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Measuring Ammonia Slip from Post Combustion NOx Reduction Systems

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ABSTRACT

Unreacted ammonia, referred to as ammonia slip, can be a by-product of certain NOx reduction processes. Facilities with NOx reduction systems that experience substantial operating problems from ammonia slip are the exceptions rather than the rule. This is largely due to improved understanding of technology application and also due to the fact that these systems are usually operated well within the operating envelopes in order to avoid problems with ammonia slip. In many facilities there may be room for process improvement that could reduce operating costs or provide revenue enhancement opportunities. Operating SNCR or SCR technology closer to its limit offers these benefits but increases the risk of high ammonia slip. The risk could be abated with the use of ammonia monitoring technology. But, except for gas-fired plants, continuous ammonia slip monitoring technologies have not been available at a practical price to facilitate these cost-saving or revenue enhancing improvements. Conditions that exist in high dust, high temperature, high NOx and/or high SO_2 environments make most analyzer methods of continuously measuring ammonia unsuitable for application to coal plants.

In this paper, the motivation to utilize ammonia slip monitoring technology will be analyzed and quantified for an example plant. As will be shown, the benefits of monitoring ammonia slip are largely realized in the ability to operate a facility in a manner that permits facility income enhancement at a lower risk. Hence, the value is in risk reduction while revenue is enhanced.

Finally, a brief overview of the technologies available for measuring ammonia in the high dust region downstream of a NOx reduction system and the status of their development will be provided.

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Introduction
For Selective Catalytic Reduction (SCR) and Selective Non-Catalytic Reduction (SNCR) technologies, the level of ammonia slip is normally controlled to levels that do not create operating problems or pollutant emission issues for users. Under the unlikely circumstances where high slip may occur, the types of problems ammonia slip can potentially contribute to are well documented and include:

- Formation of ammonium salts on air preheater and other downstream surfaces.
- Ammonium Chloride plume from the stack.
- Ammonia odor in fly ash.
- Emission of gaseous ammonia.

The first, second and third problems are of most concern to boiler operators, particularly the first. The third problem is of greatest concern to air regulators. This paper will not explore these problems in detail, since they are mostly well understood and operators of facilities and air regulators are well aware of them.

Reference 1 evaluated the use of NOx reduction technologies on several U.S. utility boilers and found that significant operating problems due to ammonia slip were rare, although there were units identified in the study that experienced some air preheater buildup. The level of slip that needed to be maintained to avoid problems varied. According to Reference 1, one unit experienced air heater plugging when ammonia slip exceeded 2 ppm while other plants could withstand higher ammonia slip levels up to 10 ppm. None of the facilities reported higher emissions than 10 ppm. While sulfur content of the fuel plays a major role in determining the level of slip that is associated with an onset of problems, boiler design, fly ash characteristics, and condition of the boiler (air in-leakage, etc.) all play a significant role.

NOx reduction plants are normally operated well within the operating limits in order to avoid ammonia slip. In many facilities there may be room for process improvement that could reduce operating costs or even provide the opportunity for revenue enhancement under allowance trading scenarios. However, such operation might risk higher slip. Ammonia slip monitoring technology has not been available to facilitate such benefits with sufficient confidence that slip won't be a problem. To date, ammonia monitoring technology application has been limited largely to natural gas fired applications or other clean gas applications. These applications could be addressed with existing monitoring techniques, such as UV photometry, ion mobility spectroscopy or differential NOx analysis following conversion of ammonia to NOx. Conditions that exist in high dust, high temperature, high NOx and/or high SO_2 environments have made these methods mostly unsuitable for application to coal plants. Moreover, most commercial embodiments of these instruments are such that a several minute time delay would exist, which may make them less useful as process control devices in SNCR or SCR systems. Therefore, other technologies must be used.

However, before embarking on a description of technology for measuring ammonia, it is worth considering the reasons for monitoring it.

Benefits of Monitoring Ammonia
The value of the benefit of monitoring ammonia slip continuously must exceed the cost or there would be no reason to pay the price of an ammonia slip monitoring instrument.

Others who have considered this issue have focussed on the benefits of process optimization or avoidance of air preheater cleaning. These are good reasons to monitor ammonia. However, as will be shown, the argument may not be compelling in many cases. However, when the facility is operated closer to the limits of the technology for the purpose of revenue enhancement, the argument becomes much more compelling.

Experience with SNCR and SCR systems in the U.S. on coal fired boilers documented in Reference 1 showed that only one of seventeen coal-fired boilers evaluated experienced an ammonium bisulfate deposition problem that forced shutdown or a derate. This one case was an unusually challenging SNCR system that required special injectors because of the required level of reduction, the boiler's size and furnace characteristics. In other cases, where air heater build up did occur, cleaning was performed during scheduled outages. Therefore, if SCR and SNCR systems continue to be operated as they have - well within their capabilities - it is reasonably unlikely that any particular boiler will experience air heater plugging that is so severe that it is forced to an unplanned shut down or take a derate. Some units may experience an increase in air-preheater build up. But, it will rarely be so severe that forced outages or derates result. Of course, air heater cleaning is a nuisance and costs money, but it probably is not as costly as purchasing replacement power. The cost of periodic air heater cleaning, which is unlikely to go away completely with an ammonia monitor, is likely to be reduced with the help of ammonia monitoring technology. If, on average, cleaning is reduced from, say, 2 times per year to one time per year. This is worth in the range of $20,000 to $40,000 per year (assuming $20,000 per cleaning). It is notable that there was at least one unit in Reference 1 that operated an SNCR system for several years without having any apparent ammonium bisulfate build-up in the air preheater. Of course, this too is probably an exceptional case. In summary, many facilities did experience some increase in air preheater deposition. However, experience shows that under current operating methods the likelihood of problems serious enough to affect operation is very low.

SNCR Process Improvement
SNCR process chemistry is such that there is a trade off between chemical utilization and ammonia slip. Chemical utilization is related to the level of NOx reduction associated with a given treatment rate. In order to assure that ammonia slip will not be a problem, SNCR operators are forced to operate the system in such a way that chemical utilization is usually less than optimal. Figure 1 shows how this trade off between NOx reduction and ammonia slip occurs largely as a function of injection temperature. The SNCR process chemistry is very complex and it is sensitive to many furnace variables. For this reason, it is very difficult to assess how much of an improvement in reagent consumption may possible through integration of an ammonia analyzer into the SNCR controls without some sort of detailed test program or computer modeling. Reference 2 discusses how New England Power used an ammonia analyzer and other control improvements to reduce reagent consumption by a total of 60%. Half of the improvement was attributed

by New England Power entirely to changes in the way the boiler furnace wall blowers were operated as a result of an on-line furnace temperature monitor that was installed. It is unclear how much of the remaining improvement could be attributed to the ammonia analyzer because substantial changes were made to the urea injection system that likely accounted for much of the improvement. If an ammonia instrument could be integrated into the controls of an SNCR system to improve reagent consumption by, say, 5%, then a unit with an annual urea bill of $500,000 (an approximate number for a 200 MW Group I boiler operating year-round at a capacity factor of 65%) would see a $25,000 improvement in the annual urea cost. A 10% improvement could be worth $50,000 per year. On the other hand, if the boiler only uses its SNCR seasonally, the cost savings are much less, because the urea bill will be much less - around 40% of the aforementioned values.

On the other hand, an ability to identify the onset of high ammonia slip and adjust the process may offer the potential for revenue enhancement through more aggressive operation of the SNCR system and sale of excess NOx credits. The additional NOx reduction could potentially result from process improvements at no additional reagent costs or from injecting more reagent while monitoring ammonia to ensure that high slip does not result.

What would it cost to equip an SNCR system to accommodate the signal of an ammonia monitor to improve controls? This depends upon the current configuration of the SNCR controls. It could be anywhere from slightly more than the cost of the analyzer to several times the cost of the analyzer if the controls needed substantial changes. Putting values to this, this could be an expenditure of no less than $50,000-$100,000 to several hundred thousand dollars.

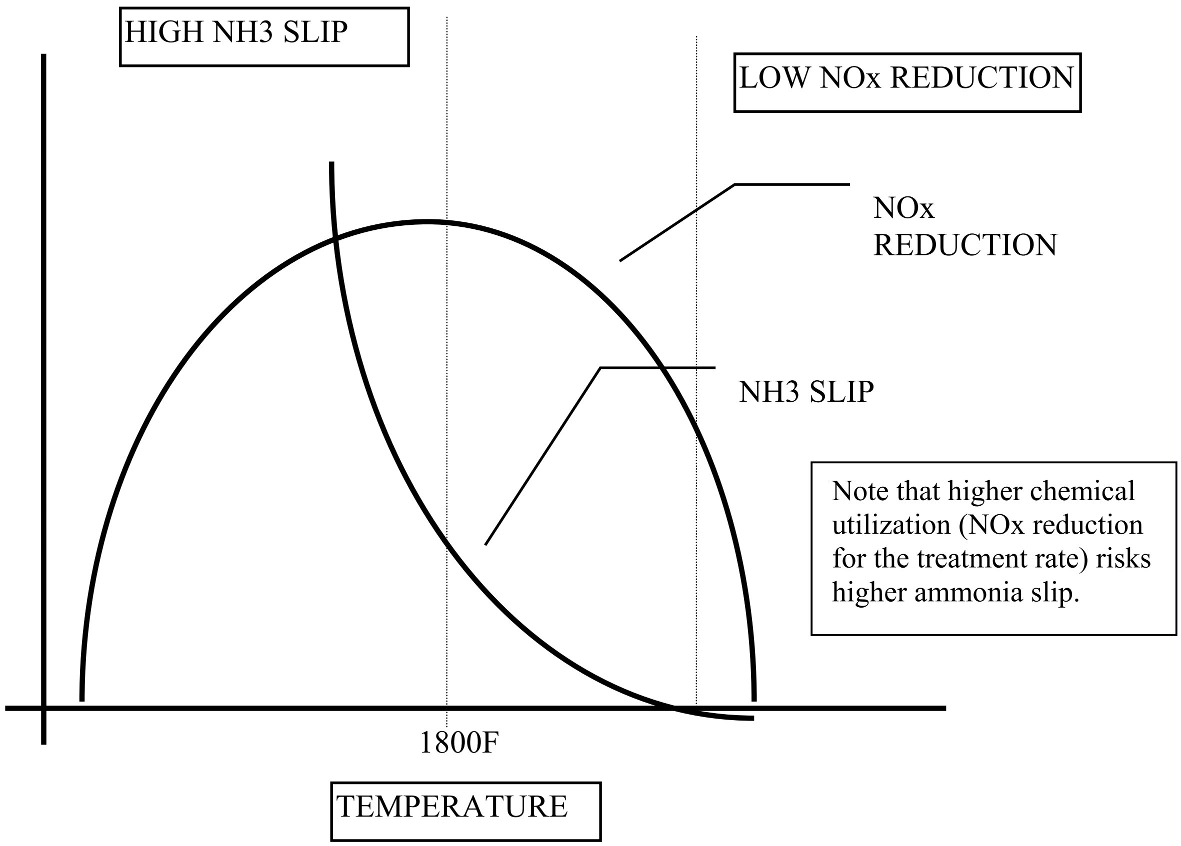
Improved SCR controls

Because of the inherent efficiency of the SCR reaction, there is little or no room for improvement of reagent consumption. An on line analyzer may enhance transient operation, avoiding high slip conditions that may occur during rapid downward load changes. In the event that the unit is expected to have frequent load changes, an ammonia analyzer may be useful in helping to avoid some of the problems identified earlier in this paper. These benefits are hard to quantify, and may not make compelling arguments for capital expenditures.

Improved SCR Asset Utilization

Asset utilization relates to the ability of an asset to generate revenues. Therefore, if an SCR or SNCR system has the ability to improve the revenues of a facility, it can potentially improve the asset utilization of the facility. However, we will return to this financial topic shortly, after discussing technically how and why these processes can improve revenues.

Figure 1. Effect of Temperature on NOx Reduction and Ammonia Slip



SCR Technical Overview
SCR's are designed to meet a guaranteed level of NOx reduction with a maximum level of ammonia slip after a specified number of operating hours.

Catalyst volume, Vcat, is approximately determined by the following equation, which captures the effects of chemical kinetics at a constant temperature [3]:

$$Vcat = \{F1 * Vfg * [-\ln (1 - \eta)] / (Asp * k*F2)\} + F3$$

where η = the fraction of NOx removed, F1, F2, and F3 are correction factors based on experience, Vfg is the furnace gas volume flowrate, k is the catalyst activity coefficient, and Asp is the specific surface area of the catalyst.

For a particular SCR reactor with a designed volume, flowrate, specific surface area and correction factors, the above equation can be reduced to:

$$(1 - \eta) = e^{-kC}$$

Of course, this is recognized by chemical engineers as the famous Arrhenius Rate expression from chemical kinetics with temperature held constant, from which the first equation is originally derived. The catalyst reactor is designed to maintain at least a certain level of activity after a number of operating hours. This is normally referred to as k/k_o , or the fraction of original activity. Figure 2 shows an example plot of catalyst activity versus operating hours. The actual value of k/k_o is determined by the particulars of the application and the volume of the reactor.

In any event, when the catalyst is new, it can achieve greater reductions of NOx while maintaining within required ammonia slip levels. The catalyst loses its activity as a result of deposition of impurities from the fuel onto the catalyst surface. It is important to note that injection of ammonia for the NOx reduction reaction does not in any way impact catalyst degradation.

For example, a catalyst with activity as is Figure 2, might reduce NOx as shown in Figure 3 if enough ammonia is injected. The shaded area indicates the unutilized outlet NOx potential if the SCR is operated only at the end of life design value of ~0.15 lb/MMBTU.

The Potential Value and Uncertainty of Excess Reductions
This excess capacity of the SCR to reduce NOx early in it's life is potentially valuable during the ozone season in the Ozone Transport Region, where emission reduction credits can be generated and traded. In fact, Public Service Company of New Hampshire used funds earned from the sale of NOx early reduction credits to pay for facility improvements.[4]

Hence, for facilities in the Ozone Transport Region, there is the potential for revenue enhancement by overcontrolling NOx and selling emission reduction credits. The marginal cost of creating these credits is largely the cost of the additional ammonia. Bear in mind that at this point in the analysis we are assuming that the additional reductions are being done with the initial catalyst charge, so that no additional catalyst is needed. That is why the potential benefit diminishes with time as the catalyst loses activity.

The value of these credits in the marketplace less the cost of generating them (mostly the cost of ammonia) will determine the degree of *income* enhancement that is possible with this approach. Figure 4 shows the potential value of this approach for three consecutive ozone seasons on a 500 MW boiler with an Ozone Season capacity factor of 70% while assuming an ammonia cost of $360/ton. Assumptions incorporated into the analysis of Figure 4 include catalyst behavior exactly as in Figure 2 and that every ton of NOx below 0.15 lb/MMBTU can be sold.

There is, however, some additional risk associated with operating in this manner. Although experience has shown that few NOx reduction systems cause their owners serious difficulties from ammonia slip, these facilities were not trying to operate at the catalyst's limit. And, in reality, the catalyst activity may not behave exactly as expected in the design curve such as indicated in Figure 2. There is an expected range of activities expected over catalyst life, as shown in Figure 5. Figure 5 shows the expected catalyst activity along with an assumed expected 95% confidence level for the catalyst.

Figure 2. SCR Catalyst Activity versus Operating Hours

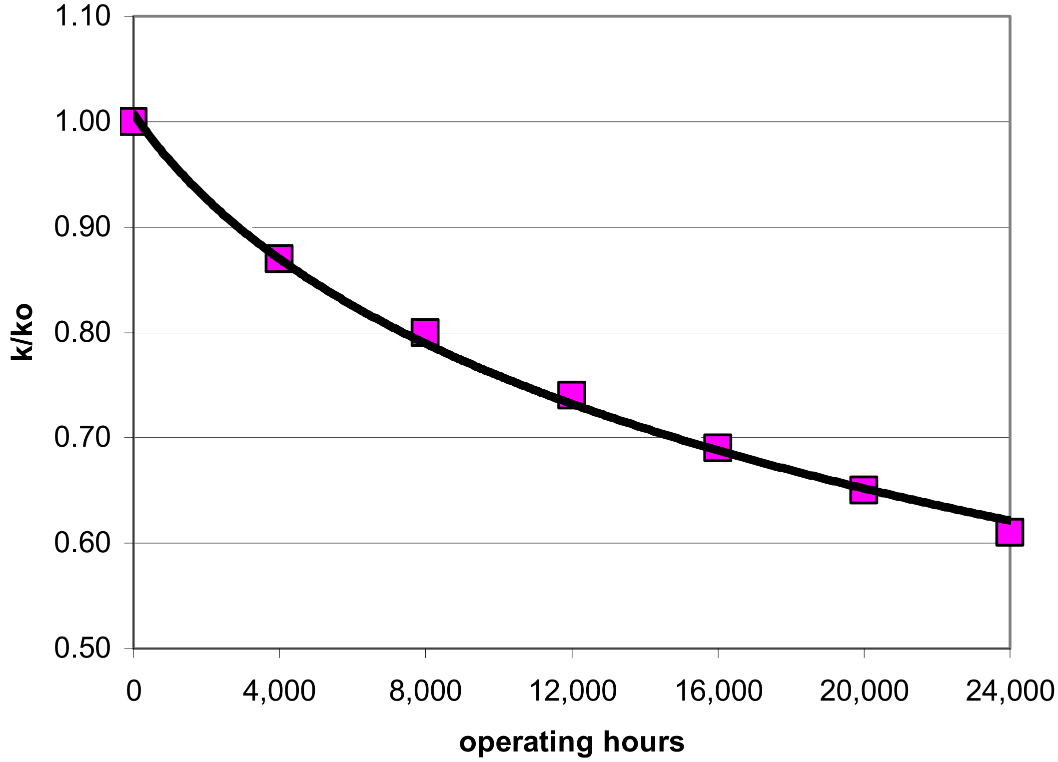


Figure 3. SCR Outlet NOx Potential

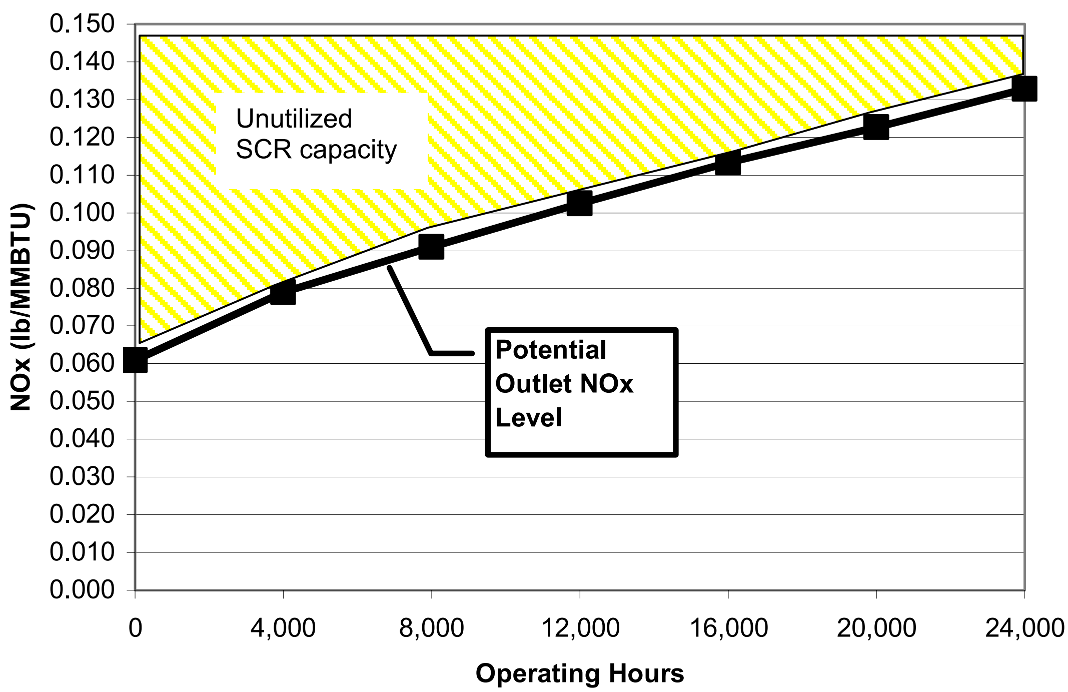
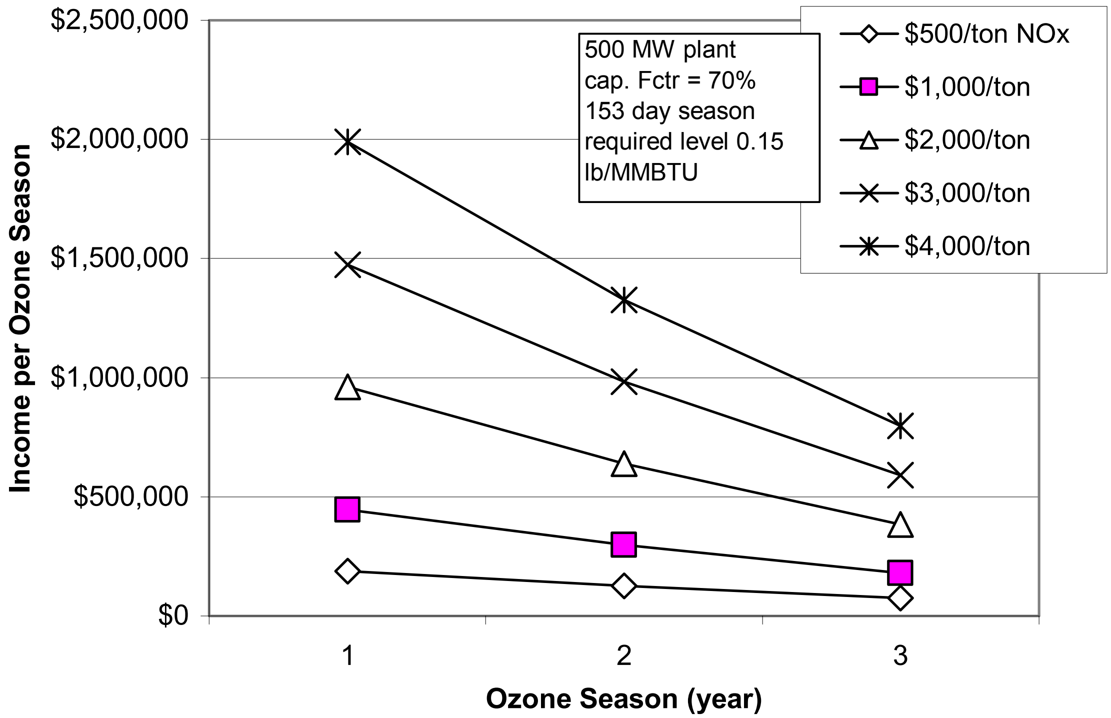


Figure 4. Potential Income Enhancement from Ozone Season NOx Allowance Sales through Overcontrol of SCR

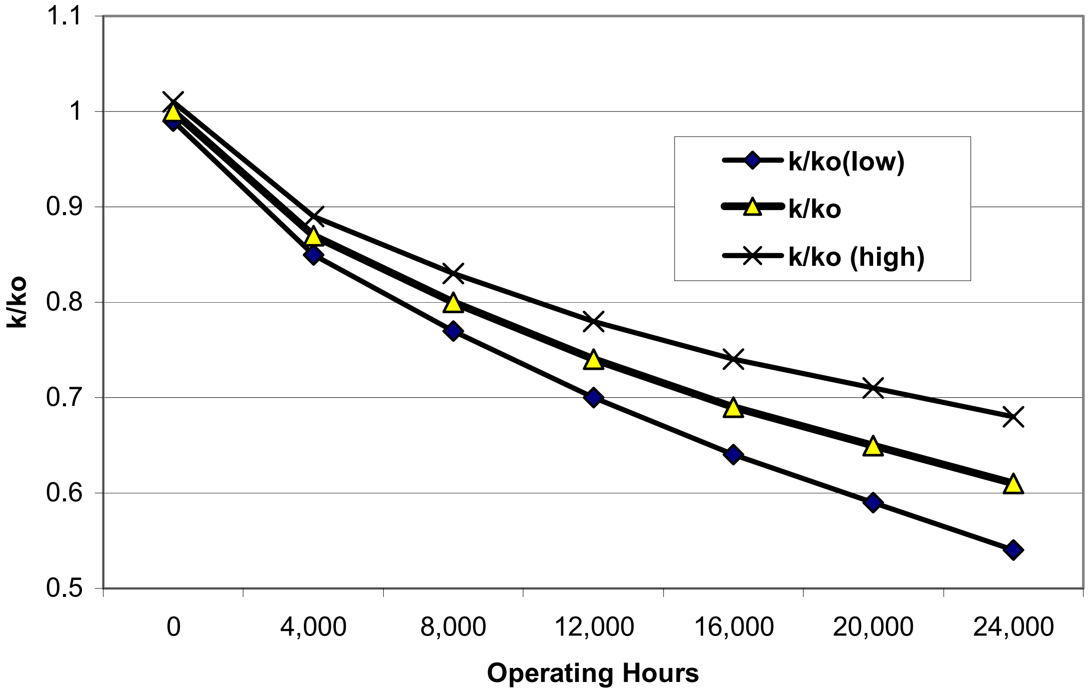


The range of uncertainty in catalyst activity will vary for each application. In some cases it will be small, in others the uncertainty can be high. The range of uncertainty will be determined by the quality of the database of the catalyst supplier, the quality of the information provided by the owner to the catalyst designer, and how closely actual operations mirror the information provided by the owner to the catalyst supplier. In general, the catalyst suppliers have very good databases and can predict performance very well for certain, well-specified conditions. However, in the authors experience, the quality of information available during the design process and how closely the actual operations match expected operations play a much greater role in determining the level of uncertainty in future catalyst performance.

Fortunately, the effects of this uncertainty can be quantitatively assessed through computer simulation. Figure 6 shows cumulative probability plots resulting from a Monte Carlo simulation of ozone season NOx allowances available for sale for each of seasons 1, 2, and 3 with the uncertainty of Figure 5 included.

The results of Figure 6 indicate the tons available for sale on a 500 MW plant with a capacity factor of 70% that only needs to control to 0.15 lb/MMBTU if the catalyst is operated at it's limit. As shown, in the first ozone season there is a 50% chance that 514 excess tons can be generated without ammonia slip problems and the uncertainty is quite low regarding how many tons. This is because the catalyst is relatively new and there is little uncertainty regarding the performance it can offer. There is about a 95% chance that up to 505 tons can be generated. Yet, there is only a 5% chance that 523 tons can be generated. In other words, risk can be substantially reduced with a penalty of only 18 tons or 3.5% of the mean expected value.

Figure 5. Expected k/ko plus and minus 2 x std. Deviation (95% confidence interval)



In the authors experience, the quality of information available during the design process and how closely the actual operations match expected operations play the greatest role in determining the level of uncertainty in future catalyst performance.

In the second ozone season, 342 tons are the mean of the projections. There is about a 95% chance that up to 315 tons can be generated. There is only a 5% chance that 368 tons or more can be generated. Hence, the spread is getting wider, to 15% of the mean expected value.

For each year the uncertainty in the projections increases. As stated earlier, this is largely due to uncertainty in how the facility is actually operated versus initial expectations. In the third ozone season, 204 tons is the value of the mean of the projections. There is about a 95% chance that 154 tons can be generated. There is only a 5% chance that 253 tons or more can be generated. The spread in uncertainty has increased to 98 tons in season three from 18 tons in season 1, or nearly 50% of the mean expected value.

Figure 7 translates the results of Figure 6 to income enhancement potential assuming NOx allowance prices of $1,000/ton and the price of ammonia is $360/ton.

As shown in Figure 7, the average (50% probability value) for the First Ozone Season is $446,000 with a Standard Deviation of only $4,800 at an allowance price of $1,000/ton. There is a 95% probability that $438,000 in income can be made and only 5% chance that $454,000 in income can be generated in the first ozone season.

In Ozone Season 2, the 50% probability value for income enhancement is just under $300,000 (~$298,000) and standard deviation is $13,720 at an allowance price of $1,000/ton. Or, there is a 95% chance that $273,000 in income can be made and 5% chance that $319,000 can be generated. This is still a fairly narrow band of uncertainty, although it is much increased from the first ozone season.

Finally, in Ozone Season #3, the 50% probability value is only $177,733 of income enhancement at an allowance price of $1,000/ton. Standard Deviation is $26,175, or nearly 15% of the mean. There is a 95% chance that $134,000 in income can be generated and only 5% chance that $219,000 in income can be generated. Clearly, the uncertainty of available allowances for trading and the uncertainty in income potential has substantially increased to nearly 50% of the mean expected value.

Finally, Figure 8 plots the 5%, 50%, and 95% confidence values from Figure 7, which demonstrates the diminishing value and increasing uncertainty of income for each ozone season.

Figure 6. Range of Potential Ozone Season Tons Available for Sale, Accounting for Uncertainty: 500 MW Plant, Catalyst activity of Figure 5

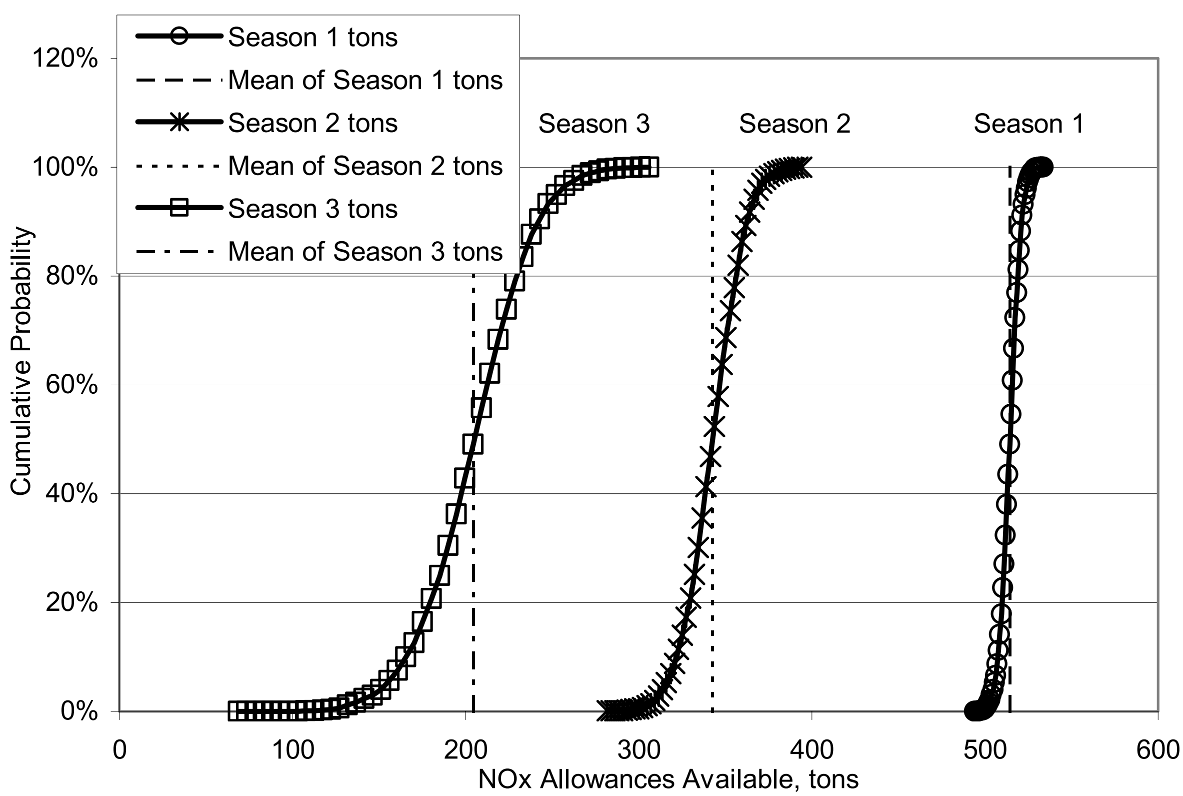


Figure 7. Range of Potential Net Income Enhancement, Accounting for Uncertainty 500 MW Plant, $1,000/ton allowance prices, Catalyst activity of Figure 5

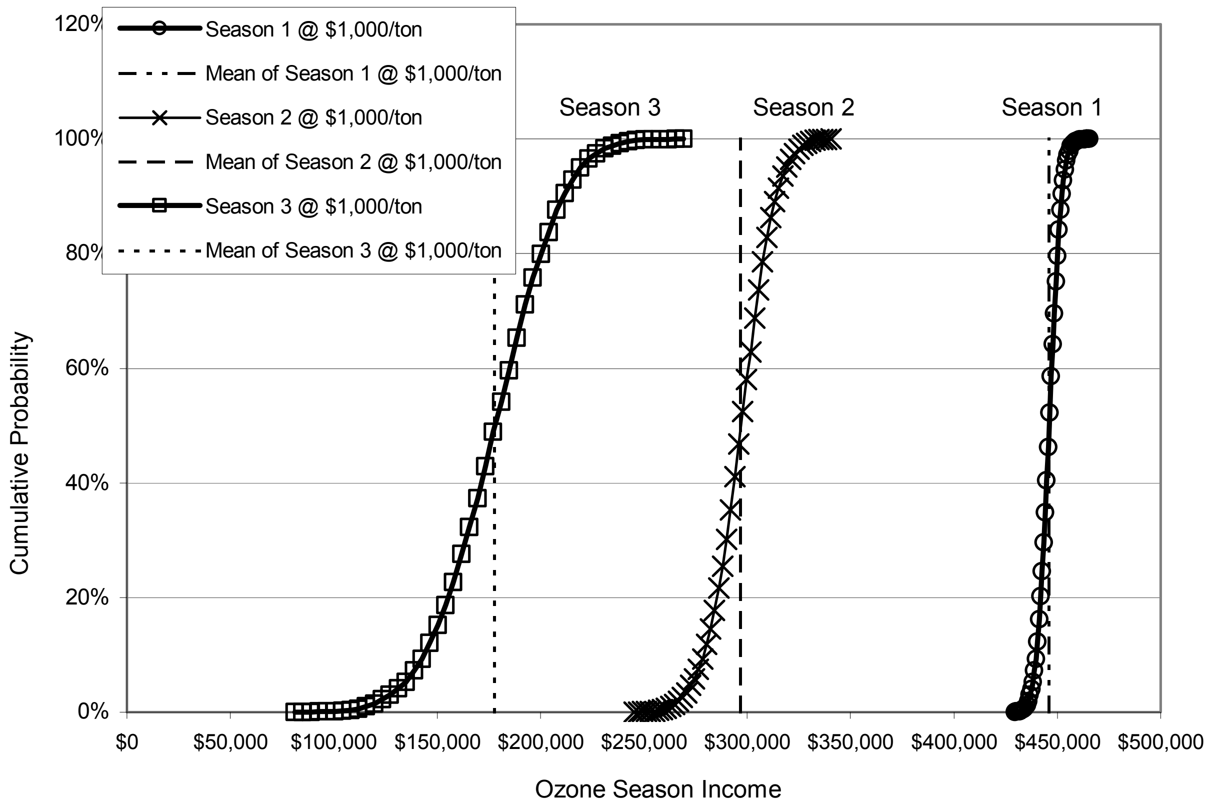
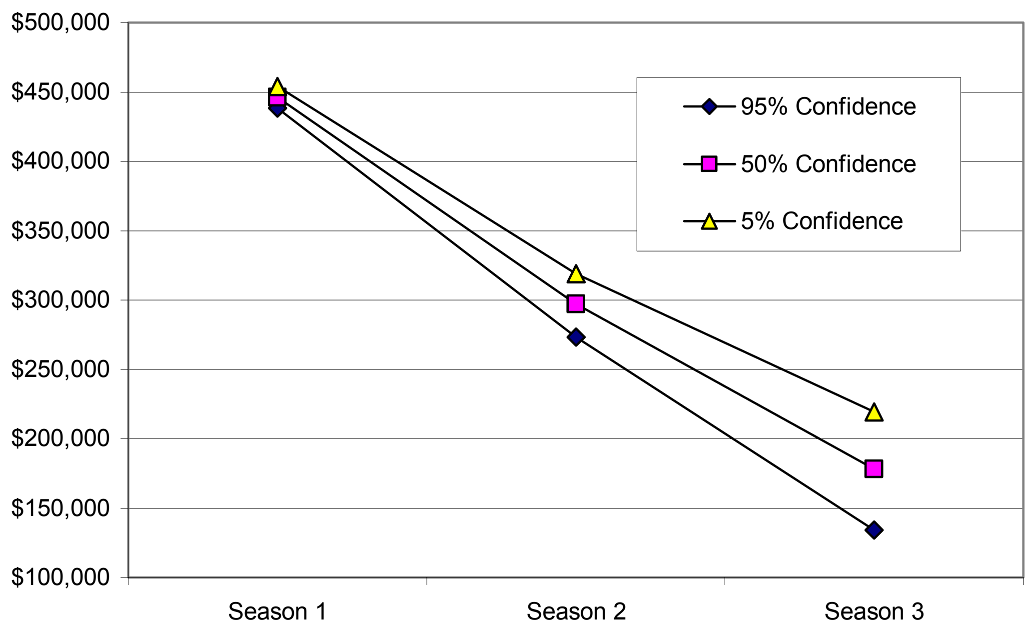


Figure 8. 95%, 50% and 5% Confidence Values of Income Enhancement from Figure 7



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Reducing the Uncertainty - The Value of Monitoring Ammonia
There is a large motivation to utilize the assets of utility plants as effectively as possible. Therefore, when it is possible to enhance revenues and income through sale of NOx allowance credits, these opportunities should be explored. The analysis in this paper showed, quantitatively, what the value of these opportunities might be for a particular situation. The analysis also showed how there can be significant uncertainty in projecting what the value of the opportunity might be. Uncertainty in the projections is determined by several things. The price of NOx credits is one. But, one of the most significant for SCR systems is the behavior of the catalyst over time. Generally, this is more a factor of how closely actual operation matches expected SCR operation than any uncertainty over how the catalyst would behave under absolutely certain conditions. For SNCR systems, there are numerous factors that affect the predictability of operation. Most important is the consistency of furnace conditions, since for SNCR catalyst degradation is not an issue.

Ammonia monitoring is one important tool in the effort to address the uncertainty of NOx reduction system operation. Other tools include periodic catalyst activity testing, periodic furnace testing, and maintaining consistent fuel and boiler conditions. However, ammonia slip is the single indicator that will provide a direct measure of whether the NOx reduction system is being operated under, at, or beyond its limitations and by how much. Therefore, the use of ammonia monitoring technology (if available) can make it possible for much of the risk to be addressed.

Unfortunately, for operators of coal-fired power plants ammonia-monitoring technology has not been available in a reliable and cost-effective form. Table 1 lists several continuous analyzer technologies. While several methods have proven very useful for gas applications where low NOx and low SO_2 exist, infra-red methods appear to offer the greatest hope for addressing this issue for coal-fired plants. Multi-component infra-red methods tend to be expensive and are not amenable to in-situ measurement. One of the most difficult aspects of measuring ammonia is getting the sample to the analyzer while maintaining sample integrity. In-situ measurement avoids the concern regarding lost sample integrity. Tunable Diode Laser spectroscopy, because it offers the potential for reasonable cost, in-situ measurements, high molecular selectivity and rapid response, is the most promising technology. Interference from moisture is a potential problem. But, some of the suppliers have developed methods for addressing this concern while maintaining adequate sensitivity. The primary disadvantages of TDL methods are that there is little commercial experience for ammonia applications and that many of the suppliers are small, overseas firms. In most cases the instruments are still development-stage prototypes. Service and application support will be important features to users of these products.

Table 1. Technologies for Continuous Measurement From Ammonia			
Technique	**Advantages**	**Disadvantages**	**Well Suited For**
NOx differential	• Experience & familiarity with method	• Measures a surrogate • Sensitivity for high NOx situations can be poor	• Low NOx (gas turbines or gas boilers)
UV photometry	• Experience & familiarity with method	• Strong Interference from SO_2	• Natural Gas applications, or other low SO_2
Ion Mobility	• Sensitivity • Fairly interference free	• Not well suited for Corrosive gases • Slow response	• Any clean, non-corrosive gas
TDL (IR)	• Relatively interference free (except for water) • Solid-state • In-Situ - no sample handling required • Sensitivity	• Limited experience • Service and Support (mostly small, foreign firms) • Moderate moisture interference must be properly addressed	• All applications, especially coal
IR (multicomponent)	• Multiple species	• Tends to be Expensive	• All applications
Automated Wet Chemistry	• Experience & familiarity with method • Can be set up quickly	• Labor intensive • Requires reagents	• Testing programs
The above are general statements that reflect the author's overall impression based upon his close familiarity with NOx reduction technology and ammonia monitoring technology. This is not intended to be a complete list. However, it is a list of the most important approaches in the author's opinion. In some cases companies may claim to have addressed certain disadvantages. The author neither disputes nor confirms their claims.			

Summary

There are large opportunities for SCR and SNCR NOx reduction system operators to enhance overall facility income. However, there are uncertainties and risks associated with operating the facility at close to the limit of system capabilities. In this paper the values and uncertainties were analyzed and quantified for a sample plant. Computer simulation of one example showed that the uncertainty can be substantial over time. Availability of ammonia monitoring technology will permit these uncertainties and risks to be addressed more effectively. Technologies have been available for monitoring natural gas fired applications. However, until recently there have not been technologies available for coal-fired electric utility plants that are of reasonable cost, sufficient accuracy, and reliability. Some new technologies, particularly TDL spectroscopy, offer excellent potential to address coal applications.

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