CATALYST DESIGN EXPERIENCE FOR 640 MW CYCLONE BOILER FIRED WITH 100% PRB FUEL

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Abstract

Unique consideration for mechanical and chemical ash properties generated from a cyclone boiler firing 100% Powder River Basin (PRB) fuel will be discussed. In addition, relationships of system design parameters, such as flow distribution, high efficiency (93%) and low ammonia slip (3 ppmvdc), will be presented. This paper will set the stage for reporting data in the future.

Introduction

Associated Electric Cooperative Inc. (AECI) contracted a joint venture of Black & Veatch and J.S. Alberici (BVCI/JSA) to provide a High Dust Selective Catalytic Reduction (SCR) system for their 640 MW New Madrid cyclone fired Units 1 & 2. Subsequently, BVCI/JSA subcontracted for catalyst supply from Cormetech. The project constitutes the world's first application of SCR to a 100% PRB coal fired boiler. In addition to the unique characteristics of the fuel the project also requires high NOx removal efficiency (93%) while maintaining low ammonia slip (3 ppmvdc). In addition, the project incorporated equipment that will improve the overall thermal efficiency of the units. The SCR process design being implemented at New Madrid is based on over 10,000 MW of SCR design, startup, and O&M experience (12 years) derived by STEAG AG, a German independent power producer.

The retrofit project for Unit 2 will be completed in December of 1999. The retrofit for Unit 1 has been released and is scheduled for completion in May of 2001.

This paper summarizes SCR system configuration and catalyst design. Catalyst design/performance is discussed as a function of fuel and ash parameters and of system components, i.e. Ammonia Injection Grid (AIG), turning vanes, and distribution devices. Additionally, a brief discussion of the "SCR ready" regenerative air heater is provided.

Scope of Supply – Table 1

By Black & Veatch /J.S. Alberici

- SCR Reactor
- Catalyst, Frames, and Seals
- Catalyst Loading System
- Ammonia Unloading & Storage
- Ammonia Vaporization
- Ammonia Injection Grid
- Sootblowers (Catalyst and Air Heater)
- Double Louver Dampers & Seal Air
- New "SCR Ready" Regenerative Air Heater
- Air Preheat Coils
- Modified FD Fan Casing
- Interconnecting Air & Gas Duct
- Tubular Air Heater Demolition
- Ash Hoppers
- Insulation & Lagging
- Expansion Joints
- Controls
- Gas Monitoring
- Electrical Modifications
- Structural Steel
- Enclosures
- Foundations
- Engineering
- Construction
- Startup and Commissioning

By Cormetech

- SCR Catalyst Design and Supply
- Flow Modeling
- AIG Design
- Performance Guarantees
- Catalyst Management Plan

Unit Description & Design Data – Table 2

Boiler Type	B&W Cyclone Fired	
Start of Operation	Unit 1 – 1972 Unit 2 – 1977	
Number/Arrangement of cyclones	14 cyclones, opposed wall	
Heat Input, MMBtu/Hr (full load)	6,234	
Air Heater Type	Ljungstrom (new)	
Baseline NOx, lbMMBtu	1.5	
Particulate Control	Cold Side ESP	
Ash Recirculation	None	
Fuel, Powder River Basin Coal		
Ultimate Analysis (%, dry basis)	Typical	Range
Carbon	69.2	64.5 – 74.5
Hydrogen	4.7	3.6 – 6.1
Nitrogen	0.9	0.6 – 1.3
Chlorine	0.03	0.01 – 0.15
Sulfur	0.3	0.2 – 0.8
Ash	6.2	5.3 – 9.8
Oxygen	18.7	16.0 – 21.0
Ash Analysis (%, Ignited Basis)	Typical	Range
P_2O_5	1.2	0.6 – 2.6
SiO_2	33.4	28.5 – 38.5
Fe_2O_3	5.2	3.6 – 7.5
Al_2O_3	16.3	14.2 – 20.2
TiO_2	1.2	0.5 – 1.6
CaO	**21.5**	**18.0 – 26.3**
MgO	6.4	4.7 – 8.7
SO_3	11.7	1.8 – 11.7
K_2O	0.35	0.2 – 0.8
Na_2O	1.9	0.9 – 2.7
BaO	0.6	0.2 – 0.9
SrO	0.27	0.01 – 0.50
MnO_2	0.02	0.02 – 0.20
Unburned Carbon	18	

Unit Description & Design Data (cont.)

Trace Element Analysis (ppm in coal dry basis)	Design
Silver	0.24
Arsenic	1.5
Boron	43
Barium	N/A
Beryllium	0.4
Bromine	N/A
Manganese	9.0
Nickel	5.0
Lead	5.0
Antimony	0.62
Selenium	0.3
Strontium	156.4
Cadmium	0.56
Cobalt	N/A
Chromium	6.0
Copper	12.0
Germanium	N/A
Mercury	0.10
Thallium	N/A
Uranium	N/A
Design Conditions, Full Load	
Flue gas mass flow rate, lb/hr	6,217,000
Flue gas temperature, ^{o}F	715 - 800
Particulate Concentration, gr/dscf	1.0
H_2O, vol %	14.9
O_2, vol %, dry	1.85
SO_2, ppmvd	170
SO_3, ppmvd	6.0
Catalyst Pitch, mm	9.2
Catalyst SO_2 conversion, %	3
Catalyst design life, hours	20,000

Catalyst Design Considerations

Catalyst design considerations can be divided into two primary topics, mechanical and chemical. Mechanical aspects include pitch selection and material hardness, while chemical considerations include fuel/ash constituents and boiler operating conditions.

Mechanical

Catalyst Pitch Selection**.** Selection of the most appropriate catalyst pitch is important to assure that ash will not deposit and bridge over the catalyst cells/openings, thus reducing the effective catalyst surface area and causing increased pressure loss. The properties of the ash generated by the New Madrid units was evaluated under various conditions and with multiple catalyst pitch selections. Catalyst selections included multiple pitches and open areas. For all cases, it is necessary that the system design i.e. flue gas and ash distribution, is performed such that the catalyst is exposed to a uniform pattern.

Table 3

Pitch, mm	Geometric Surface Area, m^2/m^3	Open Area, %	Relative Blockage, %
9.2	383	79.8	< 1
8.2	426	78.3	< 3
7.4	468	77.0	< 10

The 8.2 mm and 9.2 mm selections performed well and the 7.4 mm pitch performed adequately, considering the advantage in surface area. After consideration of the engineers and owners preference, the 9.2 mm pitch product was selected. An added benefit of the product selected, beyond the resistance to ash bridging, is a very low pressure loss. Further catalyst pitch optimization for future catalyst additions/replacements will be considered with the benefit of long term operating experience.

Catalyst Hardness. Catalyst erosion is a function of dust loading, velocity, angle of incidence, particle size, time, and catalyst hardness. New Madrid conditions compare favorably to the existing experience base.

The environment created in the application for the New Madrid SCRs consists of:

- Standard flue gas velocity (15.8 ft/s at the catalyst)
- Low total dust loading (1 gr/dscf)
- Particle size and duration of exposure within the experience range (mps = 23 um)
- Flue/reactor design performed to minimize the angle of incidence to the catalyst

Catalyst hardness is controlled through product porosity i.e. the lower the porosity the harder the product. However, catalyst porosity also dictates catalyst performance potential, i.e. the higher the porosity the greater performance potential. Thus the two parameters counter each other and a trade-off is required.

In order to maximize both the catalyst erosion resistance and performance potential, a unique "edge hardening" solution was applied for the New Madrid catalyst. Edge hardening allows a high porosity product to be used without sacrificing erosion resistance.

Chemical

Chemical deposits/reactions on or within the catalyst are the primary cause for loss of NOx removal performance over time. General descriptions of catalyst deactivation mechanisms can be read in "Optimizing SCR Catalyst Design and Performance for Coal-Fired Boilers" Pritchard, Et al.

The table below compares New Madrid to the "Experience" for seven primary components of ash and fuel for which catalyst deactivation is typically attributed.

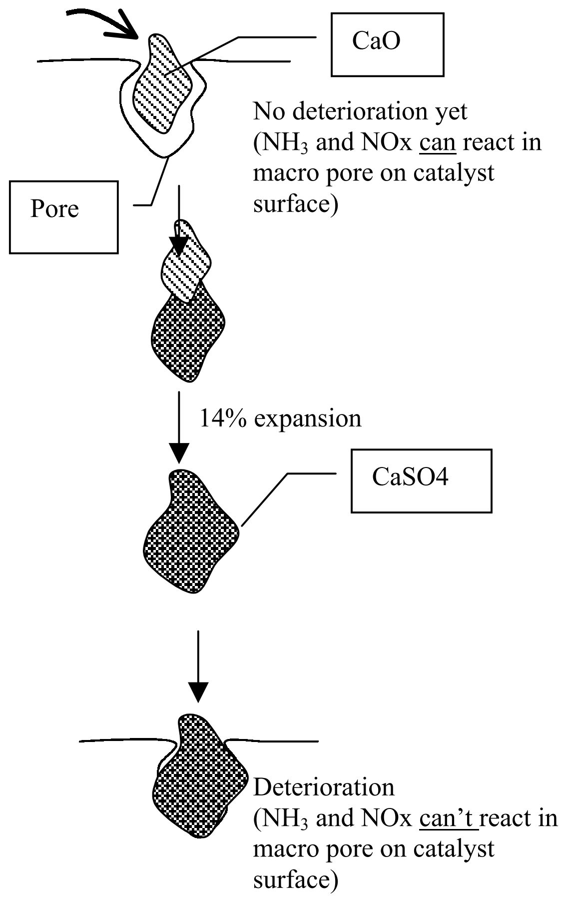
Table 4

Component	New Madrid	Experience
Dust Loading, gr/dscf	1.0	0.7 to 10
Arsenic, ppm in fuel	1.5	1 – 25
Total CaO, % ash	18 – 26.3	2.4 – 12
Free CaO, % ash	11.9 – 17.4	0.9 – 8
Na_2O, % ash	0.9 – 2.7	0.05 – 1.6
P_2O_5, % ash	0.6 – 2.6	0.06 – 1.3
K_2O, % ash	0.2 – 0.8	0.1 – 4.0

The primary focus of catalyst performance degradation associated with the New Madrid units is attributed to the deposition and conversion of CaO to $CaSO_4$ within the catalyst pore structure. Deactivation caused by arsenic, and components such as sodium, potassium, and phosphorous will be relatively small in comparison to $CaSO_4$, although some interactions may occur. This is shown, with the exception of arsenic, by the comparison of the product of dust loading and dust constituent. Due to the combination of low ash content and low flyash levels generated from cyclone boilers the effective level of contaminant that reaches the catalyst is well within experience levels and can be accurately predicted. Gaseous arsenic levels will be extremely low due to the combination of low fuel arsenic and available CaO.

The deposition rate of CaO onto/into the catalyst surface is a function of the mass transfer rate within the catalyst cells. Therefore it is extremely important to model/test the catalyst under "SCR-like" conditions when judging deactivation. The following table describes the mechanism of $CaSO_4$ formation within a catalyst pore. It is important to note that the deterioration caused by $CaSO_4$ is primarily dependent on the CaO content because it is the rate limiting step of the reaction. Therefore the content of SO_3 in the fluegas has a very limited affect on deterioration caused by this mechanism.

Figure 1

Step	Process	Model	Process Time
Step 1	CaO is caught in macro pore on a catalyst. This phenomenon depends on probability which CaO is caught in macro pore which depends on the quantity of CaO.		It takes **<u>~10,000 hrs</u>** to change the concentration on the catalyst which we can confirm the change from actual data. **(rate controlling)**
Step 2	Diffusion through gas film.		(R=1μm) ι=5.6 hrs (R=0.5μm) ι=2.8 hrs **< 10Hrs**
Step 3	Diffusion through ash.		(R=1μm) ι=22.5 hrs (R=0.5μm) ι=5.6 hrs **< 30Hrs**
Step 4	Chemical reaction. $CaO + SO_3 \rightarrow CaSO_4$ (0.297 cc/g) → (0.338 cc/g) 14% expansion The rate of these reactions for Step 2,3,4 depends on CaO and SO_3 concentrations.		<u>Faster than Step 2,3</u>

Summary of CaO Poisoning Mechanism

This poisoning mechanism consists of 4 steps:

Step 1 – CaO becomes attached to macro pore on catalyst surface.

Step 2 – SO_3 diffuses through gas film surrounding CaO particle.

Step 3 – SO_3 diffuses into CaO particle.

Step 4 – As SO_3 diffuses into particle, it reacts with CaO to form $CaSO_4$. The particle expands with the reaction and becomes lodged in the catalyst pore blocking diffusion of NH_3 and NO and therefore reduces the deNOx reaction rate.

The relative rates of each of these steps is:

Rate of Step 4 > Rates of Steps 2 & 3 >> Rate of Step 1

Step 1 is the rate controlling step. The rate of this step is dependent on the CaO content in the flue gas and independent of SO_3 content.

Catalyst Management

Once the catalyst is in service a testing series to monitor the performance capability of the installed bed will be implemented. The testing will aid/confirm the understanding of impacts of various parameters on catalyst performance including, fuel constituents, ash constituents, and boiler operation over time.

This objective will be met through a series of steps. Each step, by itself provides useful information and when combined, fully addresses the performance capability of the catalyst within the application. Each of the individual steps is shown below.

- Catalyst performance potential (Ko) and change in potential over time $(K/Ko)_{time}$ including specific deactivation mechanism(s) via pilot test facility and specific chemical analyses
- Review and analysis of field operating conditions and ash test results
- Review and analysis of catalyst outlet NOx traverse data

The methodology of combining the results is too broad to discuss herein, but will be utilized to construct an optimized catalyst management plan.

System Design

The design performance for New Madrid is 93% from an inlet of 1.5 lb/MMBtu with a maximum of 3 ppmvdc ammonia slip for a minimum of 20,000 operating hours. In order to achieve the stated performance and assure that there is limited impact on downstream equipment, both the system and catalyst must be designed properly. Key components of the system include flues and hoppers, turning vanes and flow distribution devices, Ammonia Injection Grid (AIG), and Air Preheater (APH).

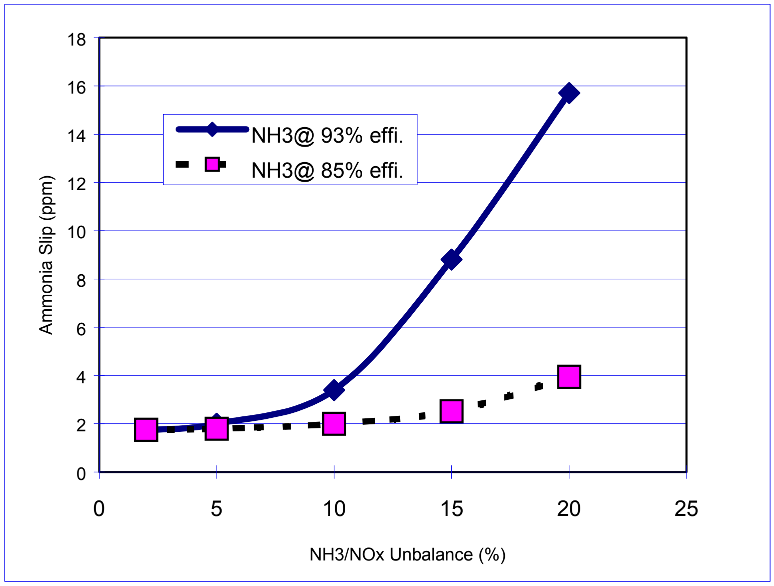
The flue and reactor schematic is shown in Figure 2. Design and optimization of the flue, turning vanes, distribution devices, and AIG was achieved via physical modeling. Computer modeling was employed to check particle distribution throughout the model under the final design layout. More than ten different arrangements of the flue internals were checked during the modeling process in order to assure the most technical and economic design.

Details of measurement methodology and location are not discussed in detail herein but should be greatly considered when evaluating results. Therefore it is important to have a good understanding of both flow and catalyst characteristics to achieve meaningful and successful results from a cold flow model.

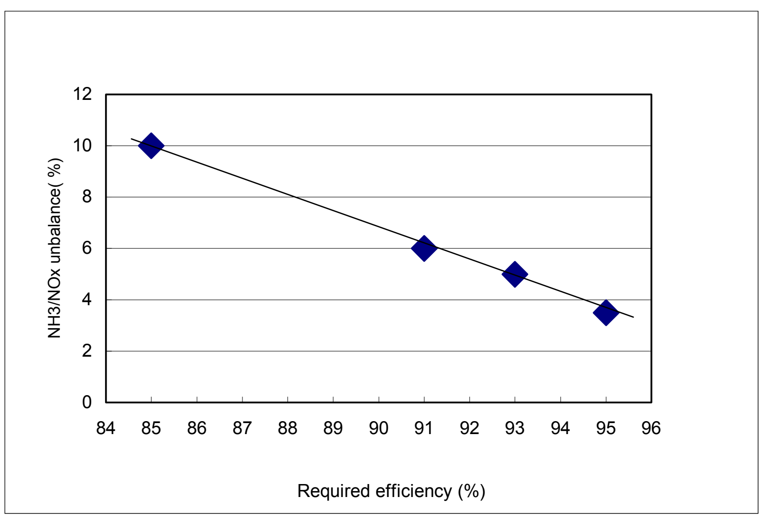
Ammonia Injection Grid (AIG)

The ammonia injection grid is one of the keys to assuring long term successful performance. The design utilizes a multi-zone grid to assure excellent coverage and tuning capability. In order to simplify the tuning of the AIG and assure excellent coverage/mixing, the velocity profile at the inlet to the AIG was controlled to less than ± 10% across the entire flue. This was achieved via the use of a simple and relatively low pressure loss flow distribution device. Due to the combination of the AIG design, the flow distribution device and the long mixing lengths inherent to the design, a static mixer was avoided. Dimensionless ammonia concentration as measured via use of a tracer gas showed excellent distribution and assure excellent long term operation at 93% reduction.

Graph 1: Ammonia slip vs. NH_3:NOx Unbalance

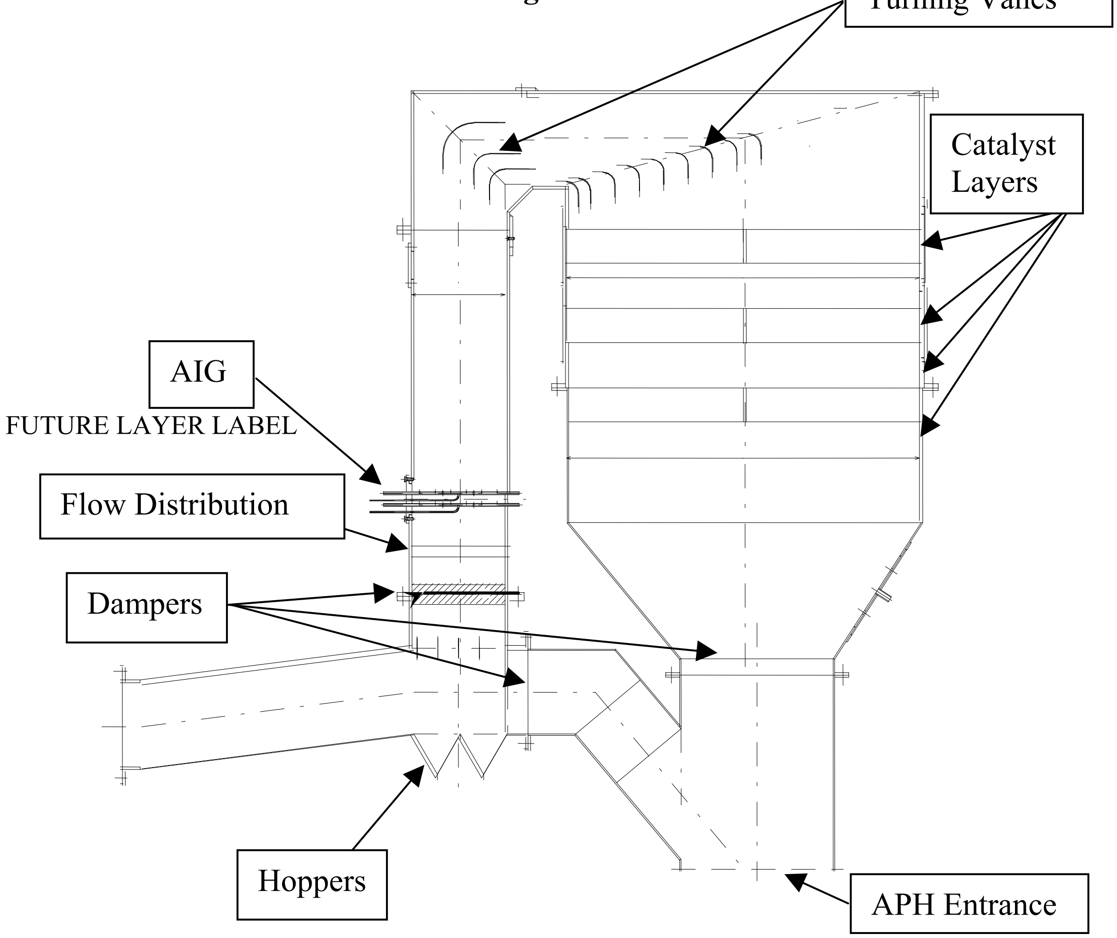


Graph 2: NH_3:NOx Unbalance vs. Reduction Efficiency



Excellent distribution assures an even NOx outlet profile and more importantly an even ammonia profile at the outlet of the catalyst. Thus the formation of any ammonia bisulfate in the APH is reduced and leads to longer APH life and lower overall pressure loss.

SCR Flue and Reactor Schematic – Figure 2



Turning Vanes

Turning vanes were installed in the flues to assure good flow distribution to the catalyst and minimize overall system pressure loss. Although the velocity distribution has limited direct impact on overall catalyst NOx reduction performance, it is imperative to assure good ash distribution and to minimize any local high or low velocity points that can attribute to excessive catalyst wear or localized plugging.

Straigtening vanes were installed at the entrance to the riser duct in order to prepare the flow to enter the AIG region. Use of the straightening vanes allowed the pressure loss of the flow distribution device to be minimized and still achieve excellent results, as indicated above.

In order to assure good flow distribution to the catalyst, a combination of turning vanes were employed at the top of the riser duct and at the reactor entrance. Flow was distributed very well before the AIG and was to be maintained around the 180 degree bend. Three vanes were used at the top of the riser duct. The vanes were spaced such that the flow was readied for entrance into the SCR reactor. Constant radius vanes were used at the inlet to the SCR reactor. Special attention was paid to assure adequate carrying velocity around the inside of the turn, a notorious place for ash accumulation. Additionally, all vane geometries were designed with consideration to avoid ash accumulation during low load operation.

Results of velocity measurements at the catalyst show velocity distribution of approximately ± 5% over 90% of the cross-section and approximately ± 10% over the remaining 10% of the cross-section.

Balance of Plant Considerations

The project offering proposed to AECI by BVCI/JSA was fully integrated to improve plant thermal efficiency and address SCR draft requirements. Since converting to Powder River Basin coal the New Madrid Plant has experienced backpass fouling and high backend temperatures. Currently, the temperatures exiting the tubular air heater are approximately 350 F. This high backend temperature debits unit heat rate performance. In addition, installation of an SCR system increases system draft losses. At New Madrid this might have necessitated the installation of booster fans.

The innovative solution to these challenges offered by BVCI/JSA was based on the removal/replacement of the existing tubular air heater with a new "SCR ready" regenerative air heater. This choice addressed draft system and unit heat rate concerns as well as minimizing the potential for air heater fouling. Removal of the tubular air heater will take place during the 6 week outage.

The pressure drop of the new regenerative air heater is substantially less than the existing tubular air heater. As such, use of a new regenerative air heater offset the need for booster fans to overcome the SCR system draft losses. In fact, with this changeout, the plant will have an improved draft margin available.

In addition, the new regenerative air heater was configured to lower gas exit temperatures to 280 F. This change will improve boiler efficiency significantly for both New Madrid units. Finally, the use of a regenerative air heater configured for SCR operation (two layer design with cold end enameled baskets) dramatically reduces the operating risk associated with SCR. The heat rate improvement and operational benefits of the BVCI/JSA project offering more than offset the cost of the new air heater system.

Summary

- The SCR systems for AECI's New Madrid Units 1 & 2 have been designed for high NOx removal efficiency with low ammonia slip while firing 100% PRB fuel.

- PRB fuel presents unique ash characteristics which influence both pitch selection and catalyst deactivation. Its use in cyclone fired boilers results in chemical ash characteristics that are within the experience base, however use on pulverized coal fired units will present new challenges. The resulting mechanical characteristics of the ash lead to the selection of larger catalyst pitches.

- The integration of system and catalyst design is crucial to assuring long term successful operation. Ammonia:NOx distribution is critical to assuring performance above 90%.

- An integrated catalyst and system parameter test program is required to fully optimize the catalyst management over time.

- The total system design/BOP must be considered when retrofitting SCR to a given application. Careful consideration of fully integrated equipment upgrades and/or replacements can greatly reduce the life cycle cost for retrofitting SCR.