Zero Ammonia Slip Technology for Combined Cycle Gas Turbine Exhaust

Thomas W. Hastings, Jun Murano and Frank Stevens
Cormetech, Inc.

Akira Hattori
Mitsubishi Power Systems, Inc.

Kozo Iida and Mashashi Kiyosawa
Mitsubishi Heavy Industries, Ltd.

Power-Gen International : Environmental Issues with Combustion Turbines
December 9-11, 2003 Las Vegas, Nevada

BREATHE IN BREATHE DEEP BREATHE EASY

CORMETECH

CORMETECH

Outline

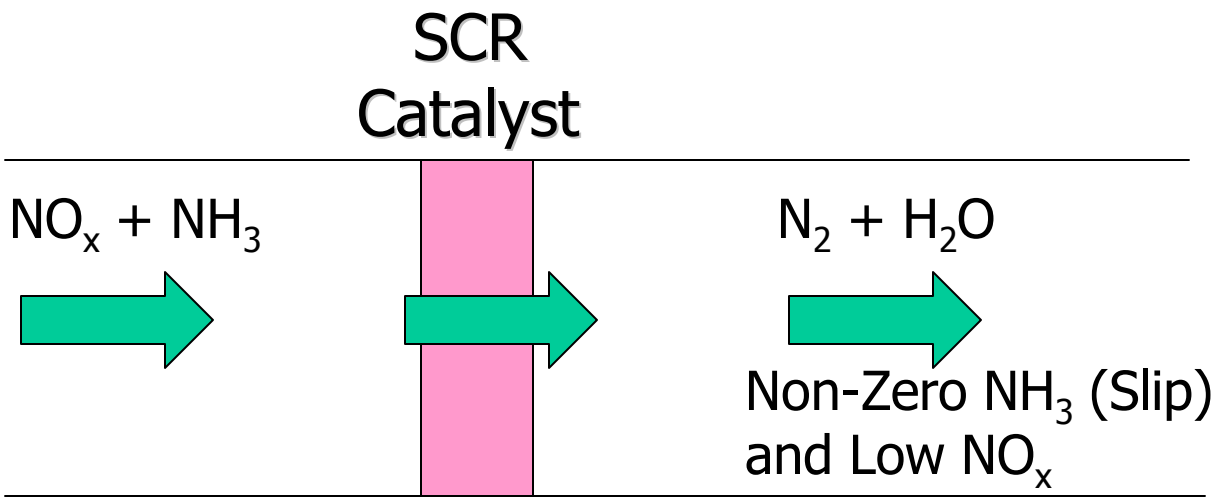
- Introduction
- Zero-Slip™ Technology Description
- Pilot Test Results
- 7 MW Commercial Demonstration
- Conclusions

Introduction

- **Selective Catalytic Reduction (SCR)**
  - Vanadia-Titania SCR Catalyst in Path of Flue Gas
    - "Honeycomb" Monolith with Channels for Gas Flow
  - Ammonia Reductant (NH_3) Injected Upstream of Catalyst
  - NO_x Reactant in Flue Gas (NO_x is an Ozone Precursor)
  - Reduction of NO_x to N_2 and H_2O ("de-NOx Reaction")
  - High Conversion of Flue Gas NO_x to Products
    - Permit Outlet NO_x Levels Typically 2-10 ppm

- **Outlet Ammonia is Termed Ammonia Slip**
  - Non-Stoichiometric Local Conditions Across Catalyst
    - Flue Gas Flow Non-Uniformities
    - NH_3 Injection Grid Tuning to Match Flue Gas Flow
    - Inadequate Mixing Time
  - Ammonia Slip Permit Levels
    - Typically 2-10 ppm or even 30 ppm

SCR NO_x Reduction – de-NO_x Reactions



NO_x Reduction Over SCR Catalyst

$$NO + NH_3 + 1/4\ O_2 \rightarrow N_2 + 3/2\ H_2O$$

$$NO + NO_2 + 2\ NH_3 \rightarrow 2\ N_2 + 3\ H_2O$$

Zero-Slip™ Technology - Purpose

- **Ammonia Slip is Regulated in Some Localities**
  - NH_3 is not a Criteria Pollutant (Federal)
  - Toxic Air Contaminant under SCAQMD Rule 1401
  - Some Local Permit Agencies Require Control of NH_3 Slip
- **Local Regulations Have Tightened**
  - NO_x < 2 – 5 ppm
  - NH_3 Slip < 2 – 3.5 ppm
- **NH_3 Salt Formation Reactions Contribute to PM**
  - $2\ NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$
  - $NH_3 + HNO_3 \rightarrow NH_4NO_3$
  - NH_3 Sources
    - Fertilizers
    - Animal Feeding Operations
    - SCR and SNCR Ammonia Slip (Relatively Small)
- **Regional Haze**

CORMETECH

Outline

- Introduction
- Zero-Slip™ Technology Description
- Pilot Test Results
- 7 MW Commercial Demonstration
- Conclusions

Zero-Slip™ Technology - Description

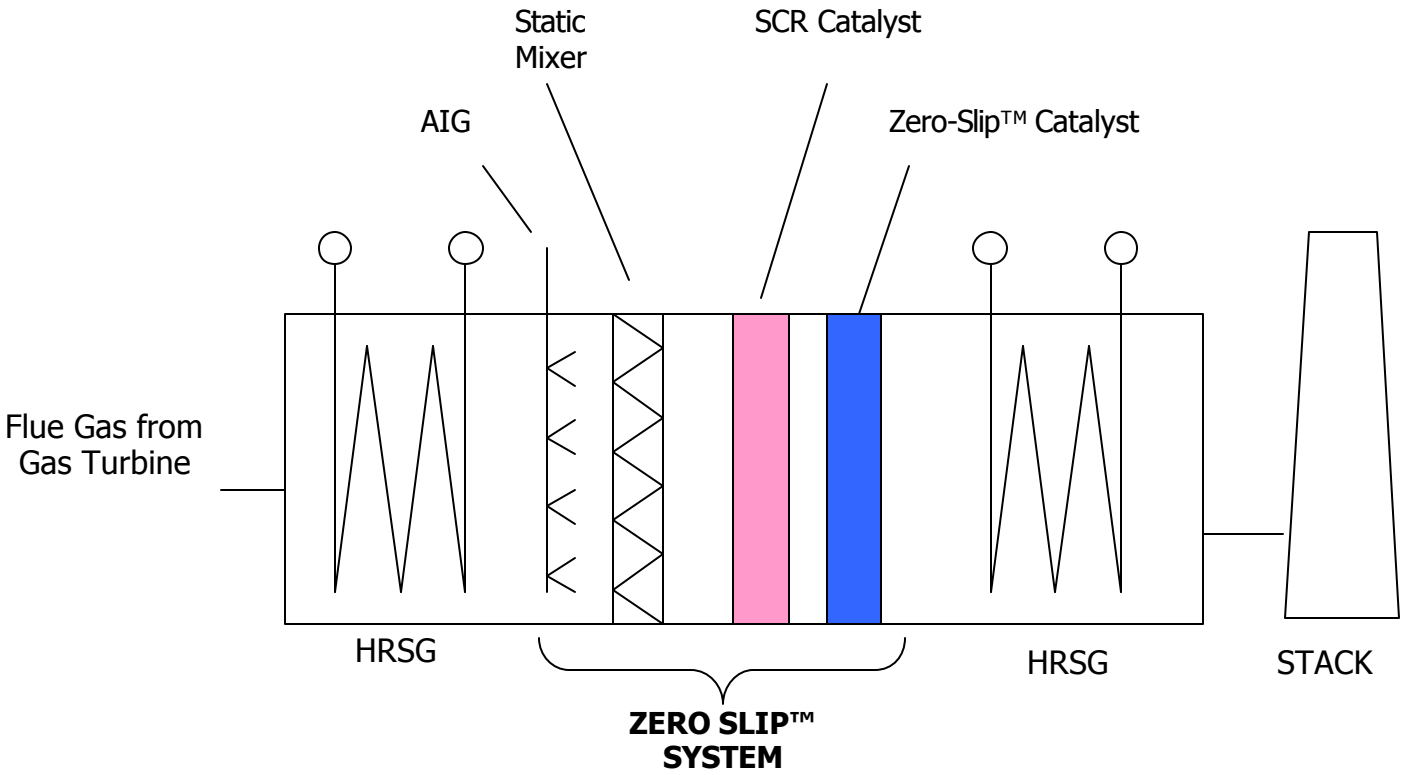
- **Enhanced SCR Technology for Combined Cycle Gas Turbines to Achieve down to "Zero" NH_3 Slip**

- **Mitsubishi/Cormetech Joint Development**
  - Patented
  - Demonstrated Commercially

- **General Features**
  - Standard SCR Catalyst and Zero-Slip™ Catalyst Layers
    - Zero-Slip™ Catalyst Composition is Proprietary
  - NH_3 Injection Above Stoichiometric
  - Promotion of Good Mixing
  - Destruction of Ammonia over Zero-Slip™ Catalyst
  - Can Achieve Down to "Zero" Ammonia at the Outlet
  - Applicable to New Units and Retrofits

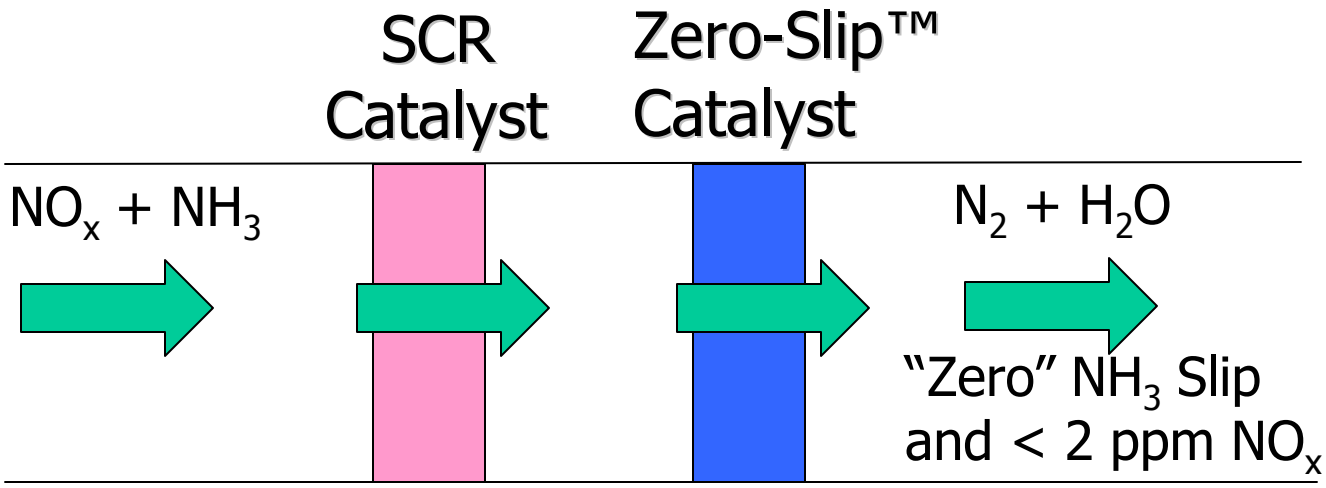
Zero-Slip™ Technology

Schematic Drawing for Typical Split Heat Recovery Steam Generator (HRSG)



BREATHE IN BREATHE DEEP BREATHE EASY

Zero-Slip™ Technology – Reactions



NO_x Reduction Over SCR Catalyst

$$NO + NH_3 + 1/4\ O_2 \rightarrow N_2 + 3/2\ H_2O$$

$$NO + NO_2 + 2\ NH_3 \rightarrow 2\ N_2 + 3\ H_2O$$

De-NO_x and NH_3 Destruct Over Zero-Slip™ Catalyst

$$NO + NH_3 + 1/4\ O_2 \rightarrow N_2 + 3/2\ H_2O$$

$$NH_3 + 5/4\ O_2 \rightarrow NO + 3/2\ H_2O$$

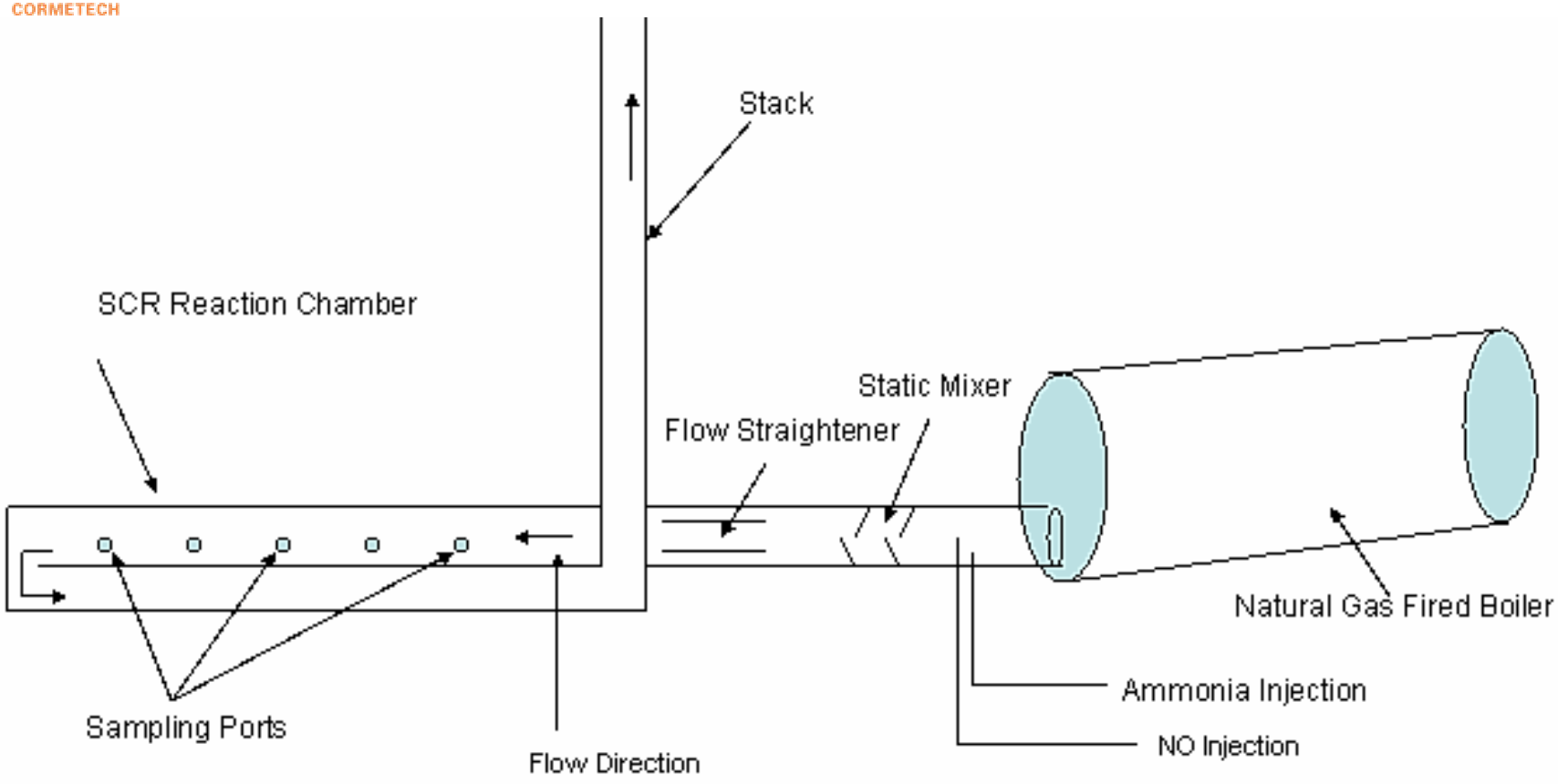
CORMETECH

Outline

- Introduction
- Zero-Slip™ Technology Description
- Pilot Test Results
- 7 MW Commercial Demonstration
- Conclusions

Zero-Slip™ Technology

Pilot Reactor

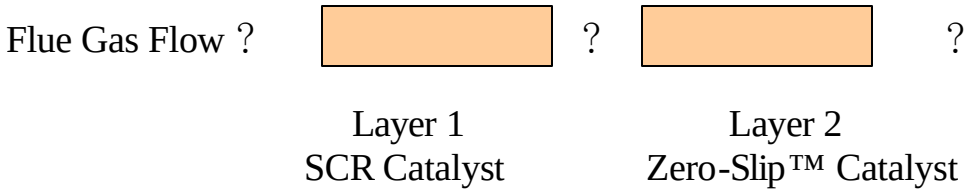


BREATHE IN BREATHE DEEP BREATHE EASY

Zero-Slip™ Technology

Pilot Study - Test Conditions

Target Test Condition Number	1	2	3	4	5
NO_x Inlet Concentration (ppmvdc)	32	32	32	32	32
O_2 Concentration (volume %)	12.4	12.4	12.4	12.4	12.4
H_2O Concentration (volume %)	10.7	10.7	10.7	10.7	10.7
Superficial Gas Velocity (Nm/s)	1.23	1.23	1.23	1.23	1.23
Gas Flow (SCFM)	61.9	61.9	61.9	61.9	61.9
NH_3/NO_x Molar Ratio	0.80	0.90	1.14	1.23	1.60



BREATHE IN BREATHE DEEP BREATHE EASY

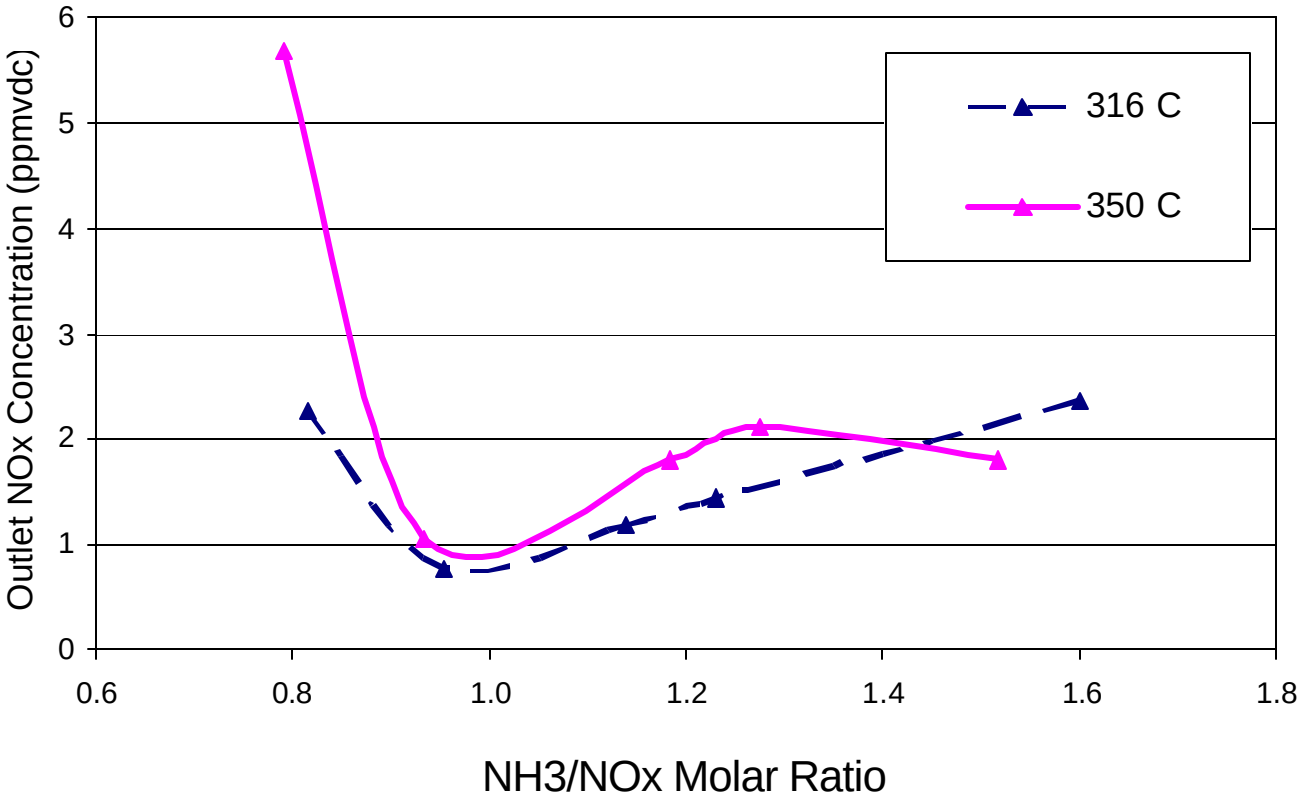
Zero-Slip™ Technology

Pilot Study - Test Results – NH_3 Slip < 0.1 ppm

NH_3/NO_x Molar Ratio (Inlet)	Temperature (°C)	Ammonia Slip by FTIR (ppmvdc)	Outlet NO_x by FTIR (ppmvdc)	Estimated NO_x Conversion (%)
0.81	316	0.01	2.3	96%
0.95	316	0.07	0.8	99%
1.14	316	0.02	1.2	98%
1.23	316	0.02	1.4	97%
1.60	316	0.01	2.3	96%
0.79	350	0.01	5.7	90%
0.93	350	0.04	1.0	98%
1.18	350	0.01	1.8	97%
1.27	350	0.01	2.1	96%
1.52	350	0.01	1.8	97%

Zero-Slip™ Technology

Pilot Study - Test Results for Outlet NO_x



BREATHE IN BREATHE DEEP BREATHE EASY

CORMETECH

Outline

- Introduction
- Zero-Slip™ Technology Description
- Pilot Test Results
- 7 MW Commercial Demonstration
- Conclusions

CORMETECH

Zero-Slip™ Technology

Commercial Demonstration

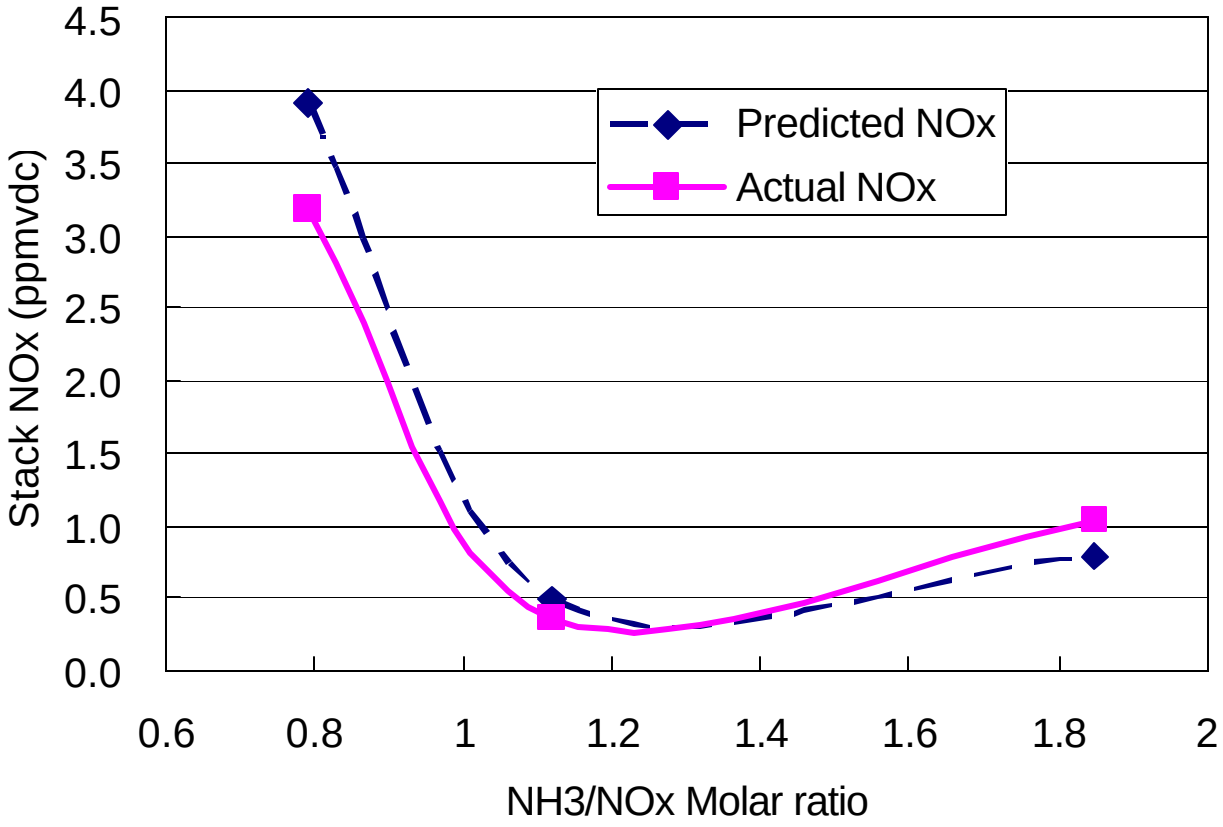
Commercial Demonstration

Initial Performance at Startup - Test Conditions

Gas Turbine Load (MW)	5	5	5
Flue Gas Temperature (°C)	355	355	355
Flue Gas Temperature (°F)	670	670	670
Inlet Oxygen (vol. %, dry)	13.1	13.1	13.1
NH_3/NO_x Molar Ratio	0.8	1.1	1.8

Commercial Demonstration

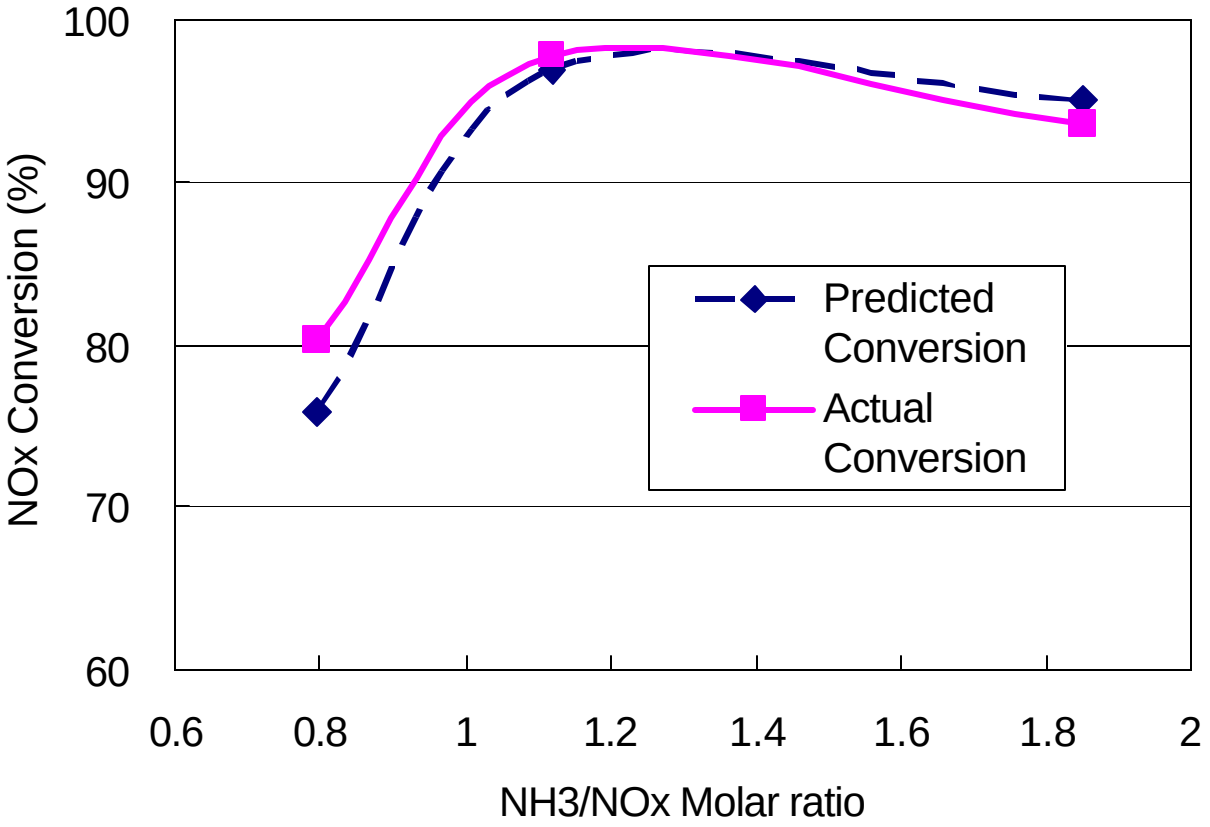
Initial Performance at Startup – NO_x vs. Molar Ratio



BREATHE IN BREATHE DEEP BREATHE EASY

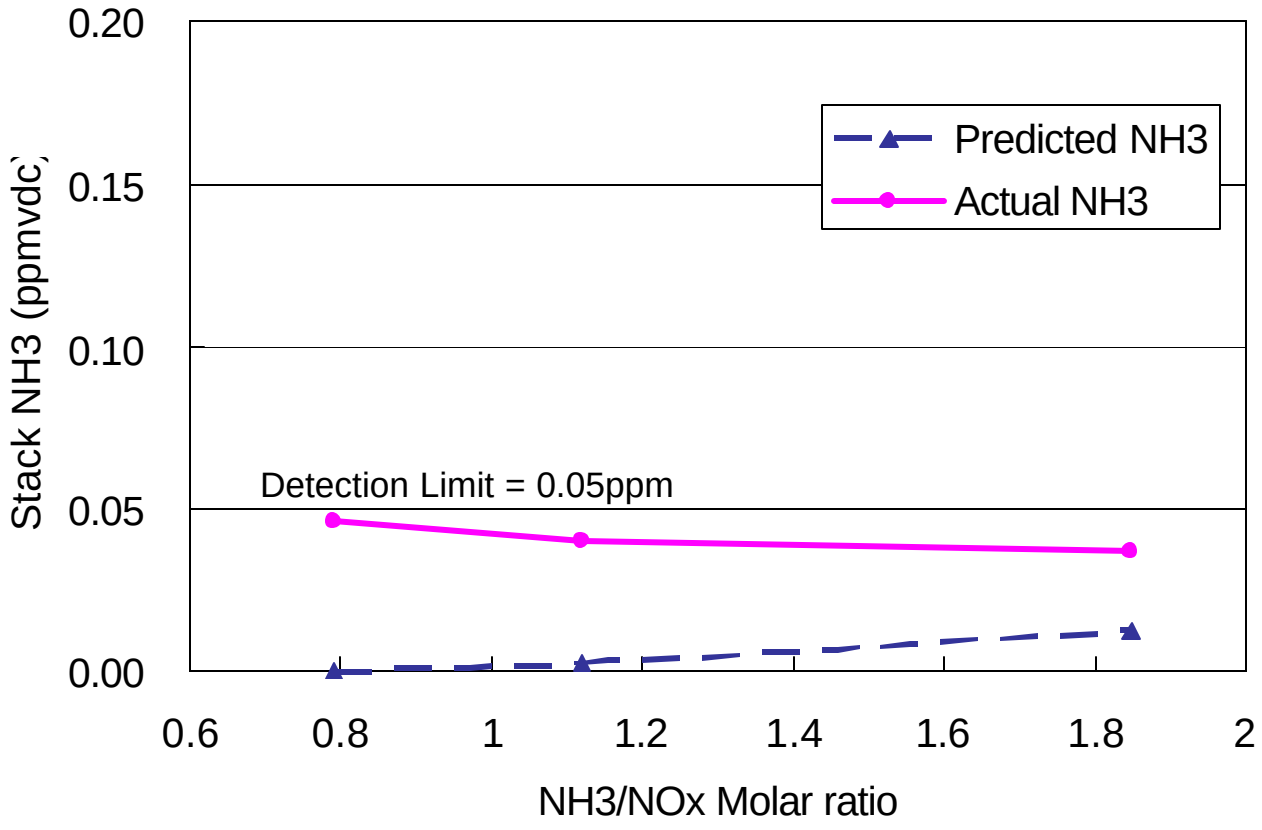
Commercial Demonstration

Initial Performance – NO_x Conversion vs. Molar Ratio



Commercial Demonstration

Initial Performance – NH_3 Slip vs. Molar Ratio



BREATHE IN BREATHE DEEP BREATHE EASY

CORMETECH

Commercial Demonstration

Performance Results after 3000+ Hours

Gas Turbine Load (MW)	5	5
Flue Gas Temperature (°C)	322	324
Flue Gas Temperature (°F)	611	615
Inlet Oxygen (vol. %, dry)	14.8	14.8
NH_3/NO_x Molar Ratio	0.9	1.3
Outlet NO_x (ppmvdc)	1.5	0.4
Outlet NH_3 (ppmvdc)	Less than detection limit	0.10 (at detection limit)

CORMETECH

Outline

- Introduction
- Zero-Slip™ Technology Description
- Pilot Test Results
- 7 MW Commercial Demonstration
- Conclusions

Zero-Slip™ Technology - Conclusions

- **A Commercial Zero-Slip™ System has been Successfully Operated for over 8 Months**
  - Achieved Ammonia Slip < 0.1 ppm (Effectively "Zero")
  - Achieved High NO_x Reduction Levels and Low Outlet NO_x
    - ~0.5 ppm NO_x Outlet Concentration Initially
    - 2.0 ppm NO_x Outlet Concentration Expected at End of Life
- **The Design Model Accurately Predicted Scale-Up**
- **Zero-Slip™ Systems are Available Commercially**
  - Applicable to Combined Cycle Gas-Fired Units
    - New and Retrofit
  - System Design is Flexible to Meet Customer Needs
    - Extremely Low NO_x Levels, and/or
    - Extremely Low Ammonia Slip

CORMETECH

Acknowledgements

- **Paramount Petroleum Corp. – for providing the host site for the commercial demonstration**
- **Midac Corp. – for providing FTIR CEM for commercial demonstration**
- **General Electric – for providing source testing services for field measurements**