CATALYST TESTING

Overview, Methodology, Reporting, and Full-Scale Application

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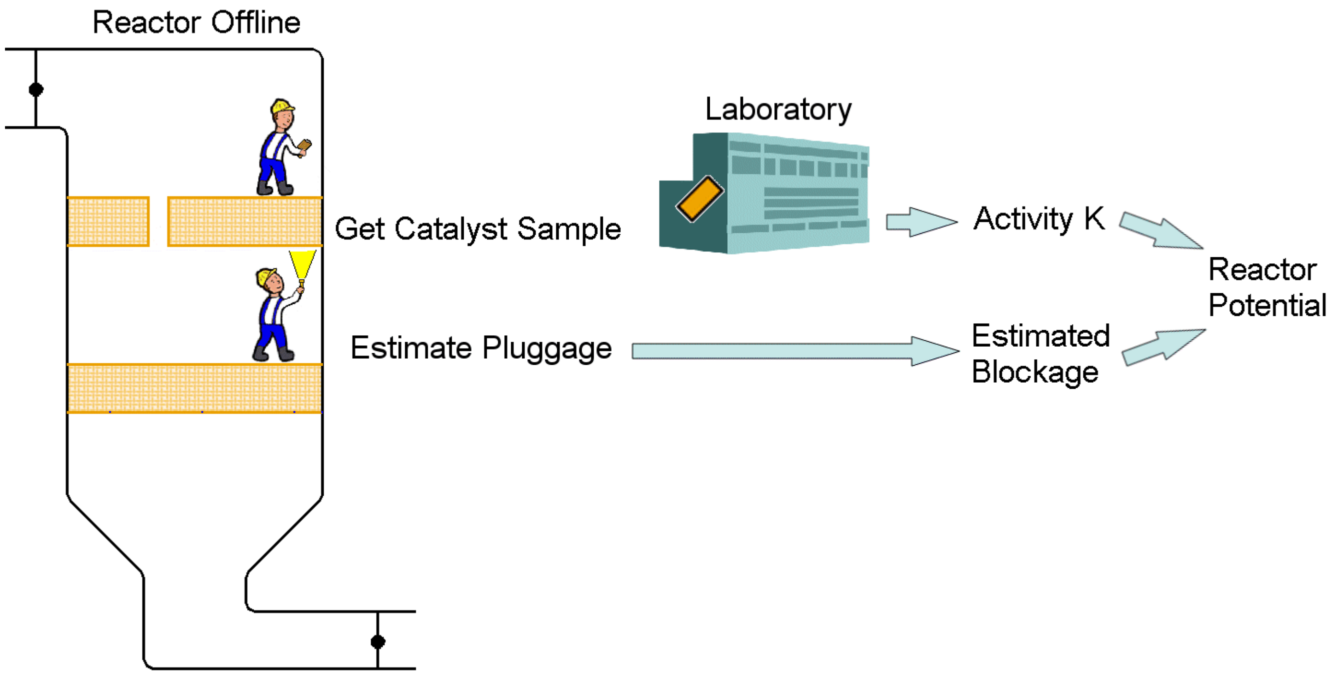
October 19, 2016

OVERVIEW

- Laboratory catalyst tests are performed as close to actual operating conditions as possible
- Catalyst sample pulled from the catalyst bed



CATALYST SAMPLES

- **SCR Catalyst Samples**
  - Catalyst cartridge
  - Test coupon
  - Core sample

- **CO Catalyst Samples**
  - Catalyst cartridge
  - Test 'button'

FERCo

MP305

LABORATORY TESTS

- **SCR Activity 'K'** →

$$K = -Av * \ln(1 - dNOx)$$

$$RP = K / Av = -\ln(1 - dNOx)$$

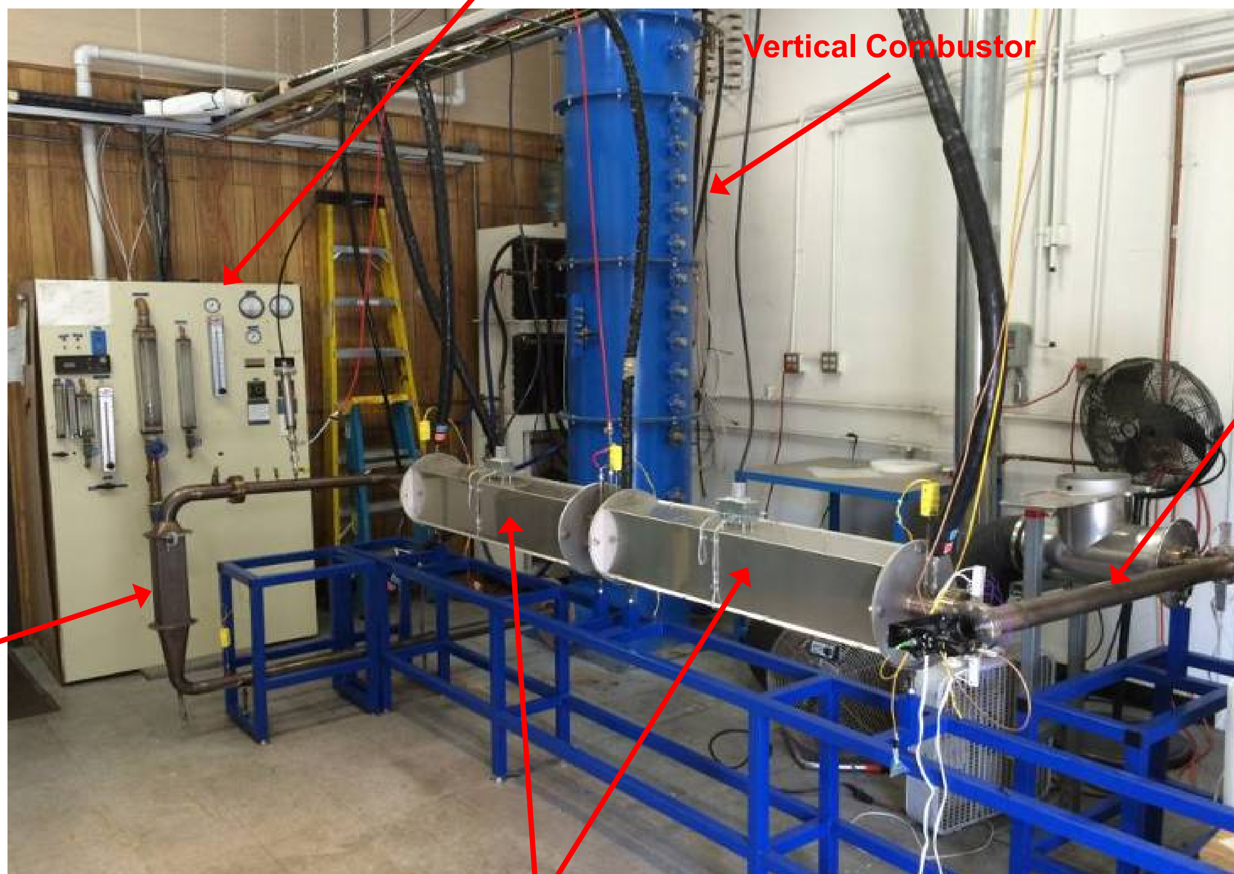
$$dNOx @ NH3 / NOX >= 1.0$$

- **NO_X Reduction @ NH_3 Slip**
- **CO Oxidation**
- **SO_2 Oxidation**
- **VOC Oxidation**
- **Chemical Analysis**
  - Usually surface & bulk x-ray flouresence (XRF)
- **Pore-Size Distribution / Surface Area Analysis**
  - Common to measure Brunauer–Emmett–Teller (BET) surface area
  - Research also showing pore-size distributions may impact deactivation effects

TEST FACILITIES

- **Bench-Scale**
  - 6” by 6” open area, up to 1.5 m long catalysts
  - NO_X reduction, NH_3 slip, CO oxidation, and SO_2 oxidation
  - Coal and gas-turbine catalyst
- **Semi-Bench**
  - Less than 6” by 6”, up to 1 m long catalyst
  - NO_X reduction, NH_3 slip, CO oxidation, and SO_2 oxidation
  - Coal and gas-turbine catalyst
- **Micro-Scale**
  - Nominally 1.25” diameter, 6” long core catalyst sample
  - NO_X reduction, CO oxidation
  - SO2 oxidation , NH_3 slip, and other wet chemical tests not usually performed
  - Gas-turbine catalyst ok, but coal catalyst more difficult given the limited surface area
    - ➢ Larger pitch coal-catalyst provides less open cells, more cells = more accurate measurement

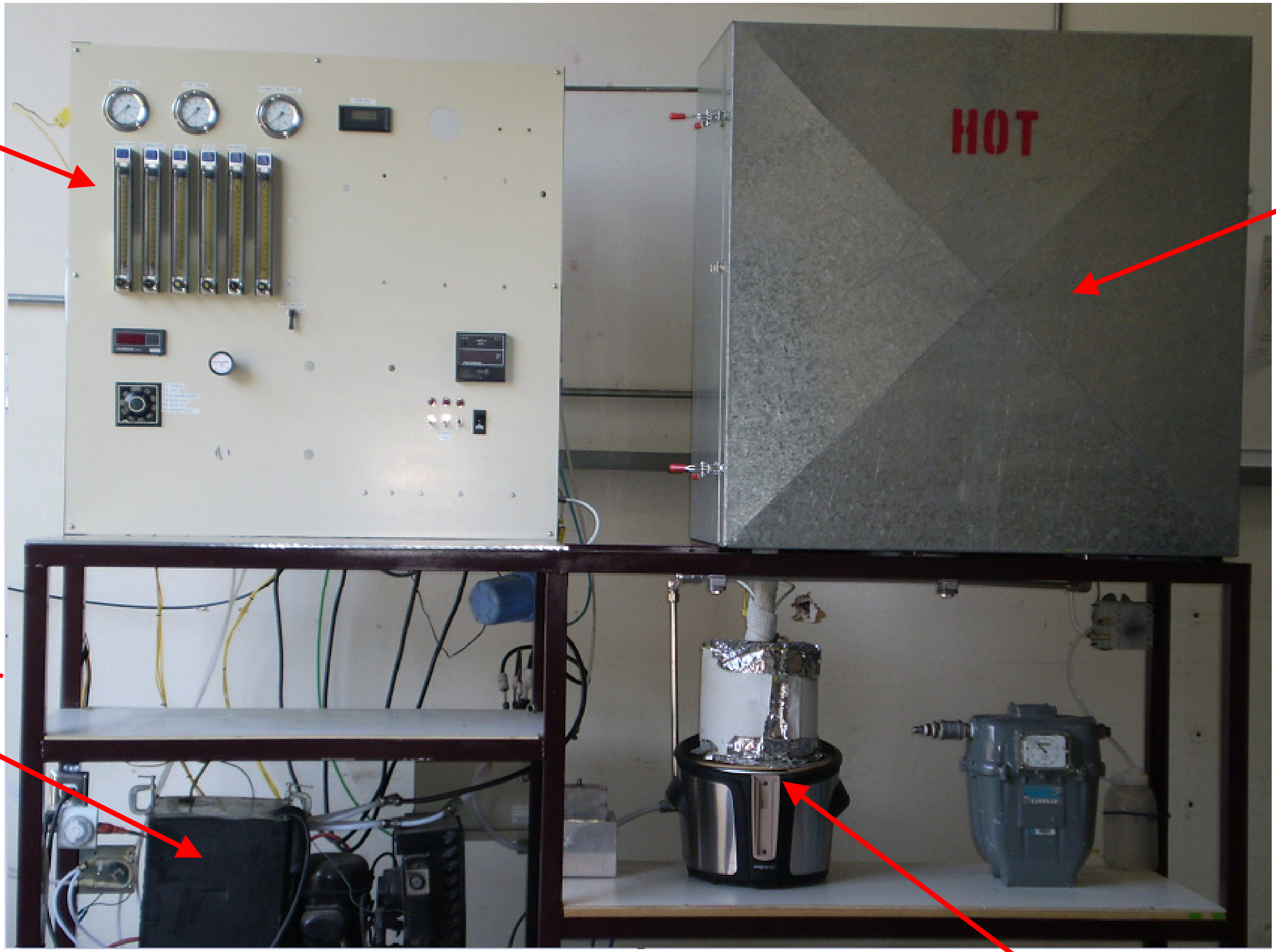
BENCH-SCALE


Combustion Air and Natural Gas Rotometers and Control Panel
Vertical Combustor
Outlet NH3 TDL
SO3 Catalyst Reactor
Isothermal SCR Reactors

MICRO-SCALE

Flow Panel

Heated Reactor Enclosure

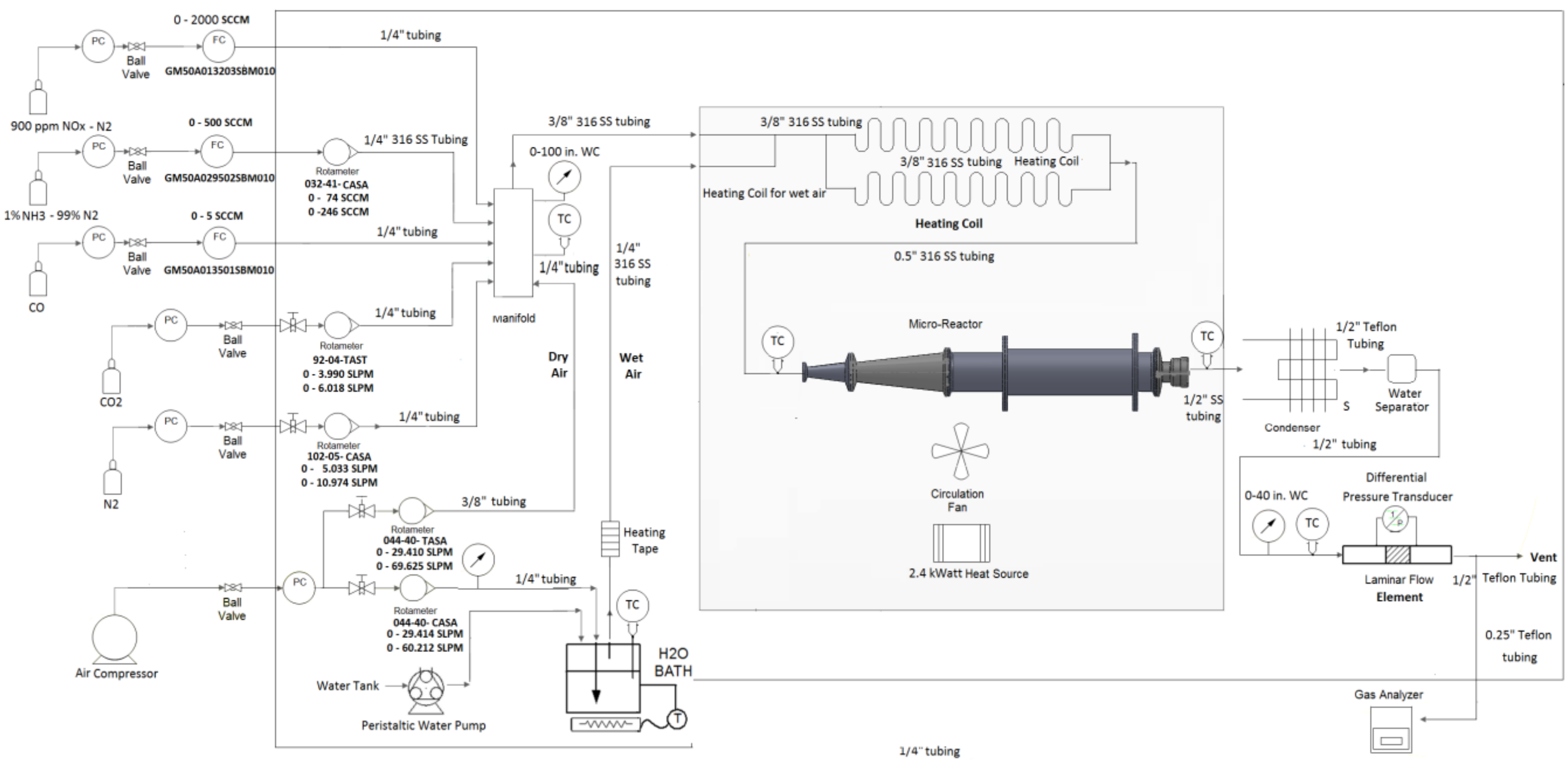


Condenser

Humidifier

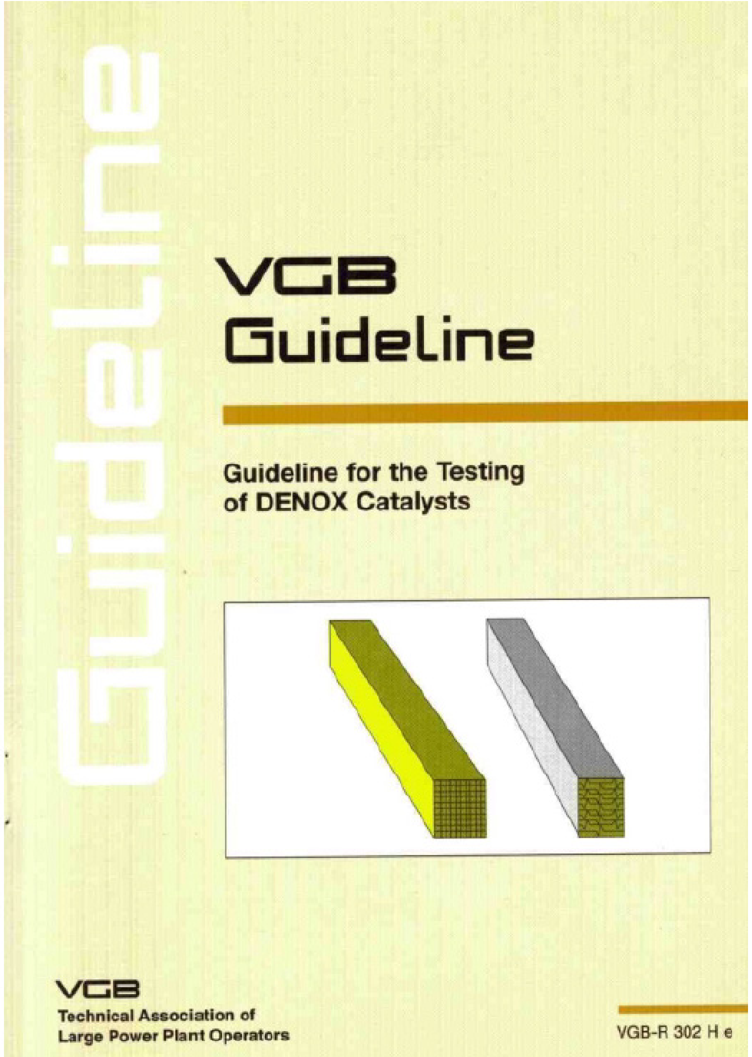
MICRO-SCALE

FERCO
Micro-Reactor
Skid P&ID



METHODOLOGIES

- **VGB Guidelines (VGB-R 302 He)**
  - Early testing document, 1st edition produced in 1988, 2nd edition published in 1998
  - Mainly deals with coal catalyst
  - Good definitions of catalyst properties and calculation procedures, but vague on actual testing methodology
  - Steag published a supplement to the VGB Guidelines in 2006 to better address actual testing methodology



METHODOLOGIES

- **EPRI Protocol (Report 1014256)**
  - 2nd edition published 2007
  - 'Replaced' VGB guidelines
  - Coal catalyst testing only
  - Defines catalyst properties and calculations as well as test methodologies

PROTOCOL FOR LABORATORY TESTING OF SCR CATALYST SAMPLES: 2nd EDITION

1014256

Technical Update, December 2007

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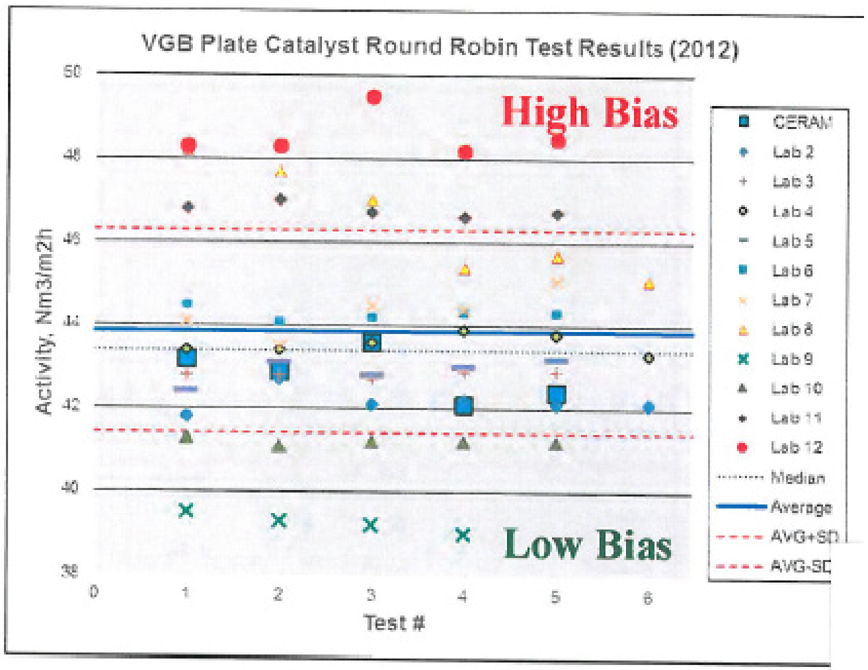
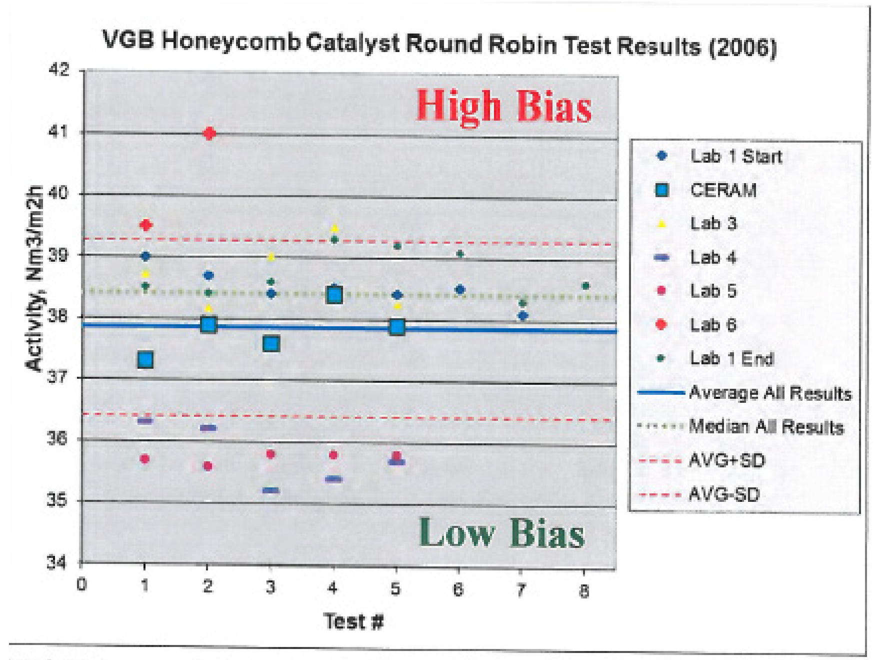
METHODOLOGIES

- **EPRI Guidelines (Report 3002006042)**
  - Published 2015
  - 1st document to provide GT SCR catalyst testing methodology
  - Gas-turbine catalyst testing and reporting
  - Defined catalyst properties and calculations
  - Provides guidelines for two test approaches – **SCR activity (‘K’)** and **NO_X reduction at NH_3 slip limit**

MEASUREMENT UNCERTAINITY

- **Lab Testing Variation**
  - Round-robin testing of the same catalyst sample in different labs provided a broad range of measured activities





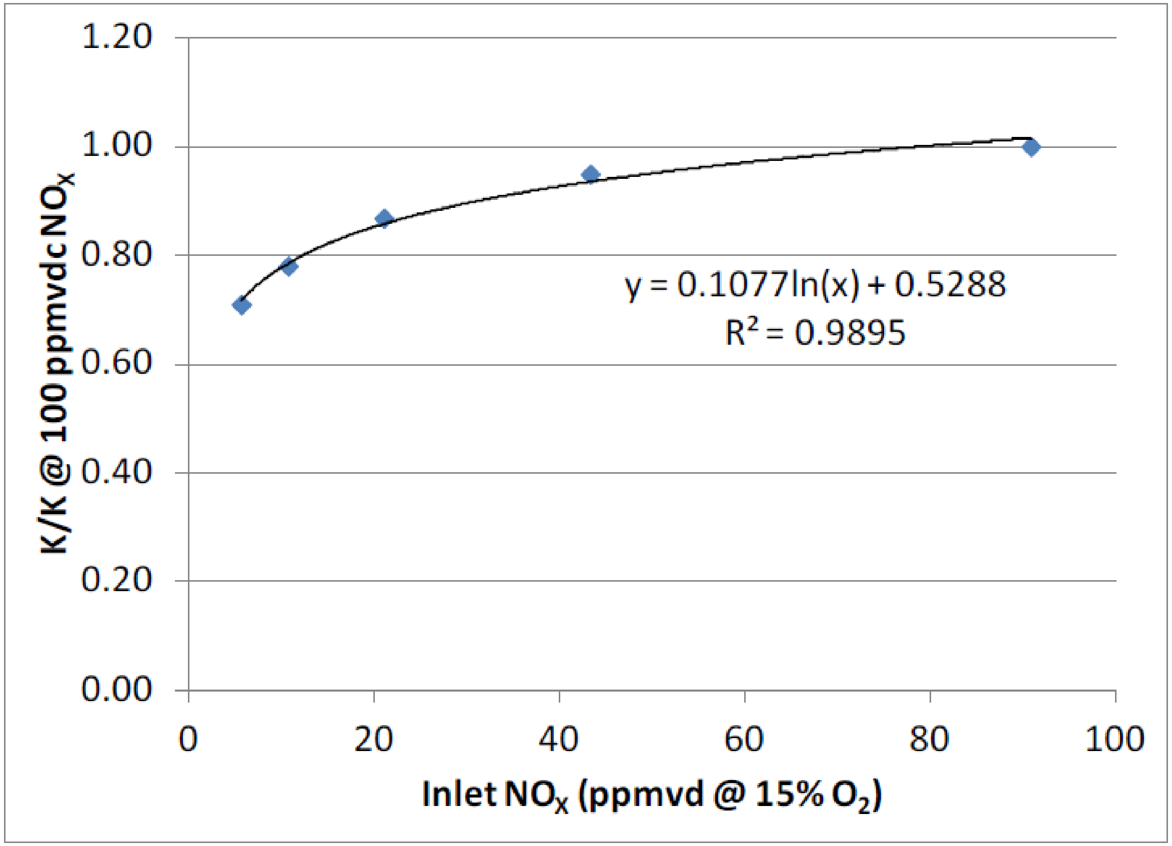
MEASUREMENT UNCERTAINITY

- **Calculation Uncertainty**
  - The activity measurement itself is prone to uncertainties
  - Example below assuming K = 85 m/hr, NOx-in=100 ppm, Av=20-45 m/hr

Parameter		Uncertainty
Flow	Q	2%
Sample X-Section Dimension	d	1 mm
Sample Length	L	1 mm
Specific Surface Area	Asp	0 m^2/m^3 (a)
Inlet NO_x	$NO_{x\ in}$	0.5 ppm
Outlet NO_x	$NO_{x\ out}$	0.1 ppm
Uncertainty	**K**	**2.3 m/hr** **2.7%**

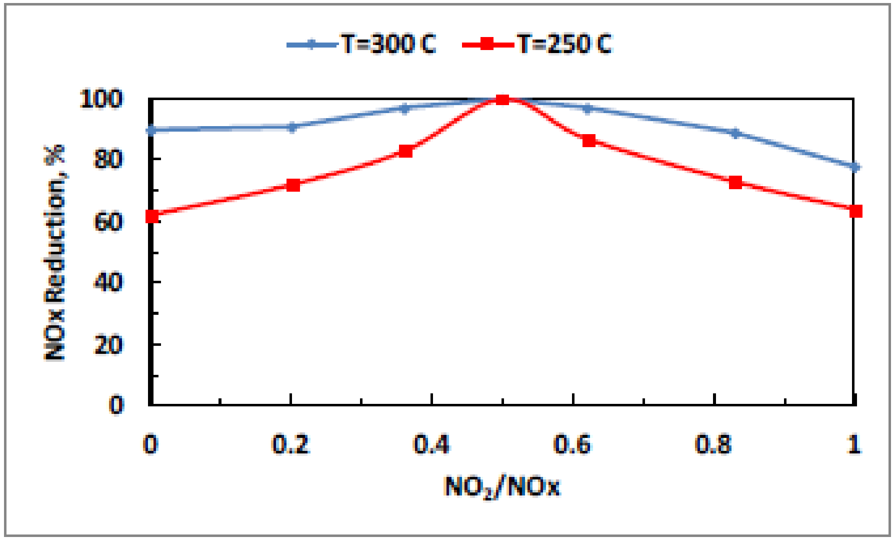
TECHNICAL CONSIDERATIONS

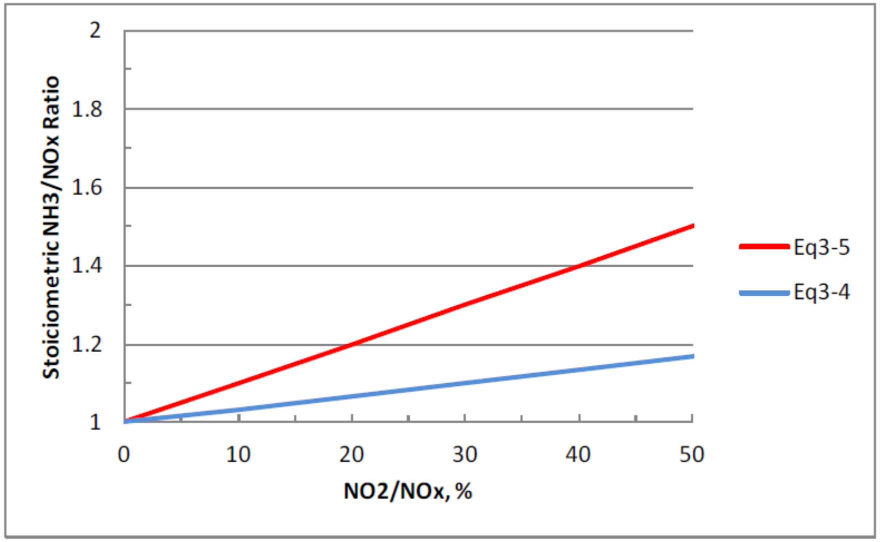
- **Inlet NO_X**
  - Low inlet NOX effects SCR activity



TECHNICAL CONSIDERATIONS

- NO_2/NO_X
  - Ratio not only effects NO_X reduction, but also stoichiometry of reaction equations
    - ➢ **What NH_3/NO_X?**
  - Held ≤ 5% during testing





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

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$$

$$NO_2 + 2NH_3 + \frac{1}{2} O_2 \rightarrow 3/2\ N_2 + 3H_2O$$

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

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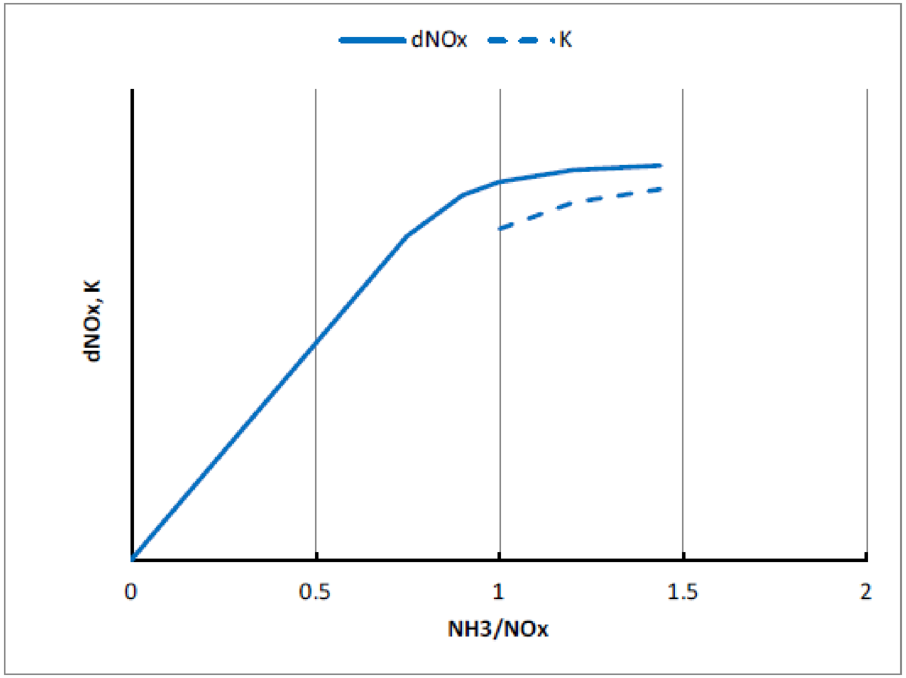
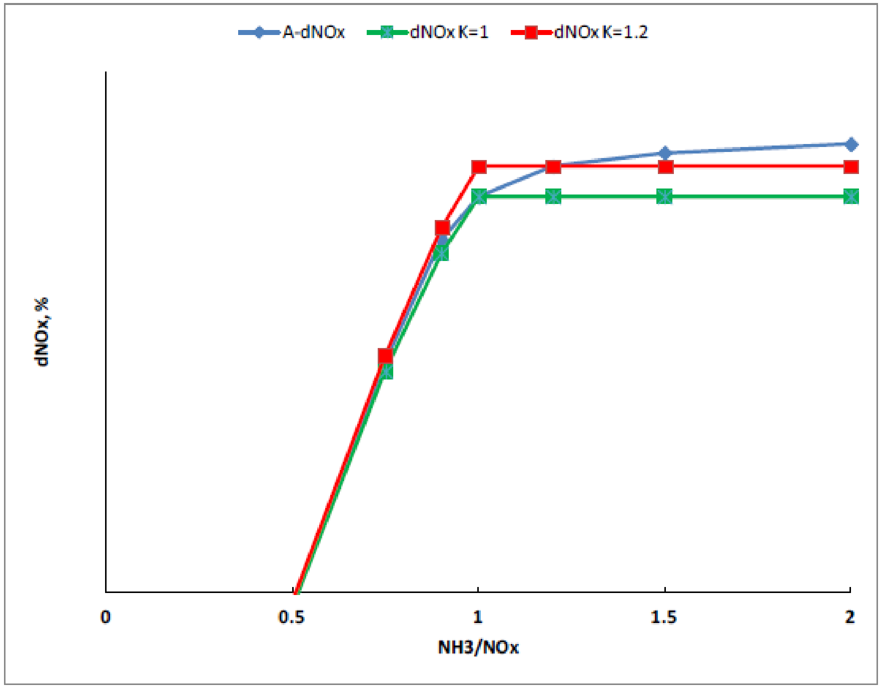
TECHNICAL CONSIDERATIONS

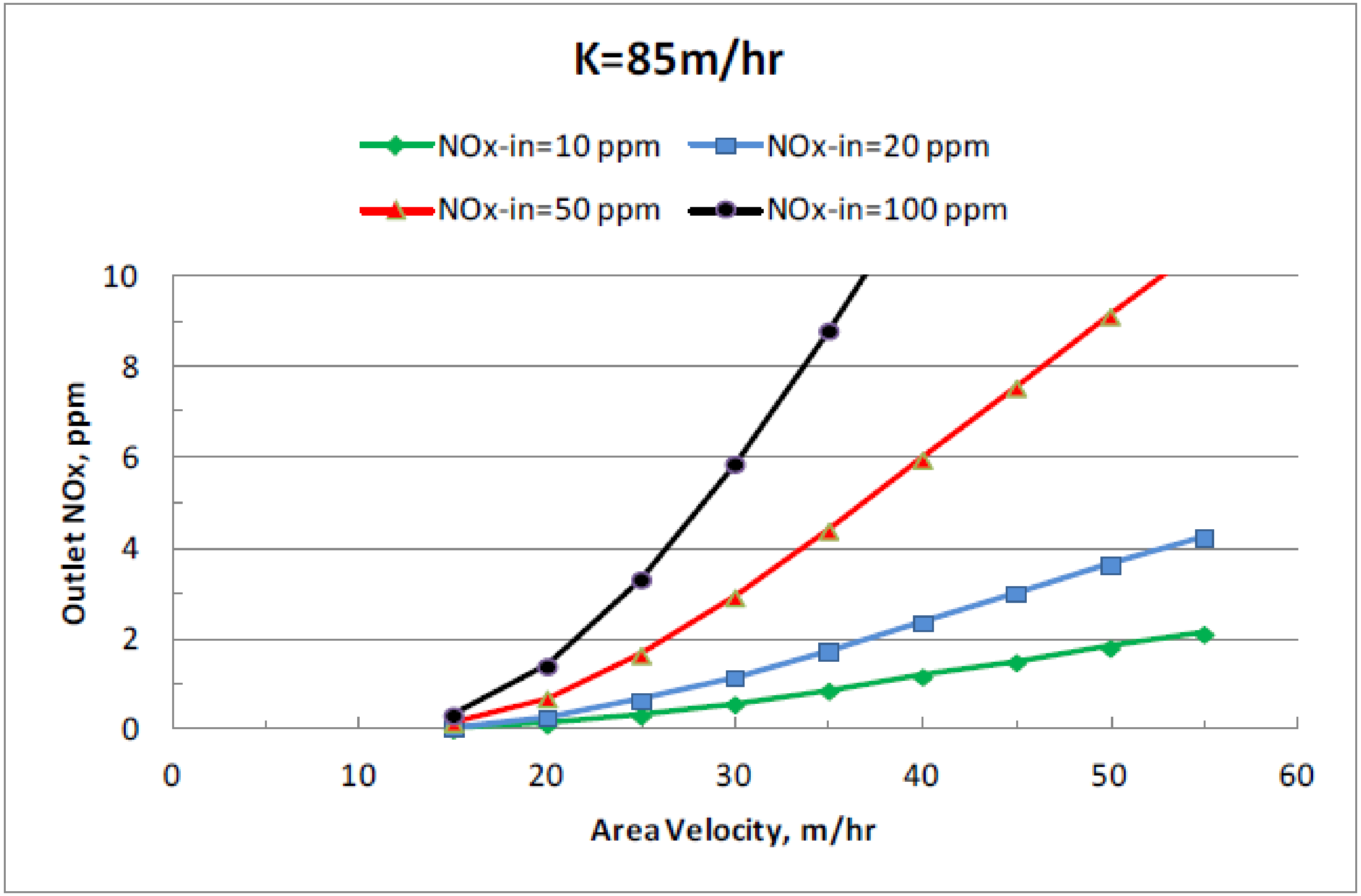
- **NH_3/NO_X**
  - Coal and natural-gas units naturally operate in different ratio regions
  - Coal catalysts usually tested at 1.0, natural-gas catalyst at 1.2





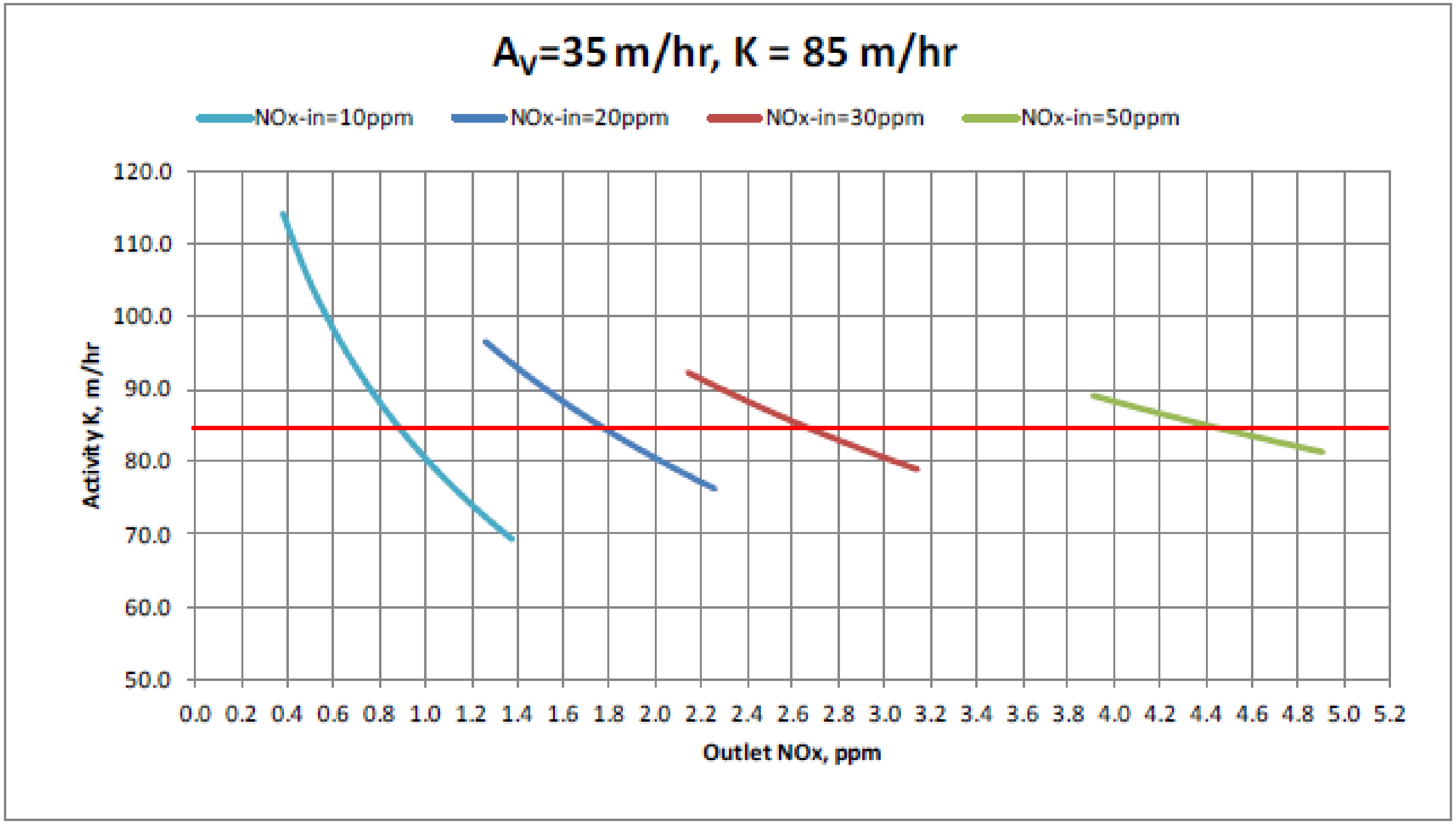
TECHNICAL CONSIDERATIONS

- **Area velocity effects on outlet NO_X**



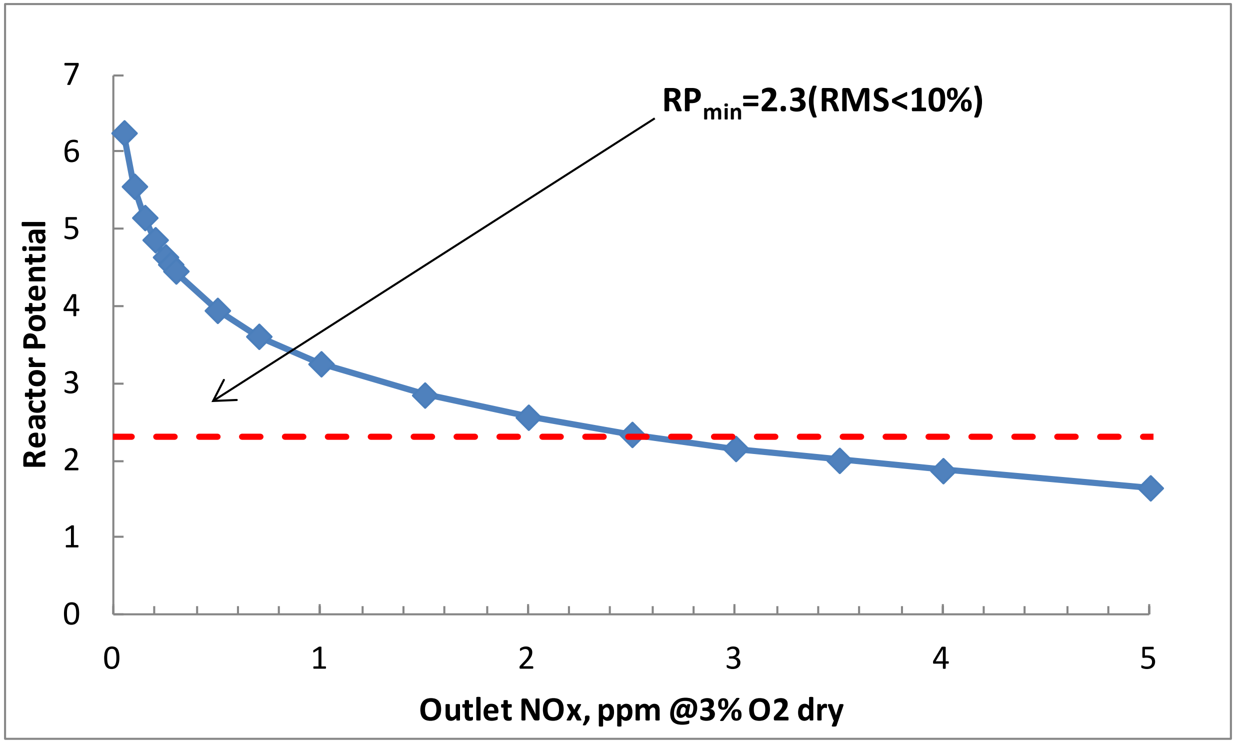
TECHNICAL CONSIDERATIONS

- **Outlet NO_X**
  - Outlet NOX measurement accuracy and variability can greatly alter activity measurement, especially for low concentrations



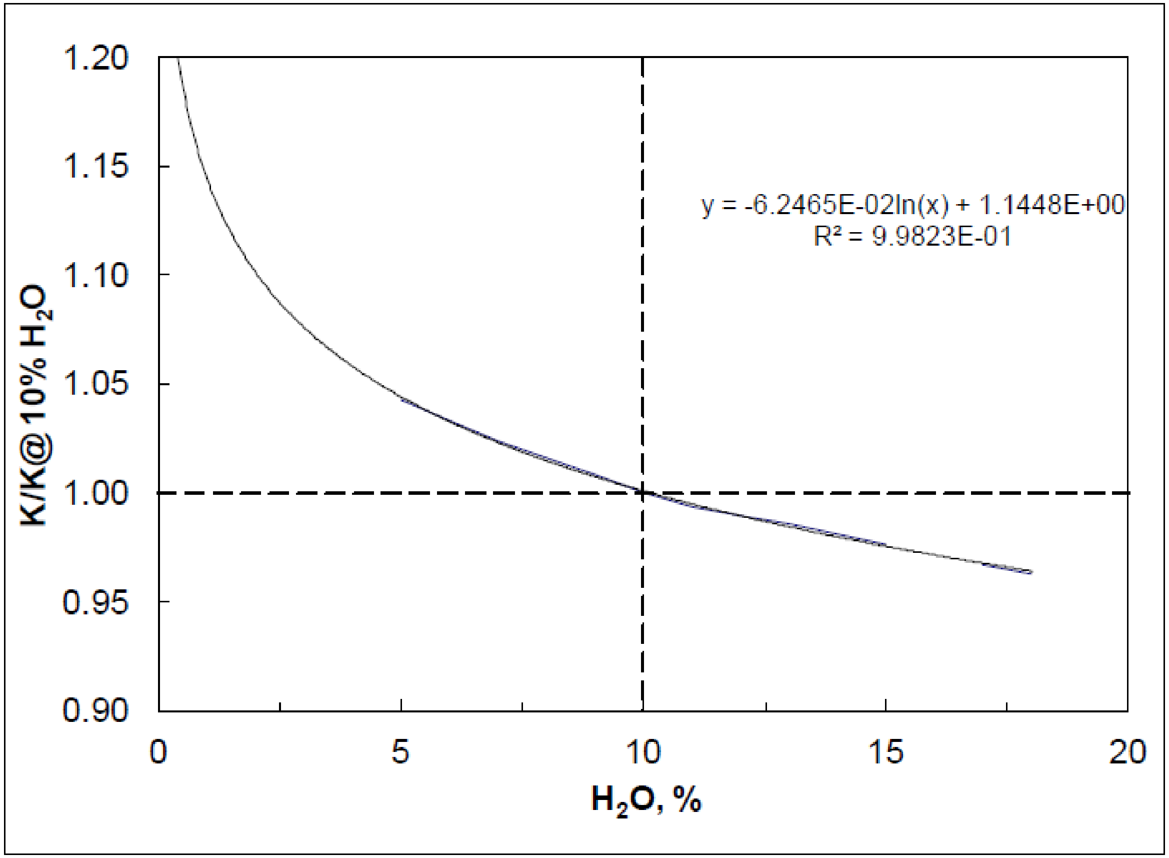
TECHNICAL CONSIDERATIONS

- **New / High-Activity Catalyst**
  - For high activity catalysts, tests at the actual inlet NO_X may lead to minute outlet NO_X measurements, even as the catalyst begins to age!
  - For GT catalysts with ≥ 95% NO_X reduction, test at A_V = 35 Nm/hr



TECHNICAL CONSIDERATIONS

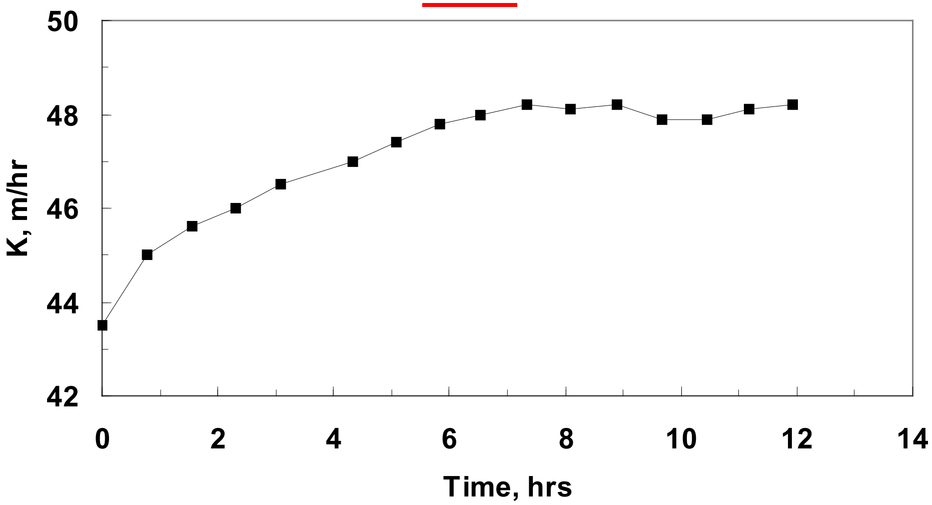
- **Moisture Level**
  - Difference between lab and field H_2O concentration can make a large difference in activity and full-scale projections



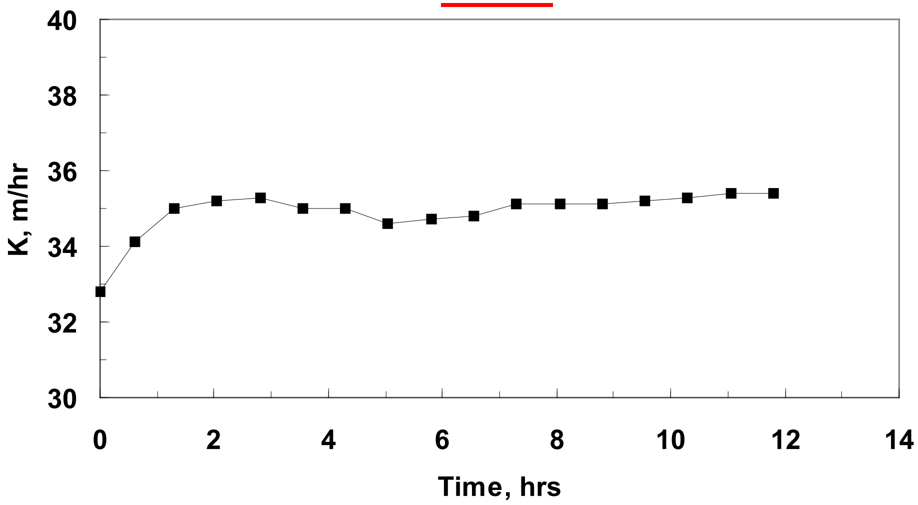
TECHNICAL CONSIDERATIONS

- **Conditioning Time**
  - New catalyst needs to be exposed to operating conditions for a long period of time (~8 hours) before reaching activity equilibrium
  - Used catalyst does not need as long (~2 hours), but still needs some conditioning

New

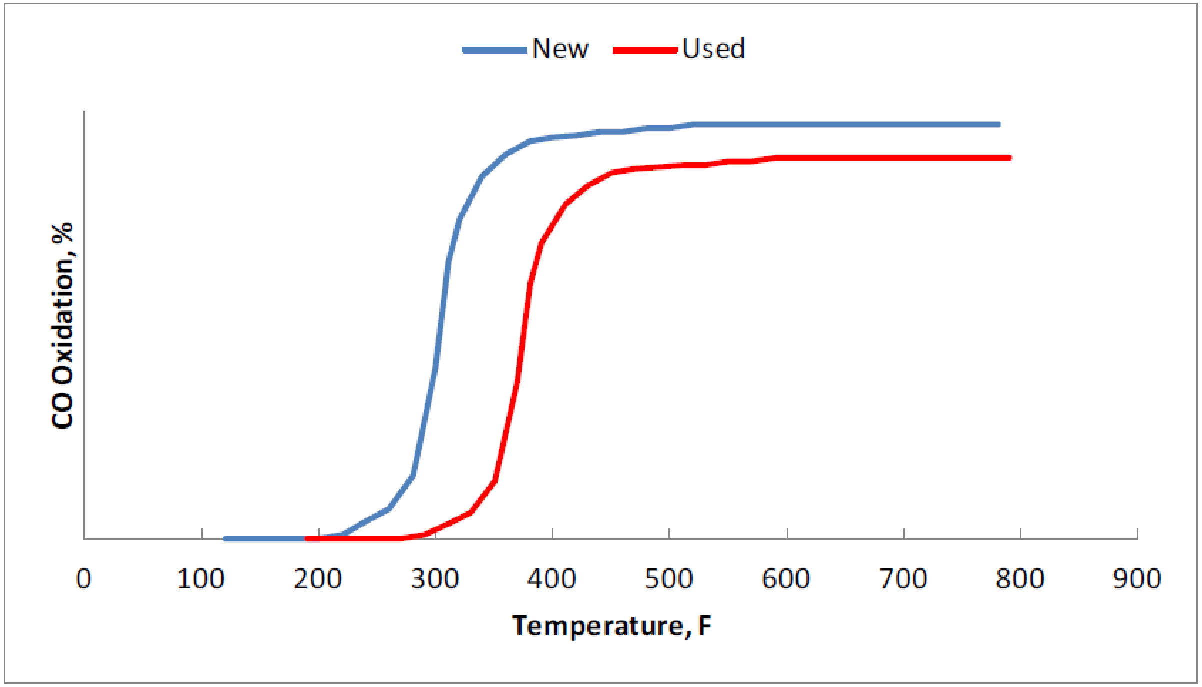


Used



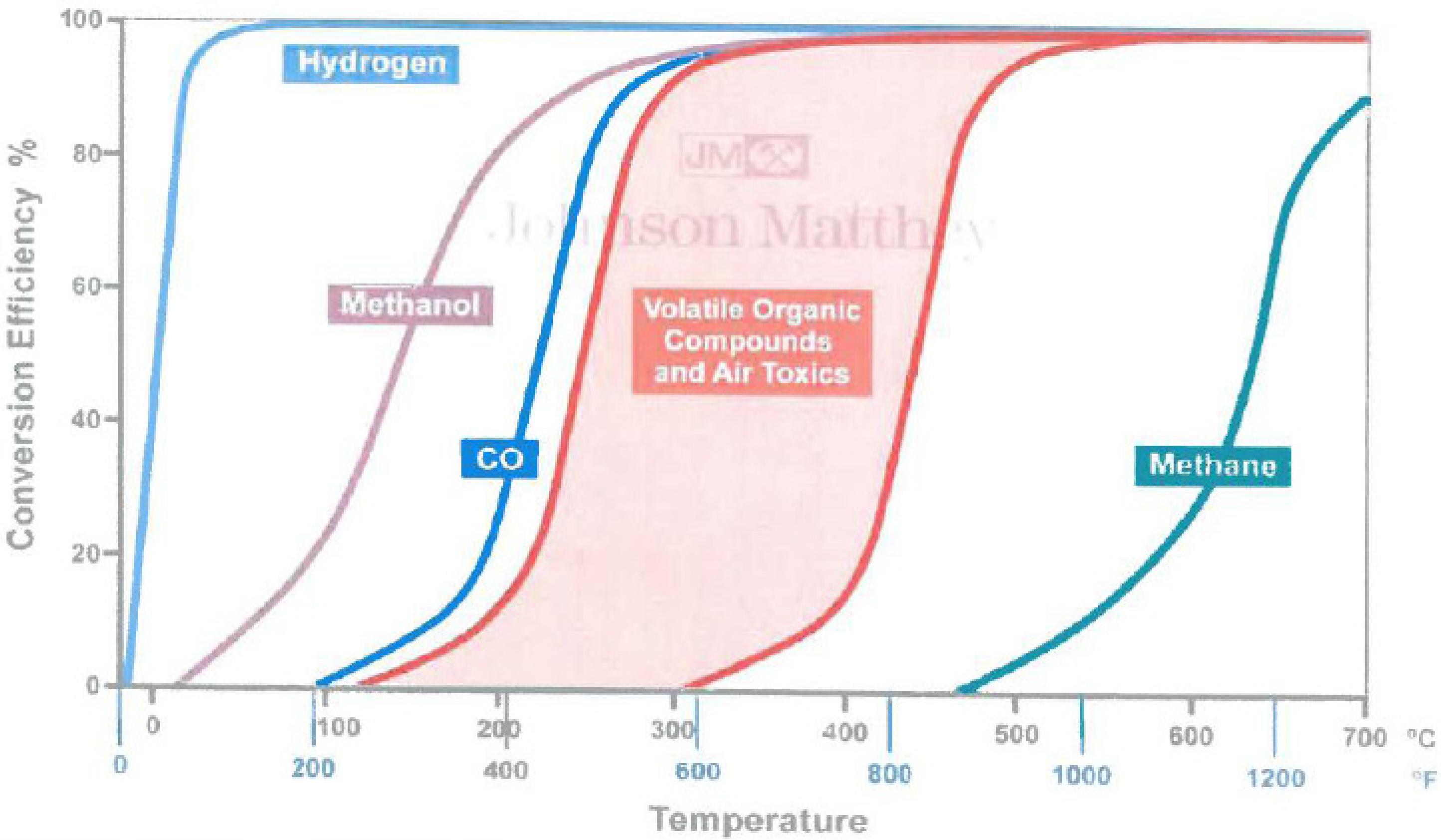
TECHNICAL CONSIDERATIONS

- **CO Catalyst Tests**
  1. Measure CO oxidation across the sample simulating full scale conditions (one test)
  2. Develop a “Light –Off “Curve for the sample
     - Reduced performance can be due to overall deactivation
     - Or, the light off curve has shifted in the operating temperate range



TECHNICAL CONSIDERATIONS

- **VOC Oxidation Tests**
  - Oxidation varies with temperature for usual species of interest



TEST METHOD

Testing methodology is dependent on:

1. **Catalyst Source**
   - *Coal / Natural-Gas*
2. **Catalyst type**
   - *SCR / CO*
3. **Size**
   - *Core / Cube / Button*

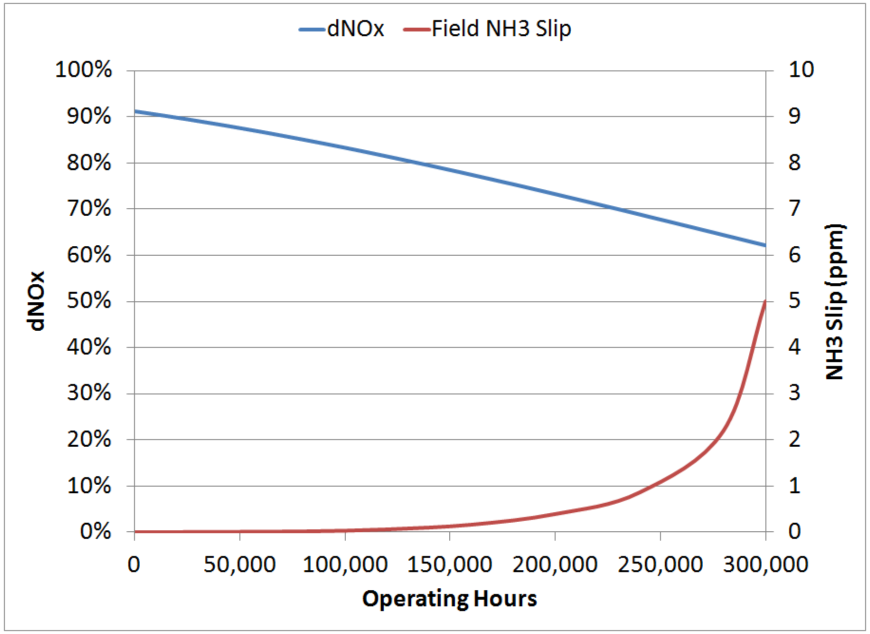
RESULTS & REPORTING

- **NO_X Reduction**
  - Activity, 'K', or NO_X reduction at NH_3 slip
  - Can be used for full-scale projections (reactor potential, RP)
  - Catalyst life estimates if starting activity/ΔNO_X and end-of-life conditions are known
  - Track deactivation over time with regular testing (often yearly or bi-yearly)
- **CO, SO_2, VOC Oxidation**
  - Percentage of inlet gaseous species' oxidation
- **Chemical Analysis**
  - Break-down of bulk and surface chemical composition
  - Useful in determining catalyst poison(s), concentration of active ingredients
- **BET Surface Area / Pore-size Distribution**
  - Useful in quantifying loss of surface area due to blinding/pluggage
  - Loss of surface area = loss of reactivity, definitely correlated but difficult to tell if it's direct (i.e. 10% area loss = 10% activity loss)

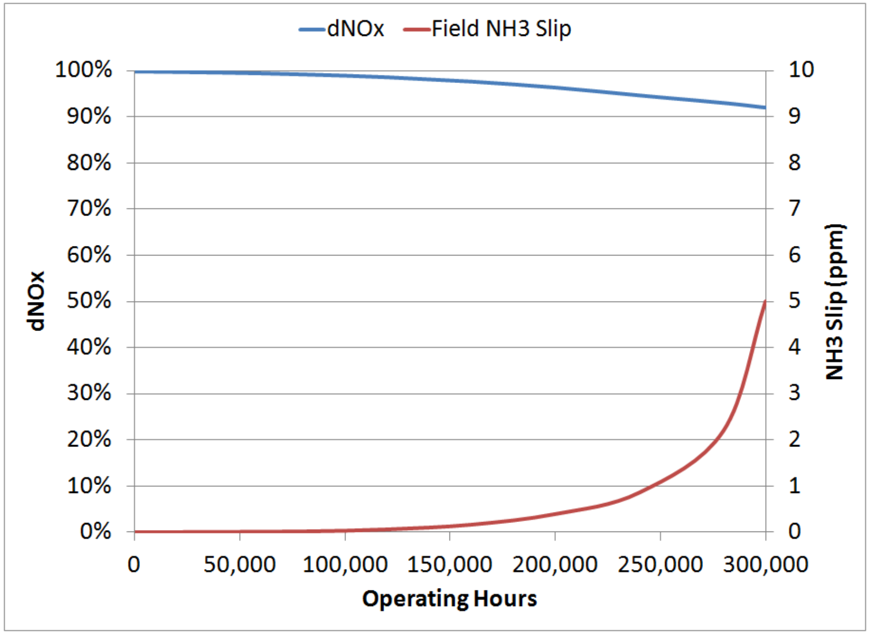
MEASURING K vs. dNOx @ NH3 SLIP

- K_0 = 85 Nm/hr
- Field A_V = 14 Nm/hr
- Deactivation = 3% per 10,000 hours
- Inlet NOx = 25 ppm
- Outlet NOx = 5 ppm
- NH_3 Slip = 5 ppm

Activity (A_V = 35 Nm/hr)

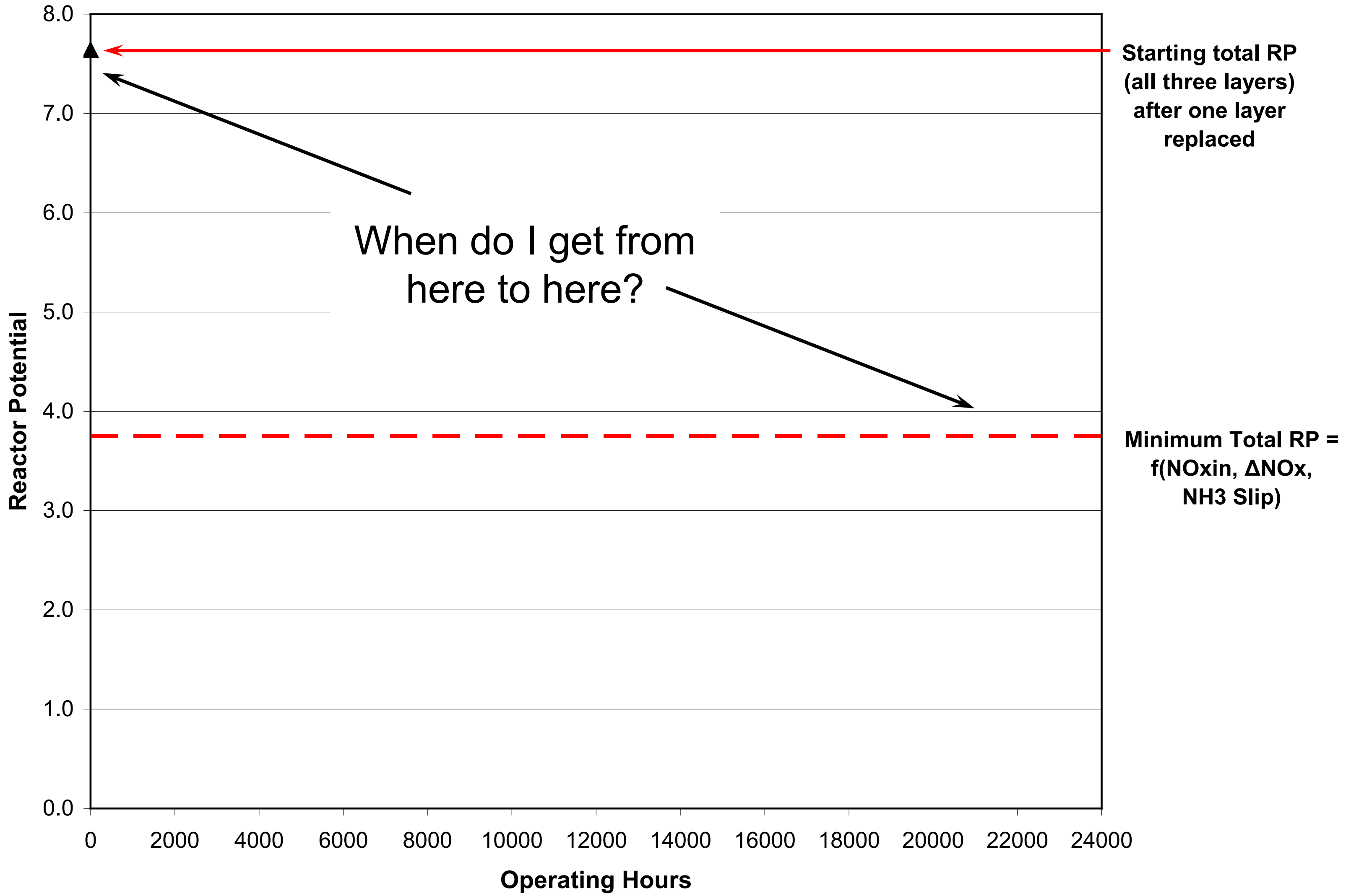


dNOx @ 5 ppm NH_3 (A_V = 14 Nm/hr)



➢NOx reduction measurements at NH_3 slip limit does not provide good resolution for high-activity GT SCR catalysts

How is Reactor Potential Used?



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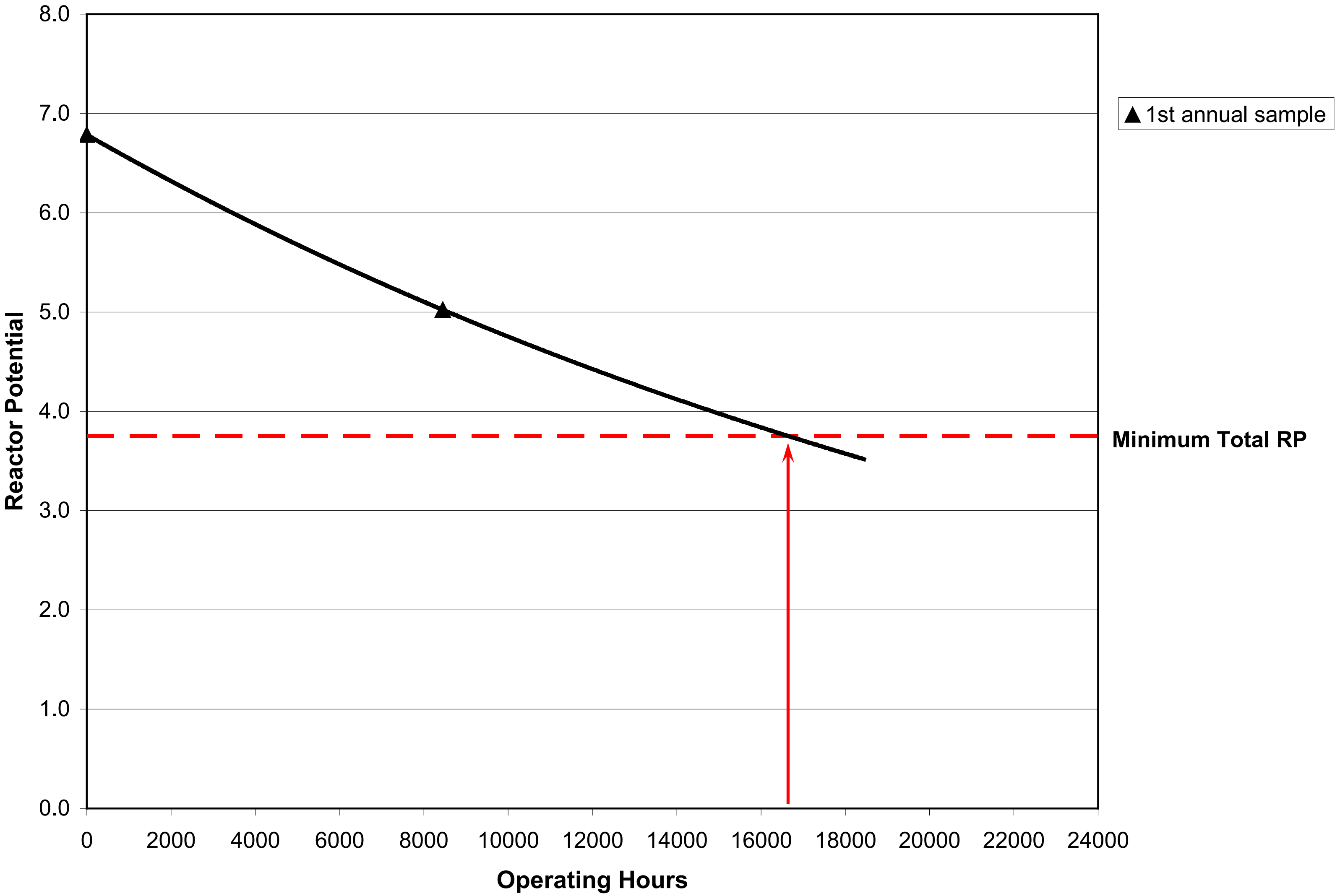
“End of Life” Prediction After 1 Year



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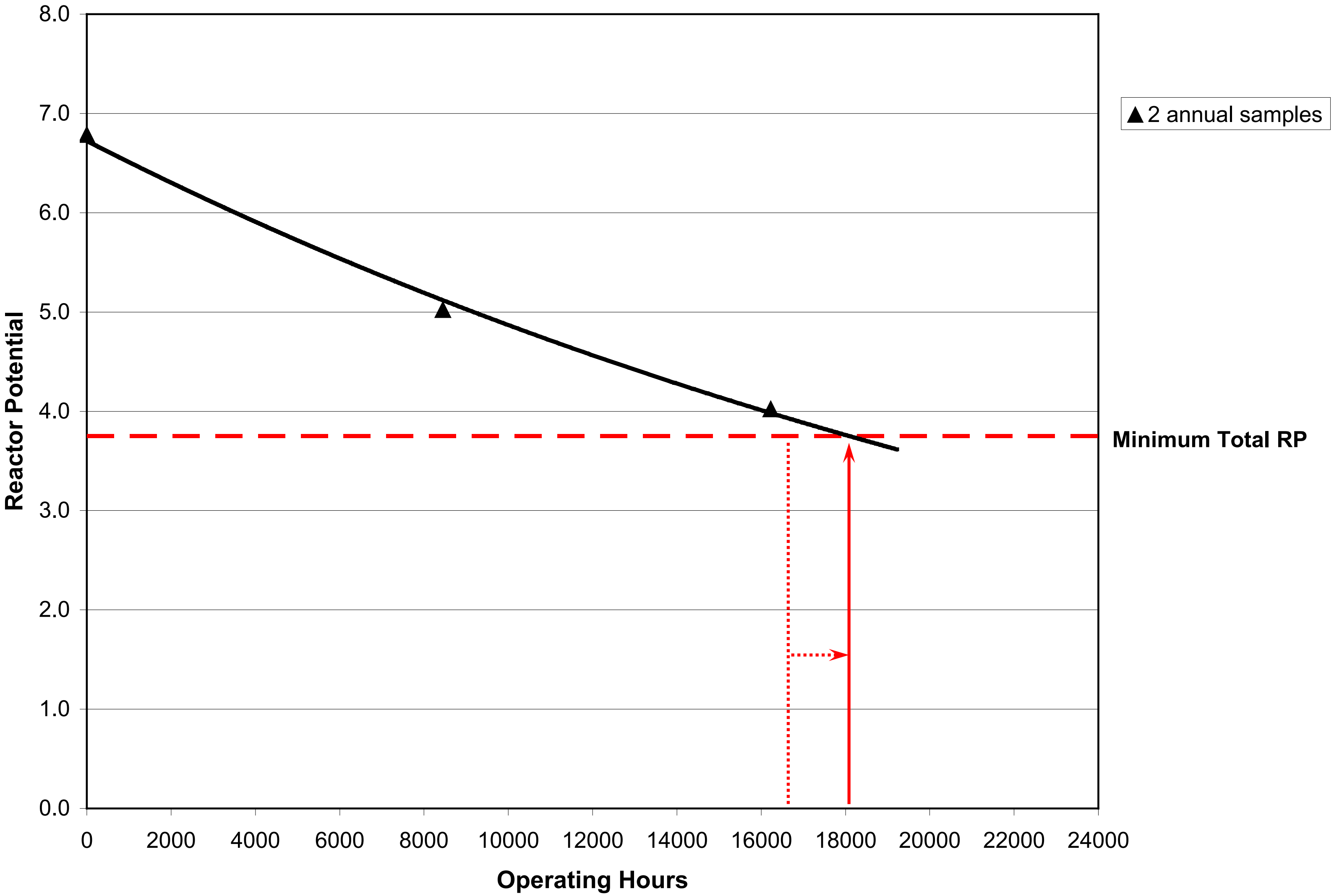
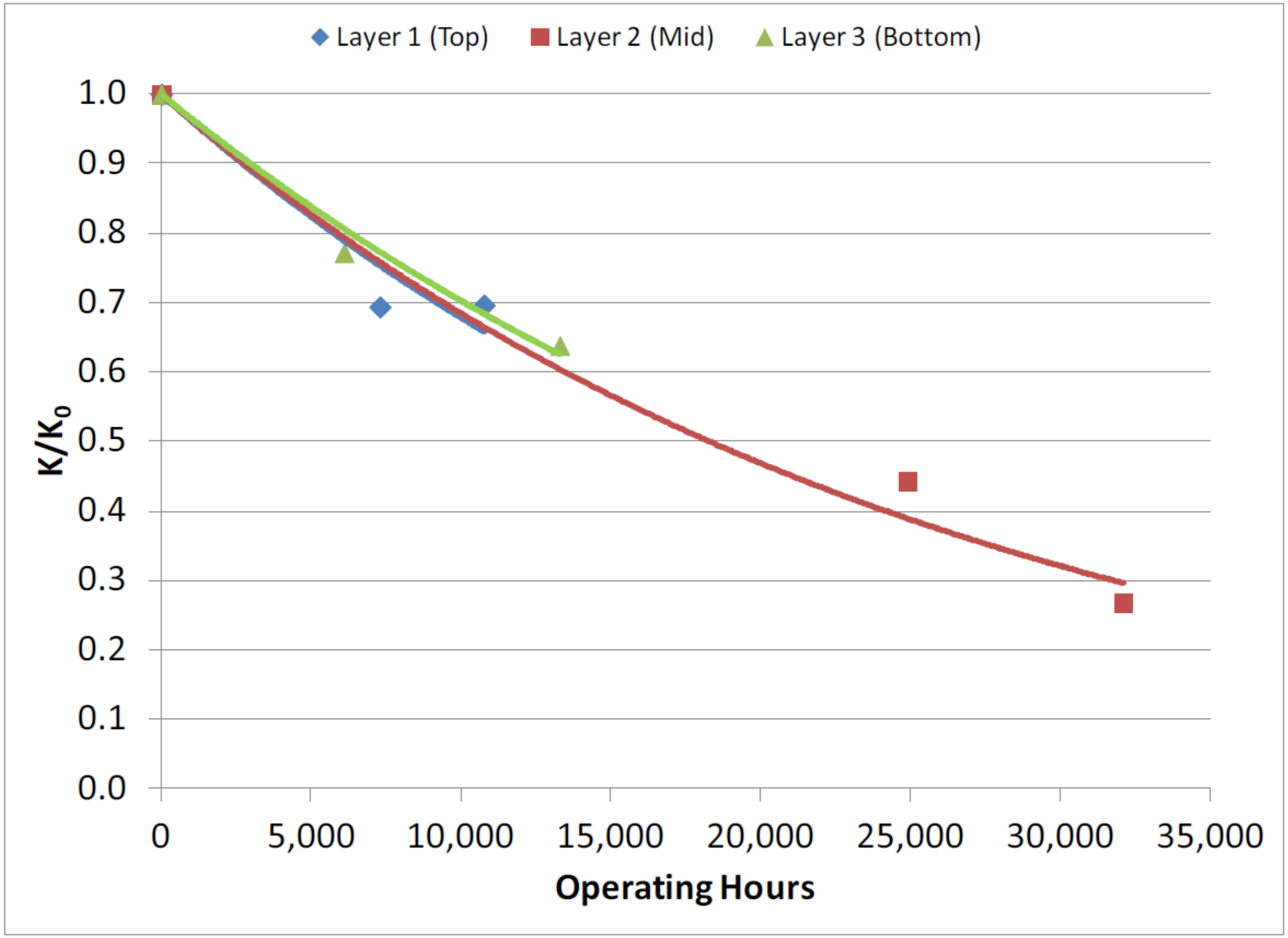
Catalyst Samples After 1 & 2 Years



FULL-SCALE APPLICATION

- **Layer-by-Layer Deactivation Tracking**



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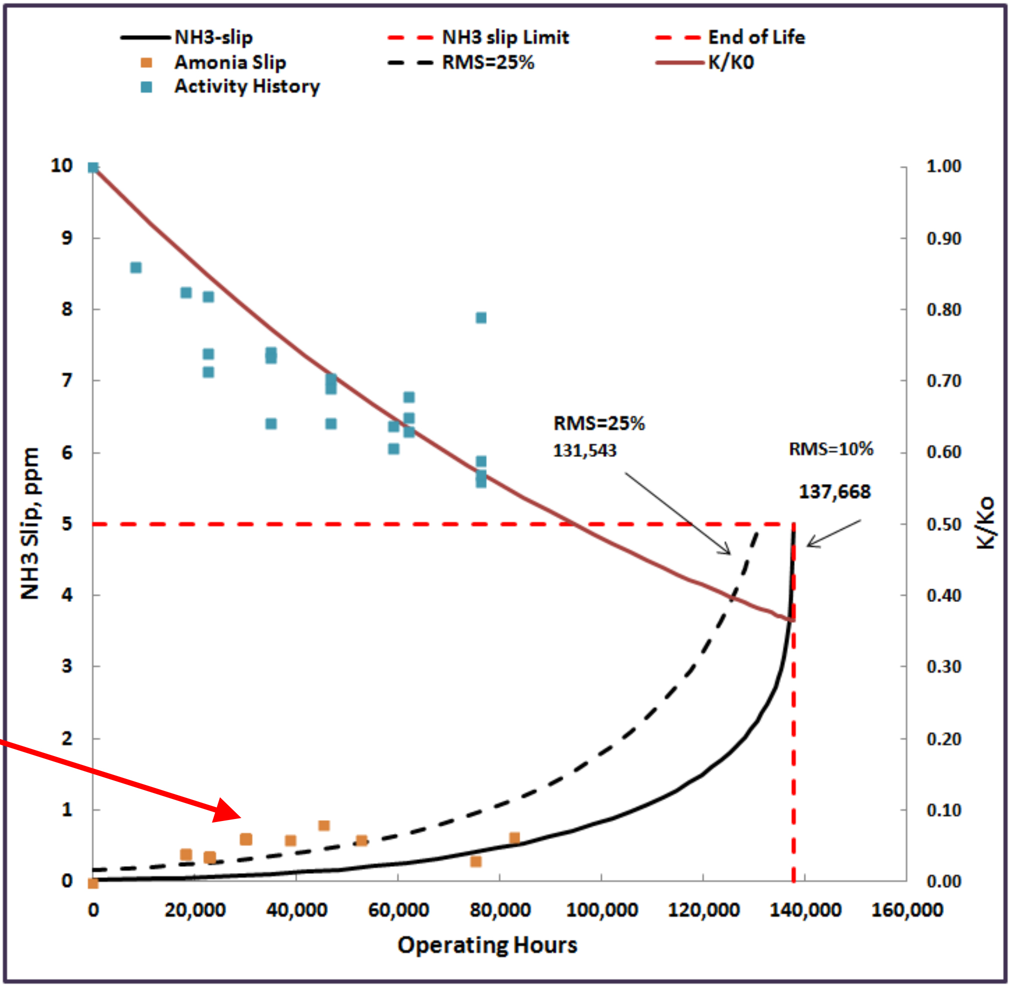
FULL-SCALE APPLICATION

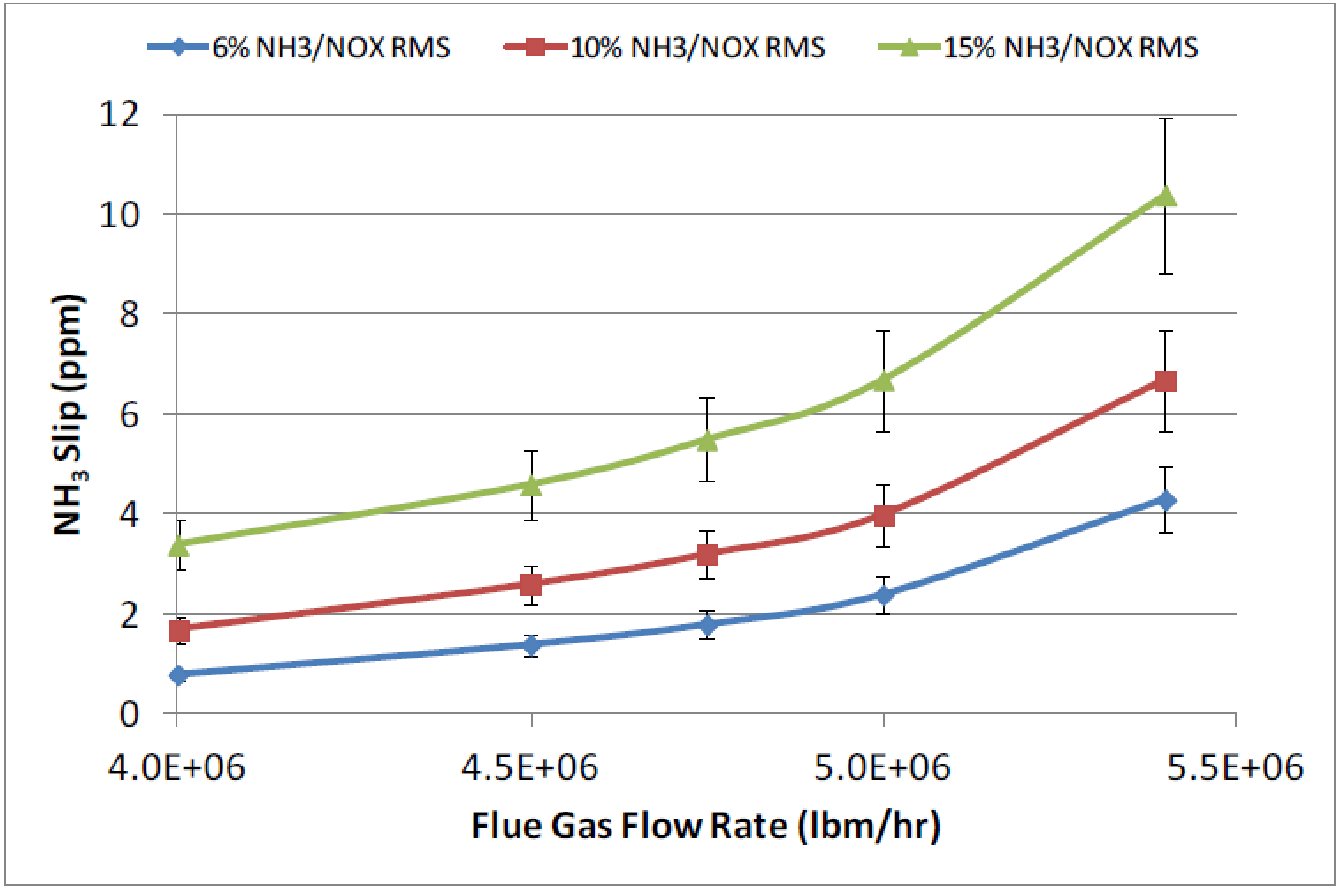
- **Life Projections**



Monitoring NH_3 slip also critical!

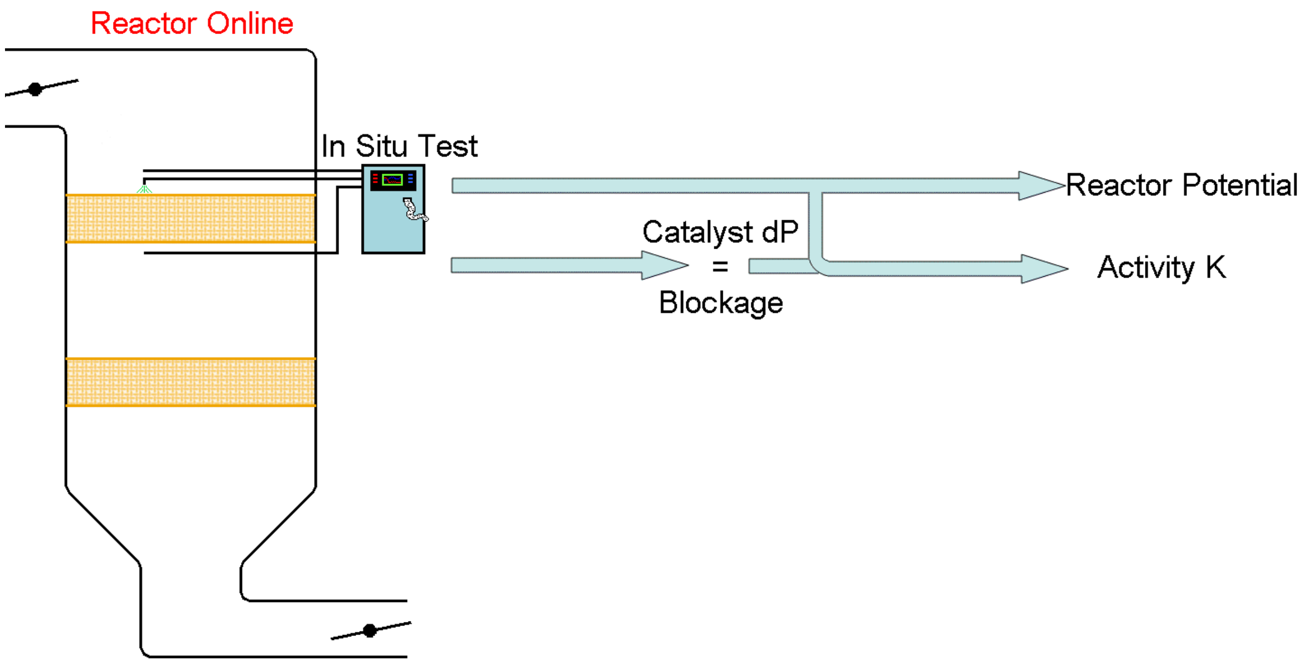
FULL-SCALE APPLICATION

- **NH_3 Slip Projections for Varying Operating Conditions**



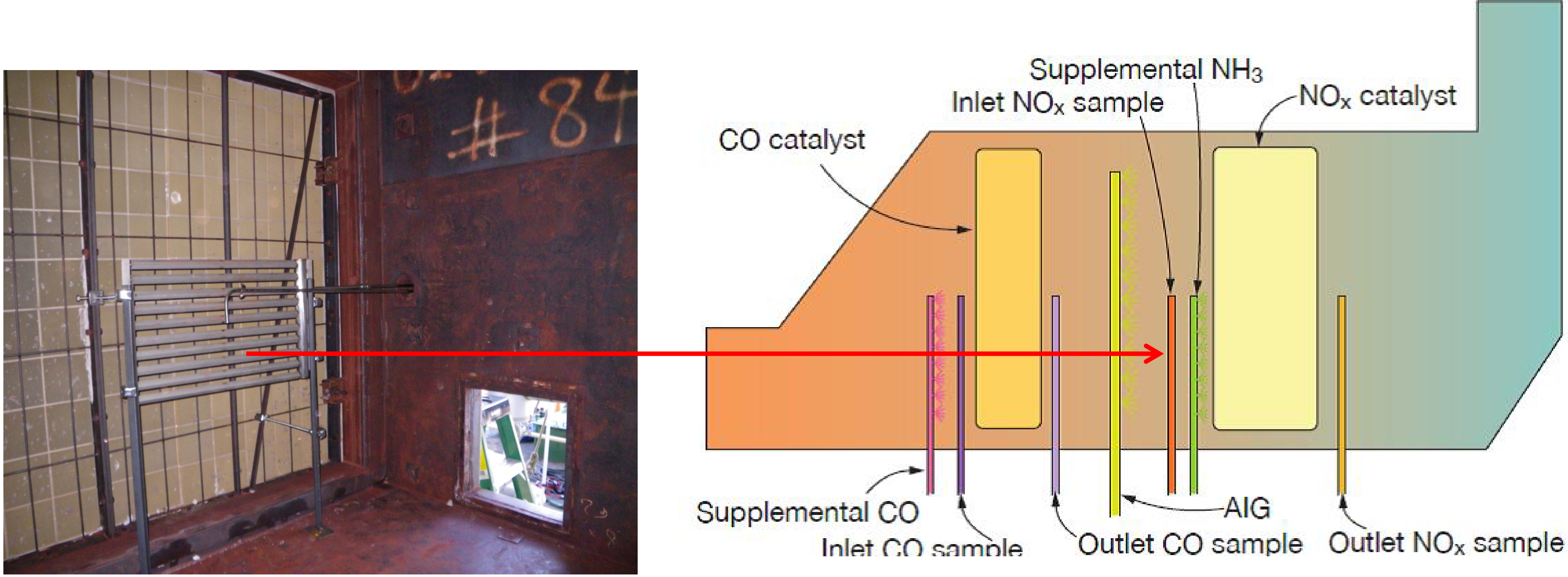
IN-SITU MEASUREMENT

- Option if lab samples are unavailable or difficult to obtain given outage schedule
  - Tests at actual operating conditions
  - Measurements anytime



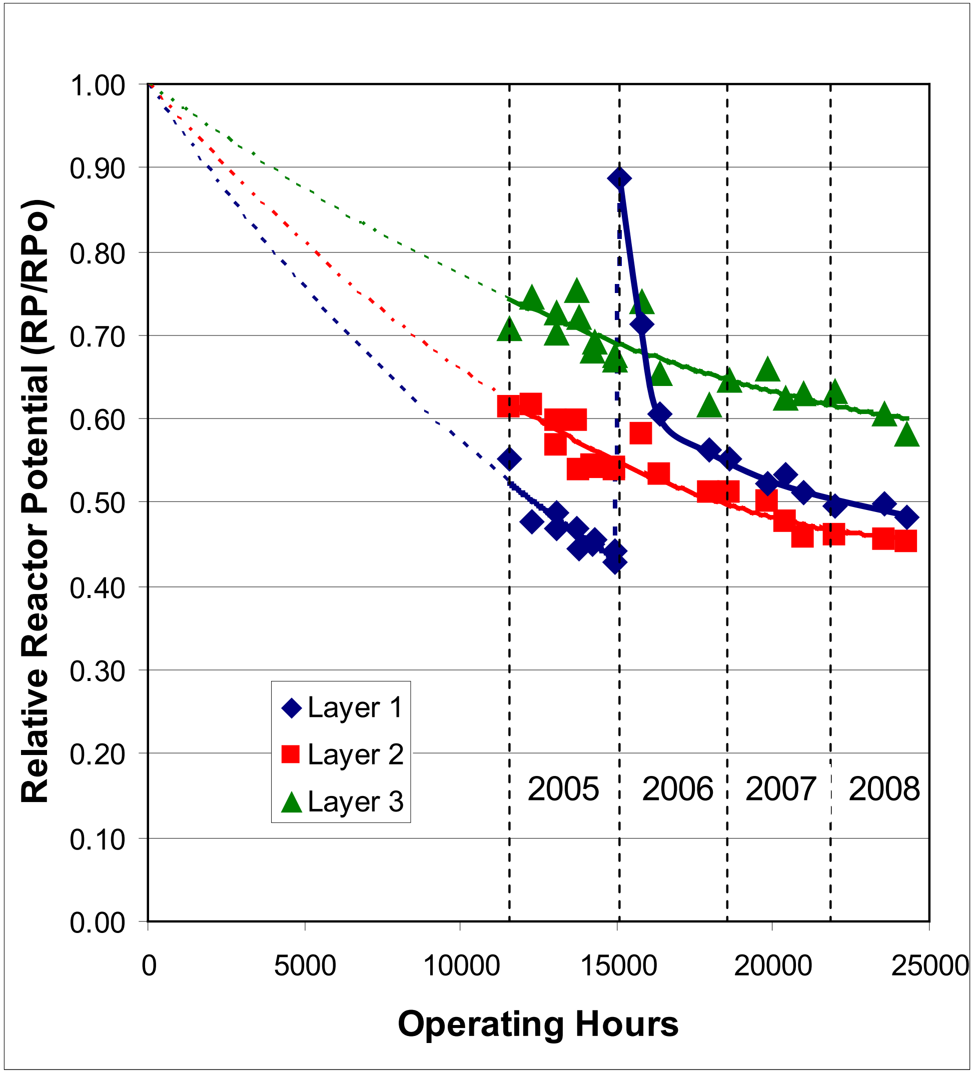
IN-SITU MEASUREMENT

- FERCo's CatalysTraK® was originally developed for coal-fired SCR's but can be used in gas-turbine as well
- Similar to the lab approach for SCR catalyst, NO_X reduction is measured across a small cross section (test section) of the catalyst bed
- A small supplemental ammonia injection grid (AIG) is permanently mounted upstream of the test section.



IN-SITU MEASUREMENT

- First 4-years of operation beginning in 2005
  - 700 MW unit
  - E. bituminous coal
  - Two reactors
  - 3 + 1 configuration
- SCR on-line May 2002
- Seasonal operation
- Initial load: 3 layers honeycomb catalyst
- Layer 1 replaced with plate catalyst prior to 2006 ozone season



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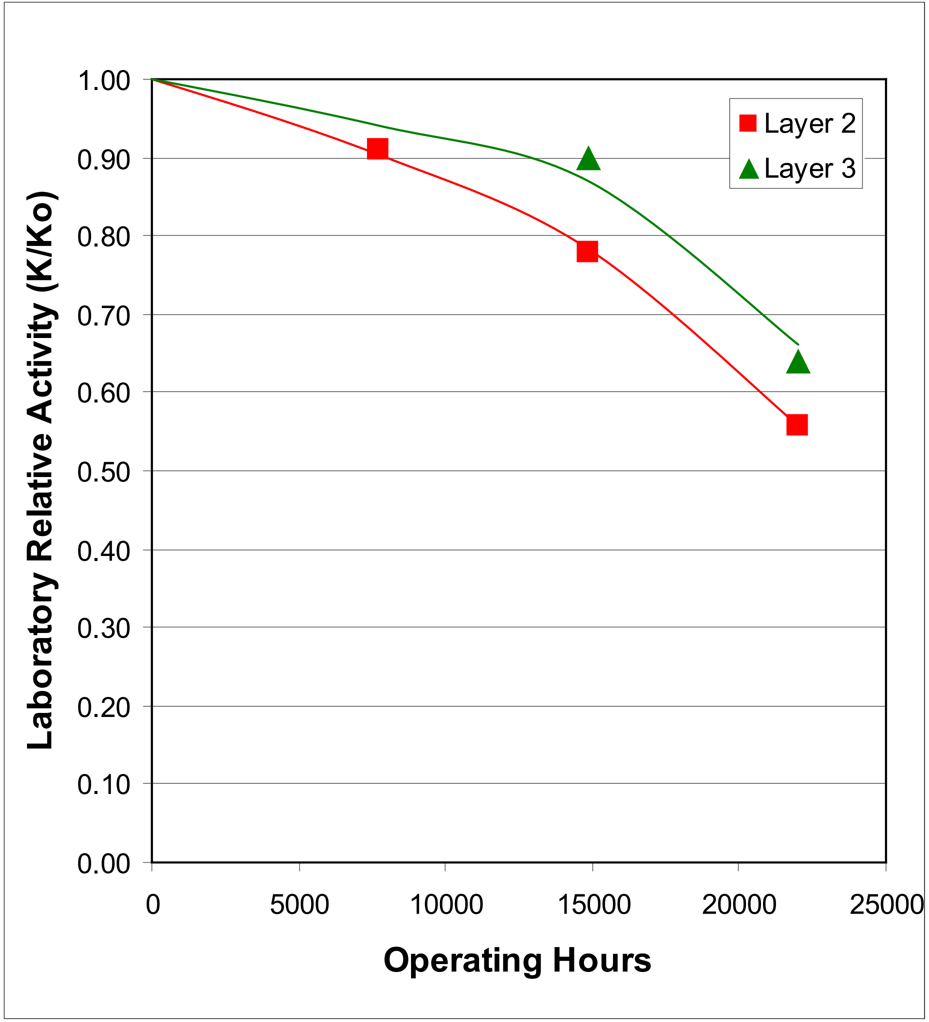
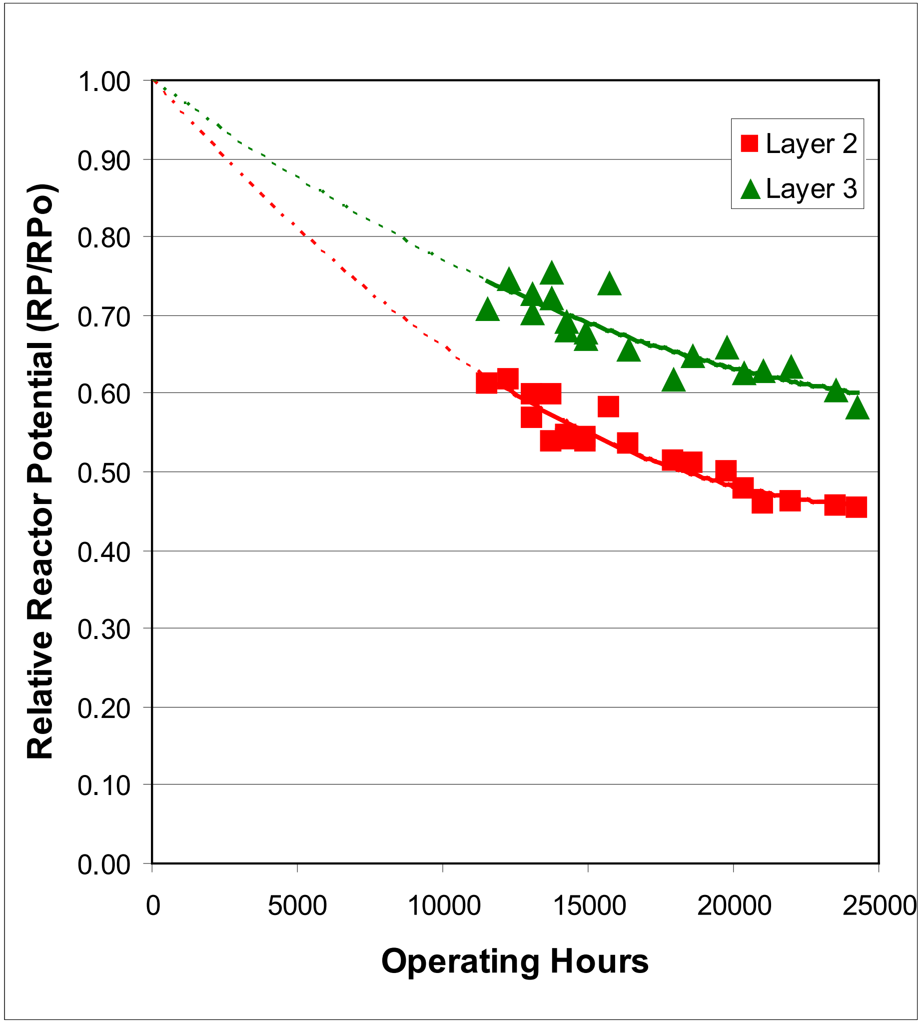
Volume of Data: Laboratory vs. *In Situ*

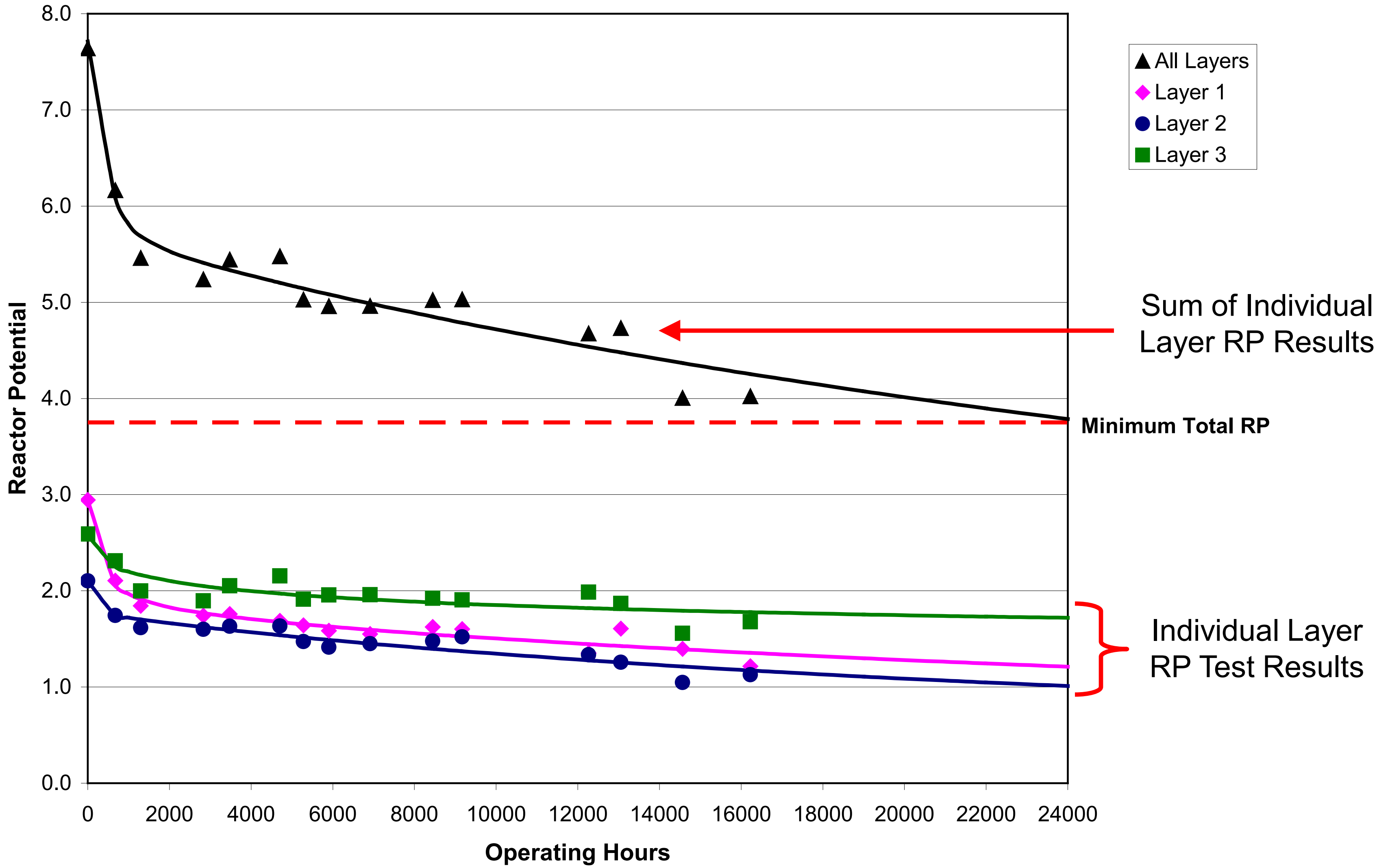
Annual Laboratory Analysis



On-Demand CatalysTrak™ Measurements

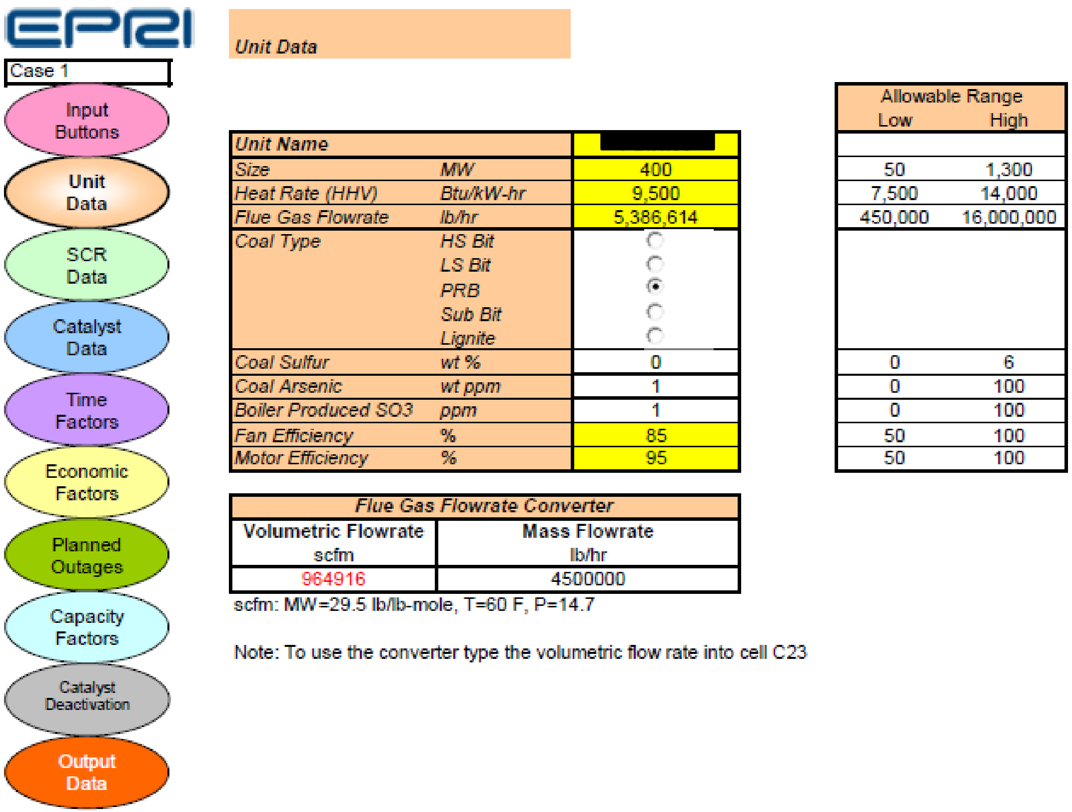


IN-SITU MEASUREMENT



CATREACT™

- **Co-developed with EPRI**
- **Comprehensive catalyst management tool – mainly multi-layer coal units**



Unit Name		[redacted]	Allowable Range Low	Allowable Range High
Size	MW	400	50	1,300
Heat Rate (HHV)	Btu/kW-hr	9,500	7,500	14,000
Flue Gas Flowrate	lb/hr	5,386,614	450,000	16,000,000
Coal Type	HS Bit	○		
	LS Bit	○		
	PRB	◉		
	Sub Bit	○		
	Lignite	○		
Coal Sulfur	wt %	0	0	6
Coal Arsenic	wt ppm	1	0	100
Boiler Produced SO3	ppm	1	0	100
Fan Efficiency	%	85	50	100
Motor Efficiency	%	95	50	100

Flue Gas Flowrate Converter	
Volumetric Flowrate scfm	Mass Flowrate lb/hr
964916	4500000

scfm: MW=29.5 lb/lb-mole, T=60 F, P=14.7

Note: To use the converter type the volumetric flow rate into cell C23

CATREACT

- **Catalyst replacement by ideal conditions or pertaining to outage schedules**
- **Scenario development and planning (1+1, 2+1, 3+1, etc.)**

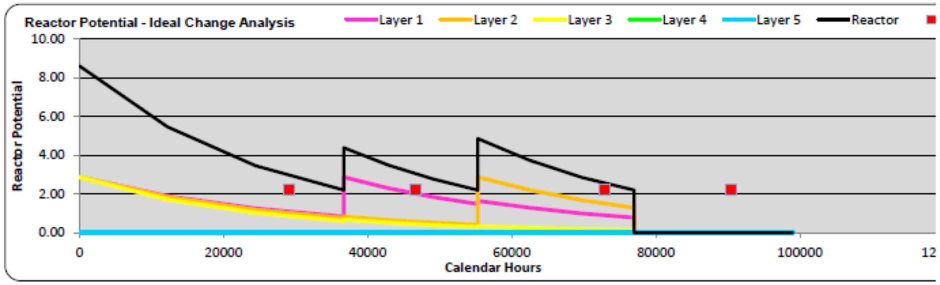
EPRI

Case 1

Input Buttons
Unit Data
SCR Data
Catalyst Data
Time Factors
Economic Factors
Planned Outages
Capacity Factors
Catalyst Deactivation
Output Data
Print All
Copy Output to Blank Sheet

CatReact

Summary Report	Raw Costs, $ Ideal	Raw Costs, $ Nearest
As of Date	6/7/16	6/7/16
Total Raw Costs, $	1,205,773	1,205,774
Catalyst Raw, $	-	-
Reagent Raw, $	1,081,376	1,081,377
Labor Raw, $	-	-
Electricity Raw, $	-	-
NOx Credits Raw, $	-	-
dP Raw, $	124,397	124,397
Catalyst Layers Installed	0	0



Layer 1	Layer 2	Layer 3	Layer 4	Layer 5		Ideal Change Analysis Date	Operating Hours (hrs)	Total Cost ($ 10^6)	dNOx (%)	NH3slip (ppm)	Cost Components (Raw) Catalyst ($ 10^6)	Reagent ($ 10^6)	Labor ($ 10^6)	Electricity ($ 10^6)	NOx Credits ($ 10^6)	dP ($ 10^6)	SO2 Conv (%)	dP (in H2O)	RP used	RP new	Sv (hr^-1)
1	1	1			Start	1/1/2014	0	-	74	0.0	-	-	-	-	-	-	0.5%	1.0		8.62	2236
1					Event 1	3/9/2018	35,970	5.00	74	5.2	1.71	1.86	0.02	1.19	-	0.21	0.5%	1.0	2.20	4.39	2236
	1				Event 2	4/21/2020	53,586	9.26	74	5.2	3.42	2.92	0.04	2.57	-	0.31	0.5%	1.0	2.20	4.86	2236
		1			Event 3	10/14/2022	73,995	13.84	74	5.2	5.13	4.20	0.06	4.01	-	0.43	0.5%	1.0	2.20	5.17	2236
1					Event 4																
	1				Event 5																
		1			Event 6																
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					Event 19																
					Event 20																

Thank You!

Questions? Comments?

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