate correction factor was then applied to the data logger data. Subsequent to these tests, the air purge flows were monitored and reduced.

A revised set of wet chemical measurements was performed for the NEO instrument in January 1999. These tests were intended to re-verify the NEO operation after revision with the reduced purge airflow rates. Table 5-1 shows a set of wet chemical and instrument data, with normal operation of the purge air. The average wet-to-dry correction factor was added to the NEO data averages, based upon the operating conditions at the time of these full load tests. The NEO data used in this comparison were the 15-minute averages recorded by the data logger. The time of each sample was matched with the closest corresponding data point recorded.

The NEO data showed very good agreement to the wet chemical measurements. The average NH_3 levels were 8.9 ppm dry for the wet chemical measurements versus 9.0 ppm dry for the NEO. The average NH_3 measurement difference was only 0.15 ppm.

Table 5-1
NEO Laser High Level NH_3 Comparison, January 1999

Sample Number	Wet Chemical NH_3, ppm dry	NEO Laser Output, ppm corrected to dry
17a	8.5	9.1
17b	8.8	9.4
17c	9.1	9.1
17d	9.0	9.2
17e	9.1	9.0
Boiler upset		
17f	8.6	8.8
17g	8.6	8.8
17h	8.9	9.0
17i	9.2	8.8
Average	8.9	9.0
Difference, average	- -	+0.15
Relative Accuracy, %		17.8

During this set of NEO wet chemical tests, a boiler or SCR upset occurred in the middle of the test. This was detected by the spot checks of the NEO instrument output, which had indicated that a rapid change had occurred and that the steady state concentrations had decreased to very low and rapidly changing NH_3 levels. The suspect wet chemical sample that was being obtained was subsequently discarded, since this sample may have included non-steady state NH_3 that resulted from the upset. The tests were suspended until boiler and SCR conditions had returned to normal. Sufficient time was allowed for the SCR reactor condition to restabilize to previous test conditions. After a couple of hours for restabilizaton, the tests were resumed and the final samples were procured.

The relative accuracy data shown in the table indicate a fair agreement of the two sets of individual measurements, however the accuracy is low relative to typical CEM measurements. This result was not unexpected, due to the methodology involved with the calculation of the relative accuracy. In general, poor relative accuracy will result when comparing very low level emissions that may be near the measurement accuracy of the analyzer and reference methods. Generally, this will be the case for these ammonia measurements, where typical measurements will be 10 ppm or lower, for a system with perhaps a 0.2 to 1.0 ppm resolution. The problem would be similar to CEM monitoring very low CO levels. In the latter and perhaps this NH_3 case, relative accuracy may not be a significant value for evaluating instrument accuracy. With even lower NH_3 slip levels, the relative accuracy value will become less meaningful.

Relative accuracy may not be of significance for NH_3 monitors, which are currently intended as SCR process monitors for checking SCR operation, or possibly for NH_3 injection control. This will be significantly different from a CEM application at the stack, where measurement accuracy and compliance with sampling protocols are the primary analyzer function.

Figure 5-1 shows the wet chemical data and the corrected data logger NEO averages cross-plotted with time. Again, the data logger 15-minute averages have been corrected to a dry gas basis for this comparison. The effect of the boiler or SCR upset was clearly seen by the significantly reduced NH_3 slip indicated by the continuous data logger output. However, the wet chemical measurement points were only taken during the time period when the boiler and SCR operation was relatively stable. The wet chemical sample measurements were in the range of 8.5 to 9.2 ppm dry, perhaps showing a gradual concentration increase with time.

The NEO corrected output appears relatively flat or constant during the sample time, with exception of the large NH_3 slip excursions that occurred during the upset conditions. Despite the presence of the upset, the NEO instrument trends appear to follow the wet chemical measurement with time. The concentrations of the NEO and wet chemical measurements were similar and were both approximately 9 ppm dry, on average. The total duration of time for these wet chemical tests was approximately four hours from start to finish, including the upset.

Although the low NH_3 levels noted from the NEO instrument could not be verified with the steady state wet chemical measurements, the data in the figure showed the rapid response of the *in situ* instrument. Also note that these 15-minute data points were smoothed by the averaging process and that the instantaneous instrument output may exhibit much faster response characteristics. The data logger did not save the instantaneous instrument output.

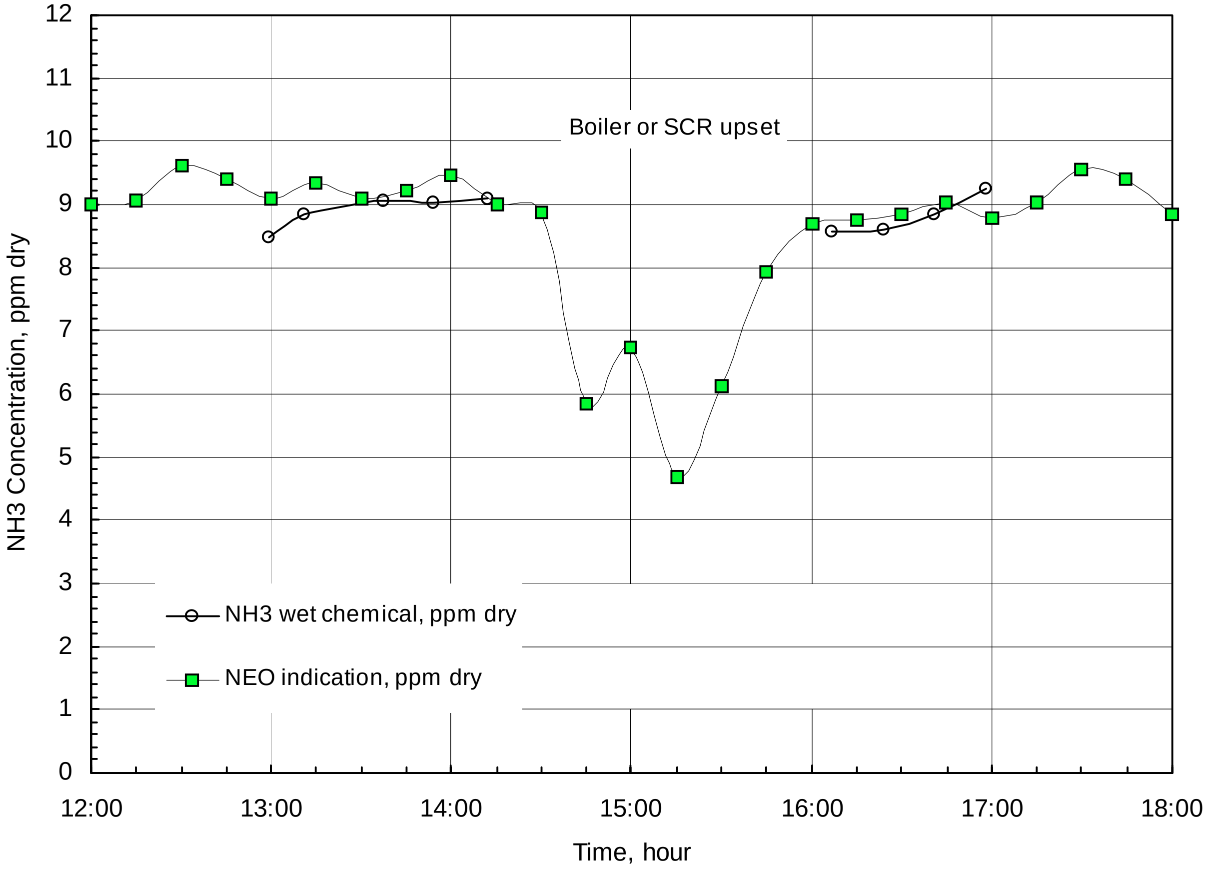

Figure 5-1
Wet Chemical and High Level NH_3 Measurements as a Function of Time

Low Level NH_3

Subsequent to the boiler outage in spring of 1999, the SCR outlet NH_3 levels were significantly reduced as a result of the addition of another layer of catalyst. The NEO analyzer output responded accordingly, typically indicating values in the range of 0 to 2 ppm. Additional wet chemical measurements were performed to evaluate the analyzer performance with these low-level NH_3 conditions. This comparison is shown in Table 5-2. As before, all data were corrected to a dry gas basis.

The data shown in the table were obtained with a glass probe, as a result of an interference that became noticeable with the low-level NH_3 measurements. The use of the glass probe apparently eliminated the interference. Additional discussion and test results are presented in a later section of this report. The glass probe was shorter than the previously used stainless steel probe, so that it did not quite reach the midpoint of the duct. This should not greatly affect the data, if the duct NH_3 concentration was fairly uniform.

Table 5-2
NEO Laser Low Level NH_3 Comparison, February 2000

Sample Number	Wet Chemical NH_3, ppm dry	NEO Laser Output, ppm corrected to dry
36a	1.34	0.72
36b	1.43	0.80
36c	1.49	0.88
36d	1.68	1.04
36e	1.74	1.06
36f	1.91	1.33
36g	1.63	1.05
36h	1.59	1.02
36i	1.62	0.76
Average	1.60	0.96
Difference	- -	-0.64

The comparison of the wet chemical measurements and NEO instrument measurements in Table 5-2 shows reasonable agreement, differing by approximately 0.6 ppm. For this measurement series, the NEO measurements were consistently lower than the wet chemical measurements. A further comparison was made by plotting the NEO and wet chemical measurements as a function of time, as shown in Figure 5-2. The NEO instrument readings reflect the small changes seen from the discrete wet chemical samples over the three-hour period.

Although the NEO instrument data were consistently lower than the wet chemical results, examination of the data trends showed that the NEO followed the individual wet chemical measurements. During the test series, there was a gradual increase in NH_3 that was indicated by both measurements. Later, the NH_3 peaked and was slightly reduced to a lower level, again indicated by both systems. The very close agreement between the wet chemical and NEO data trends gave additional confidence that the NEO appeared to be closely following the duct NH_3 trends.

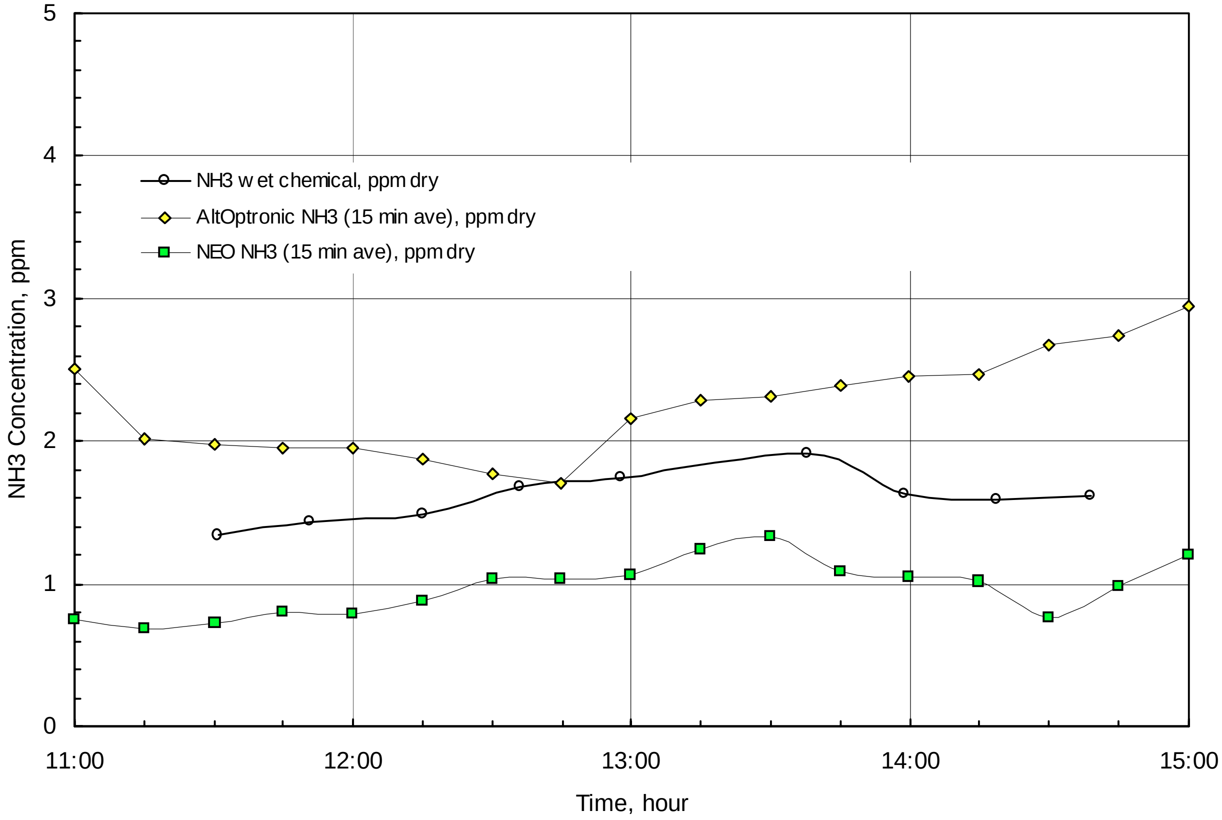

Figure 5-2
Wet Chemical and Low Level NH_3 Measurements as a Function of Time

AltOptronic Wet Chemical Comparison Results

All operating experience with the AltOptronic instrument has been obtained with the lower NH_3 levels resulting from operation after catalyst addition to the SCR. A set of wet chemical measurements was performed with the AltOptronic instrument in February 2000, at the same time that the NEO was being evaluated. The wet chemical measurements were the same as the NEO wet chemical results presented earlier. These wet chemical comparisons were performed prior to the installation of the longer shields on the instrument.

Table 5-3 shows a comparison of the wet chemical and instrument data for the AltOptronic instrument. The average wet-to-dry correction factor was also added to the instrument data for these full load tests. The AltOptronic data showed consistently higher readings relative to the wet chemical measurements. The average NH_3 levels recorded from the AltOptronic instrument data averaged 2.18 ppm dry, which were typically 0.6 ppm higher than the wet chemical measurements. This was consistent with the observation that the AltOptronic instrument typically showed a higher output than the NEO instrument. At the time, 2 ppm NH_3 levels were typical for full load operation on the AltOptronic instrument.

Table 5-3
AltOptronic Low Level NH_3 Comparison, February 2000

Sample Number	Wet Chemical NH_3, ppm dry	AltOptronic Output, ppm corrected to dry
36a	1.34	1.98
36b	1.43	1.95
36c	1.49	1.88
36d	1.68	1.77
36e	1.74	2.16
36f	1.91	2.32
36g	1.63	2.45
36h	1.59	2.47
36i	1.62	2.68
Average	1.60	2.18
Difference	- -	+0.58

The AltOptronic measurements were also shown as a function of time in Figure 5-2. The instrument readings indicated an overall, increasing NH_3 trend with time, which was similar to the general, wet chemical data trend. Examination of the data showed that there were some differences between short-term data trends of the AltOptronic instrument relative to the comparable wet chemical readings. The cause or the significance of these differences was not evident.

All wet chemical measurements with the AltOptronic instrument were performed at full load conditions; therefore, the low transmittance effects noted at the low load operation would not be applicable.

6

SAMPLING AND CALIBRATION GAS ISSUES

During the NH_3 monitoring test program, some issues concerning the accuracy of NH_3 calibration gases and the wet chemical measurements were noted. This section further discusses these issues and their potential effect upon NH_3 measurements.

Calibration Gas Issues

Ammonia span gases are not in common use, particularly when compared with the gases commonly required for a typical utility CEM system. Therefore, gas suppliers and users may not be aware of some of the particular difficulties in handling and producing acceptable NH_3 span gases. In general, it is more difficult to obtain high accuracy, NH_3 span gases, particularly as the required NH_3 concentration decreases.

In some cases, the NH_3 calibration gases (NH_3 in N_2) may have been used to calibrate, or check the calibration of analyzers evaluated in this test program. However, calibration gases were not always required in normal instrument operation, particularly for the *in situ* analyzer systems.

Unlike typical CEM calibration gases, the NH_3 species is more difficult to handle, and accuracy of the gas bottle concentration is less certain. Since these bottles may indirectly affect the accuracy of some analyzers, the bottle concentrations were verified. Wet chemical samples were obtained from the gas cylinders in the same manner as the flue gas samples and were analyzed to verify accuracy.

Initial verification of two NH_3 span gases showed good agreement with the indicated concentrations on the bottle. For example, one 50 ppm span gas averaged 50.5 ppm from wet chemical measurements. These initial wet chemical verifications were performed approximately seven months after delivery of the gases.

Approximately eight months later, the same 50 ppm calibration gas was re-verified following a relatively low reading during an instrument span check. It was determined that the 50 ppm span gas was now indicating 42 ppm by wet chemical measurements. This decrease was also similar to the low span check indicated by the instrument. A second span gas bottle showed similar reduction by the instrument span check. This apparent long-term reduction in NH_3 concentration may be a critical issue if attempting to determine instrument drift or performing re-calibrations from a span gas bottle that also changes with time.

Problems may also occur from new span gases that have been recently received from a supplier. For example, another NH_3 span gas bottle was later purchased with a similar 50 ppm specification. The gas bottle was tested approximately five months from the date of delivery at the time of wet chemical verification tests. In this case, the previously unused bottle showed only 32 ppm NH_3 concentration.

These span gas errors could be extremely significant if the monitors rely upon the gases for initial set up and/or periodic calibration. NH_3 span gases should be at least cross checked with other span gases or subjected to wet chemical measurements for verification. In addition, these NH_3 span gasses were procured based upon some of the early instrument requirements. If a typical 0 to 20 ppm NH_3 instrument requires a span gas within this low range, additional difficulties may be expected. Gas suppliers may require less accurate analysis specifications as the NH_3 levels drops below the 25 ppm range.

Wet Chemical Sampling Issues

At the start of the wet chemical accuracy tests, a few samples were acquired with a short quartz probe and compared to the results obtained with the stainless steel probes. No significant differences were noted for the measured NH_3 levels (with relatively high NH_3 levels at that time). Since no differences were noted, use of the stainless steel probe was continued.

However, some wet chemical samples obtained in November 1999, with lower NH_3 levels indicated a bias of the measurements. The comparison between the analyzer output with extractive wet chemical NH_3 measurements indicated the existence of a low NH_3 slip, wet chemical measurement interference. The exact cause of the interference was not determined; however, it resulted in higher than expected wet chemical results.

The interference was confirmed by comparisons with a limited number of diagnostic tests at the economizer exit (with no NH_3 slip present) and with quartz versus stainless steel probe measurements. The extent of this interference is shown in Table 6-1, which shows the results of wet chemical NH_3 measurements obtained ahead of the SCR ammonia injection point.

Table 6-1
Wet Chemical Interference Results
(Samples obtained at the economizer exit, upstream of the SCR system)

Test Location	Probe Material	Indicated NH_3, ppm
Ahead of SCR	8’ Stainless (Long probe)	1.72
Ahead of SCR	3’ Stainless (short probe)	0.67
Ahead of SCR	3’ Quartz (short probe)	0.09

Table 6-1 shows the results from flue gas wet chemical NH_3 samples obtained at the economizer exit, ahead of the SCR ammonia injection grid (AIG). At this location, there should be no NH_3 present in the flue gas, yet the flue gas conditions should be similar in temperature and gas composition to the SCR outlet. As can be seen in the table, sampling with the stainless steel probe in flue gas, where no NH_3 should be present, yielded an indicated NH_3 concentration of 0.67 and 1.7 ppm. At first this was thought to be a problem with the specific ion electrode analysis. Samples were reanalyzed with similar results.

Selected samples were also reanalyzed with an ion chromatograph by an outside laboratory. These ion chromatograph analyses were similar to the specific ion electrode results, indicating that the problem was related to the stainless steel probe and not the analysis of the collected sample. Also, as seen in Table 6-1, sampling with a quartz probe showed virtually no NH_3 to be present with the economizer exit samples.

The problem may be associated with the stainless steel probe; however the exact reason was unclear. Similar probe tests conducted during previous wet chemical evaluations, early in the NH_3 monitoring program, showed that the interference problem was not significant. This may suggest that the aging of the stainless steel probe could be a factor; however, this is currently only a hypothesis. If so, the type of stainless steel utilized may be an important factor.

Stainless steel probes have been routinely utilized for NH_3 sampling in utility boiler testing, generally with good success. The existence of very low NH_3 levels required in this program may have allowed better detection of this potential interference problem. A quartz (or glass) probe appeared to be unaffected; however, use of these fragile probes is often impractical for utility boiler sampling situations. Additional investigation of the extent of the interference was performed during later wet chemical measurement tests.

Additional measurements were performed to determine if the type of probe material was a factor (see Table 6-2). New stainless steel probes of different materials were procured. Stainless steel (304, 316), Inconel, and glass probes were tested. Some stainless steel probes were "aged" by subjecting them to the flue gas and rinsing with the NH_3 sampling solutions. Other probes were "new" and had only brief conditioning to the flue gases. All tests were conducted before the NH_3 injection grid; therefore, no NH_3 should be present.

It appeared that the lower grade 304 stainless steel affected the sample to greater extent than the 316 or Inconel; however, significant interferences were noted with all of the metals tested. It was not clear if aging of the stainless steel probes was a factor, but it appeared to be important for the 304 stainless material.

A glass probe showed a small effect sampling from the ash laden, flue gas stream; however, this difference may be insignificant. The analysis of a blank solution of the dilute acid (that was not subject to sample conditions) showed essentially a zero NH_3 level. All samples were analyzed with the specific ion electrode method.

The use of stainless steel probes may result in a positive NH_3 indication from sampling typical flue gases at the economizer exit or SCR exit conditions. The significance of the interference may depend upon the magnitude of NH_3 measurements that are required. Low levels of NH_3 measurement appeared to be affected to the greatest extent. The use of, or comparisons with, glass or quartz probes may be warranted under these conditions.

Table 6-2
Wet Chemical NH_3 Sampling Probe Material Tests

Probe Material	Condition	Indicated NH_3, ppm
6’ Stainless 304	New	0.89
6’ Stainless 304	Aged	1.51
6’ Stainless 316	New	0.92
6’ Stainless 316	Aged	0.60
10’ Stainless 316	Aged	0.69
6’ Inconel	Aged	0.68
6’ Glass	New	0.17
Blank solution	- -	0.02

Also, the extent to which this effect depends on the flue gas and ash composition is not known. In other words, this potential interference problem may be site-specific. For example, at the EPRI Cardinal Unit 1 SNCR demonstration, NH_3 samples were obtained during operation with no reagent injection (no NH_3 slip). NH_3 results with a stainless steel probe showed very low NH_3 measurements (~0.10 ppm), which indicated no significant interference.

7

SUMMARY AND CONCLUSIONS

An evaluation of continuous ammonia monitors has been ongoing at OUC's Stanton Unit 2 since early 1998. Tests of the two *in situ*, tunable infrared laser-based ammonia analyzers (NEO and AltOptronic) have demonstrated good reliability and accuracy over a long operating period. Both instruments follow the expected trends with varying SCR operating parameters. At relatively low NH_3 slip levels, 1.6 ppm as determine by wet chemical measurements, the measurements have been within 0.6 ppm with both instruments.

At the low NH_3 slip levels downstream of the Stanton 2 SCR, the use of metal probes to extract a wet chemical NH_3 sample were found to produce a nominal 0.7 ppm positive interference relative to a glass or quartz probe. The reason for this interference is not currently known. Additional investigation into the cause of wet chemical interference problem is warranted, since wet chemical measurement techniques are routinely utilized for evaluating SCR and SNCR processes.

Procurement of accurate NH_3 calibration gases may become a significant issue, particularly if an analyzer requires a periodic span gas for normal operation. In some cases, the measured NH_3 concentrations in new bottles differed significantly from the manufacturer's analysis. Also, the NH_3 concentrations in the bottles appeared to decrease with age.

An NH_3 analyzer used for a SCR or SNCR utility boiler installation will be primarily a process monitor for evaluating system operation and, possibly, for reagent injection control. Short term, minute-by-minute NH_3 data may not be the primary requirement for this type of analyzer application. Long-term analyzer monitoring can be invaluable for evaluating system trends on a monthly, or yearly, timeframe.

For example, at Stanton Unit 2, the NH_3 analyzer could be used to evaluate long-term catalyst life and/or overall SCR system operation. Initial NH_3 analyzer operation during this demonstration program showed unexpectedly high NH_3 slip levels. Thereafter, more frequent air heater water washes and confirmation with wet chemical NH_3 measurements indicated advanced catalyst deactivation. This eventually required an early installation of another layer of catalyst. An NH_3 analyzer installed at the startup of the SCR would have shown the gradual increase of NH_3 slip, well in advance of the high NH_3 slip effects encountered later.

Target:
Post-Combustion NO_x Control

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