

Reinhold Environmental Ltd.



2010 NO_x-Combustion Round Table & Expo Presentation

February 8 & 9, 2010

Chattanooga, TN

All presentations posted on this website are copyrighted by Reinhold Environmental, Ltd (RE). Any unauthorized downloading, attempts to modify or to incorporate into other presentations, link to other websites, or obtain copies for any other uses than the training of attendees to RE's Conferences is expressly prohibited, unless approved in writing by RE or the original presenter. RE does not assume any liability for the accuracy or contents of any materials contained in this library which were presented and/or created by persons who were not employees of RE.

High Volume Testing for SCR Catalyst



Reinhold Environmental LTD.
2010 NOx-Combustion Round Table & Expo

Mike Cooper
CoaLogix
VP Technology

Agenda

- **SCR catalyst sampling and testing to improve QA/QC for production scale regeneration**
- **Intelligent catalyst sampling strategies**
- **Catalyst test and analysis: DeNOx kinetics**
- **Catalyst test options**

Challenges in SCR Catalyst Testing **CoaLogix™**

➤ **Variances in:**

- **Catalyst manufacturing**
- **Flue gas composition**
- **SCR system design**
- **Testing methods**



➤ **Large Catalyst Volume – Typical 600Mw unit with 192 modules**

- **14,400 honeycomb elements or**
- **245,000 plates**
- **3,072 corrugated cassettes**

➤ **Limited sampling opportunities (frequency and quantity)**

➤ **Limited independent testing capacity**

Data Gathering

- **Plant operating conditions establish sample test conditions**
 - Temperature
 - Catalyst type and geometry
 - Volumetric flow per catalyst facial area: $\text{Nm}^3/\text{hr} / \text{m}^2$
 - in channel velocities derived from catalyst geometry and temperature
 - Inlet gas concentrations: NO_x SO_2 H_2O O_2
- **Evaluate available test and analysis data**
 - **Test** new catalyst DeNO_x activity and SO₂ oxidation rates (K_0 & K_{23_0})
 - New catalyst chemistry – bulk & surface vanadium content...
 - DeNO_x and SO₂ oxidation rates over time
 - deactivation rate models predict performance
- **Deactivated (current state) test and analysis data**
 - **Test** DeNO_x activity and SO₂ oxidation rates (K_d & K_{23_d})
 - Deactivated catalyst chemistry – bulk and surface

➤ Goals

- Develop and execute a regeneration process which meets customer requirements
- Test regeneration cycle – Full production simulator
 - **Test** DeNOx activity and SO₂ conversion after treatment / before vanadium re-impregnation
 - **Test** DeNOx activity and SO₂ conversion *after* vanadium re-impregnation
 - Iteration as required until performance targets achieved...
- Production quality control / quality assurance testing
 - Sampling and **testing** during production – *Production Control Samples*
 - Assurance that regeneration process in “under control”
 - Assure product meets previously agreed upon performance guarantees

Sampling Basics: Confidence Intervals

- Unless you sample and test 100% of population you produce an ***estimate*** of catalyst performance
- All catalyst performance estimates based on population sampling have a measurable probability of being wrong!
- Most common measure of error in a sample based estimate is the ***confidence interval*** and ***confidence level***
 - At a 95% confidence level there is one chance in 20 (5% probability) the “true value” of DeNOx potential lies outside the calculated confidence interval around the mean

The narrower the interval the better the data quality

Intelligent Sample Design Strategy

- Intelligent sampling strategies produce small confidence intervals at lowest possible cost
- Confidence interval formally described by *sample standard deviation* and square root of *number of samples*

$$\text{Interval} = \text{SampleMean} \pm t_{crit} \cdot \frac{\sigma}{\sqrt{\text{numSamples}}}$$

- Too few samples give unacceptably wide error band
- More than minimum provide no added value at high cost!

Sample Strategy Basics

- **Statistical tools require “normally distributed” samples – SCR**
DeNOx activity often not normally distributed
 - Inlet more deactivated than outlet – high velocity regions in layer more deactivated than low
- **Simple random samples** helps reduce bias -- every member of population has an equal chance of being selected
 - A simple random sample of non-normally distributed sample is normally distributed! (“central limit theorem”)
 - Intelligent sampling avoids plugged elements in sample selection
- **Choose sample size based on desired confidence interval width and population standard deviation**

$$numSamples = \left[\frac{2 \times t_{crit} \times \sigma}{desiredWidth} \right]^2$$

Recommended Sample Size Vs Population Size

Goal: Provide 95% confidence interval “error band” ± 2 m/hr around mean value

Assumption:

- **Mean DeNOx activity 40 m/hr**
- **Simple random samples provide “normally distributed” sample means**

Modules per layer	Elements	$\sigma \pm 1.5$ m/hr	$\sigma \pm 3$ m/hr
36	2,592	2	3
72	5,184	3 to 4	4 to 5
144	10,368	4 to 5	5 to 6
192	13,824	5 to 6	6 to 7
240	17,280	7 to 8	8 to 9

As you learn more about population the ability to estimate sample requirements improves – fewer or more may be required!

Production Process Control

- **Build data centered model of how process *expected* to perform**
 - Example: RSD around mean DeNO_x activity of regeneration process A determined to be $\pm 3\%$ Thus DeNO_x test results from....
45m/hr target expected to be $\pm 1.4\text{m/hr}$ 55m/hr expected to be $\pm 1.7\text{m/hr}$
...total sample variance combination of process variance and test variance
- **Calculate process control limits**
 - Conventional ***process control limits set at $\pm 3\sigma$***
 - $< 1/1,000$ chance a sample mean value will fall above UCL or below LCL!
 - Samples outside calculated control limits likely due to an assignable cause
- **Collect data over time and compare against control limits**
- **Examine sample data outside control limits to determine if they are part of the population from which original model was built**
 - Re-compute process control limits
 - Identify and remediate process variance → narrow process limits
 - Continual process improvement

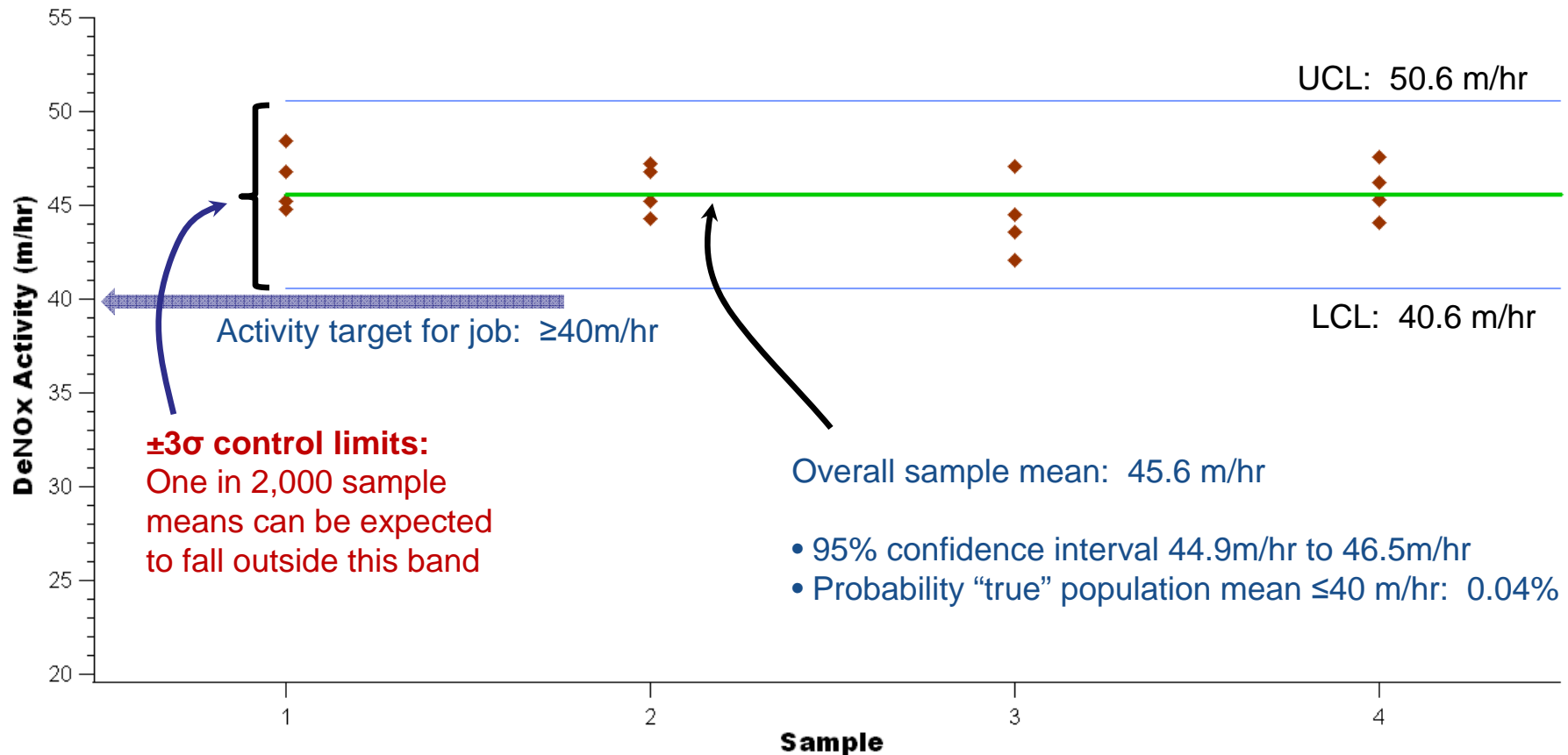
Process Control Chart Example

Sampling strategy:

Four simple random samples taken four times over course of production regeneration job

Mean DeNOx activity: 45.6 m/hr

Standard deviation: 1.67 m/hr



Deactivation Rate Analysis

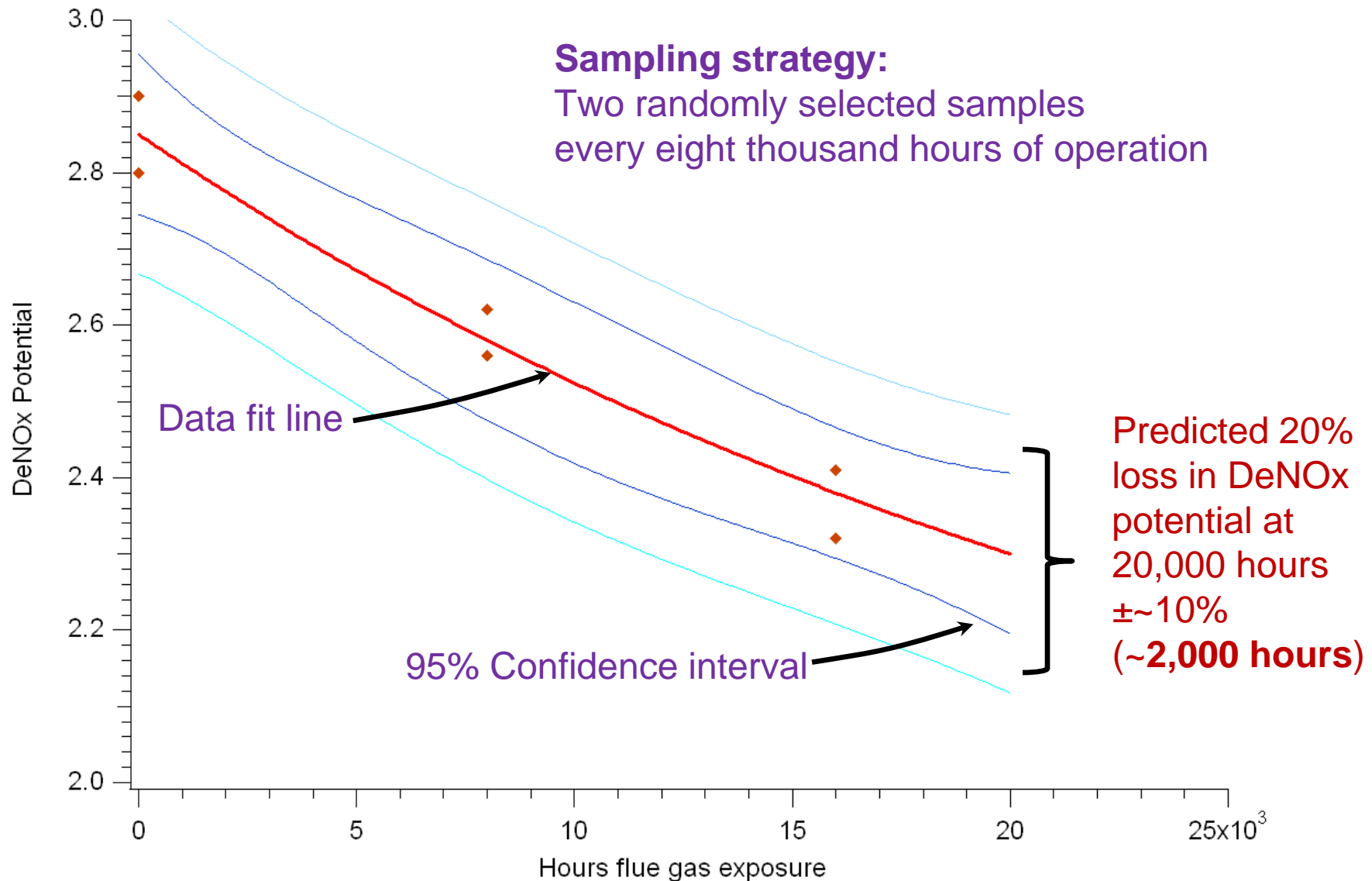
- Mean sample DeNOx activity over time allows development of a predictive deactivation rate model
- Common metric: catalyst DeNOx *Potential* a unit-less number

$$Potential = -\ln\left(1 - \left(\frac{NOx_{in} - NOx_{out}}{NOx_{in}}\right)\right)$$

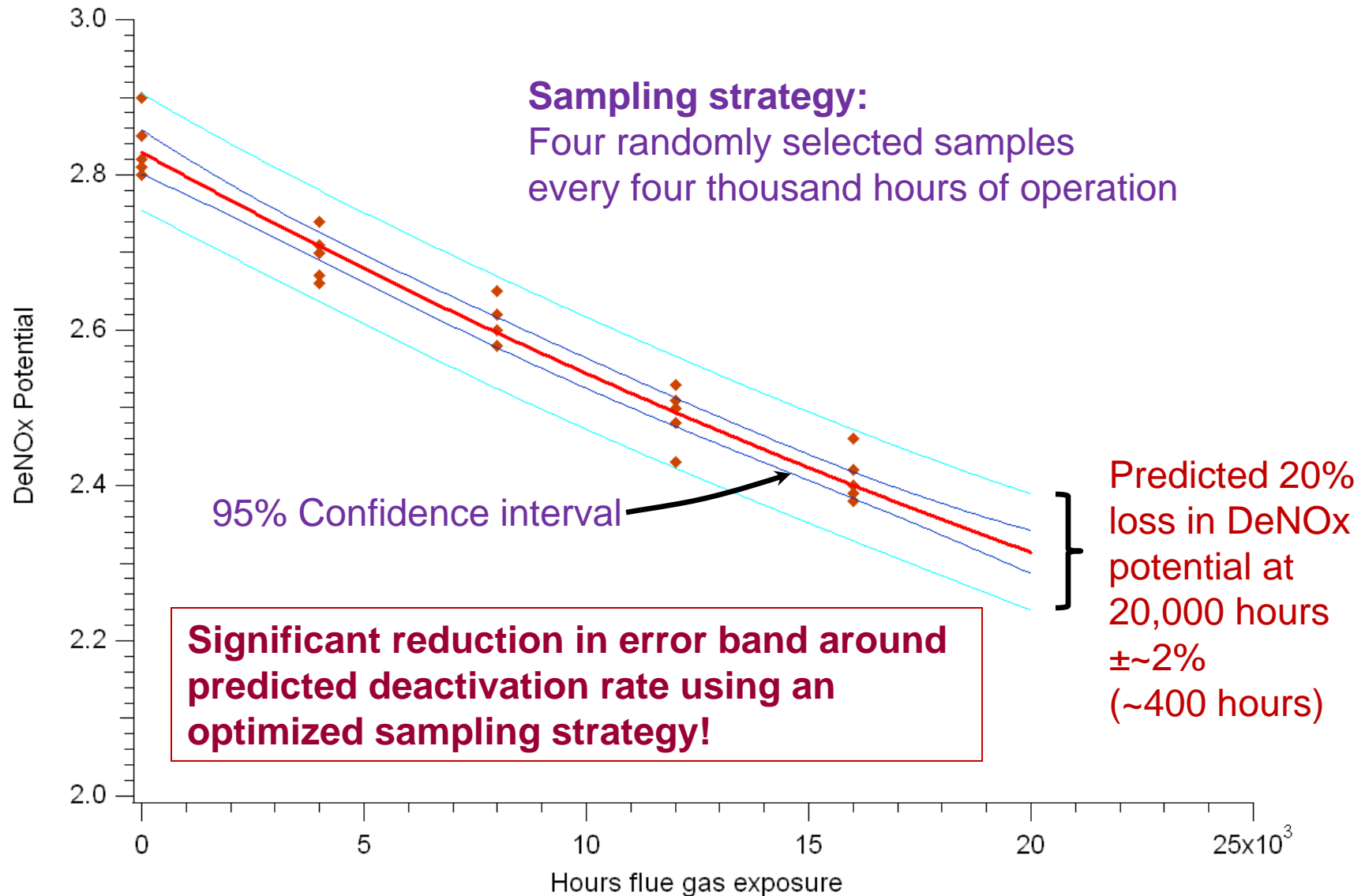
- Or simply the –log of the outlet NOx concentration...
- Mean sample DeNOx potential data over time is fit to exponential decay model in the form...

$$Potential = y_0 + A \bullet e^{-\frac{(time - time_0)}{\tau}}$$

Sample Size Error Band Example



Optimal Sampling Size Error Bands



SCR Reaction Model Overview

➤ SCR reaction rate models – why does it matter?

- SCR catalyst test reactors provide steady state sample inlet and outlet NO_x, NH₃, SO₂ and SO₃ concentrations under constant conditions
- True predictive power of data derived from how they are processed
- Reaction rate models provide guidance on data processing methods – ultimate interpretation

➤ Chemical reaction kinetics

- Study of how fast a mixture of chemical species approaches equilibrium
 - NO_x, NH₃, H₂O, N₂, SO₂ and SO₃ are not at equilibrium when they enter reactor
 - Equilibrium concentration approached as function of residence time in reactor (bed length) and intrinsic catalyst activity (turnover rate)

➤ Three kinetic rate models used to describe SCR

- Gas phase homogeneous kinetics
 - Based on collision theory
- *Eley-Rideal mechanism (gas / surface)*
 - One molecule reacts with surface – second reacts with first directly from gas phase
- Langmuir-Hinshelwood Mechanism (gas / surface)
 - Both molecules adsorb to surface then undergo bi-molecular reaction

Reaction Rate Models

- **Published DeNOx kinetic models:** **15**
 - 1st order NOx / 0 order in NH₃ 2
 - Eley-Rideal 10
 - Other 3

- **Common assumptions for all models**
 - Isothermal conditions
 - Laminar flow in channels
 - Isobaric (no axial pressure drop)
 - Single channel approach: what happens in one channel adequate to model entire monolith

- **Simplest model for industrial application – Eley-Rideal**

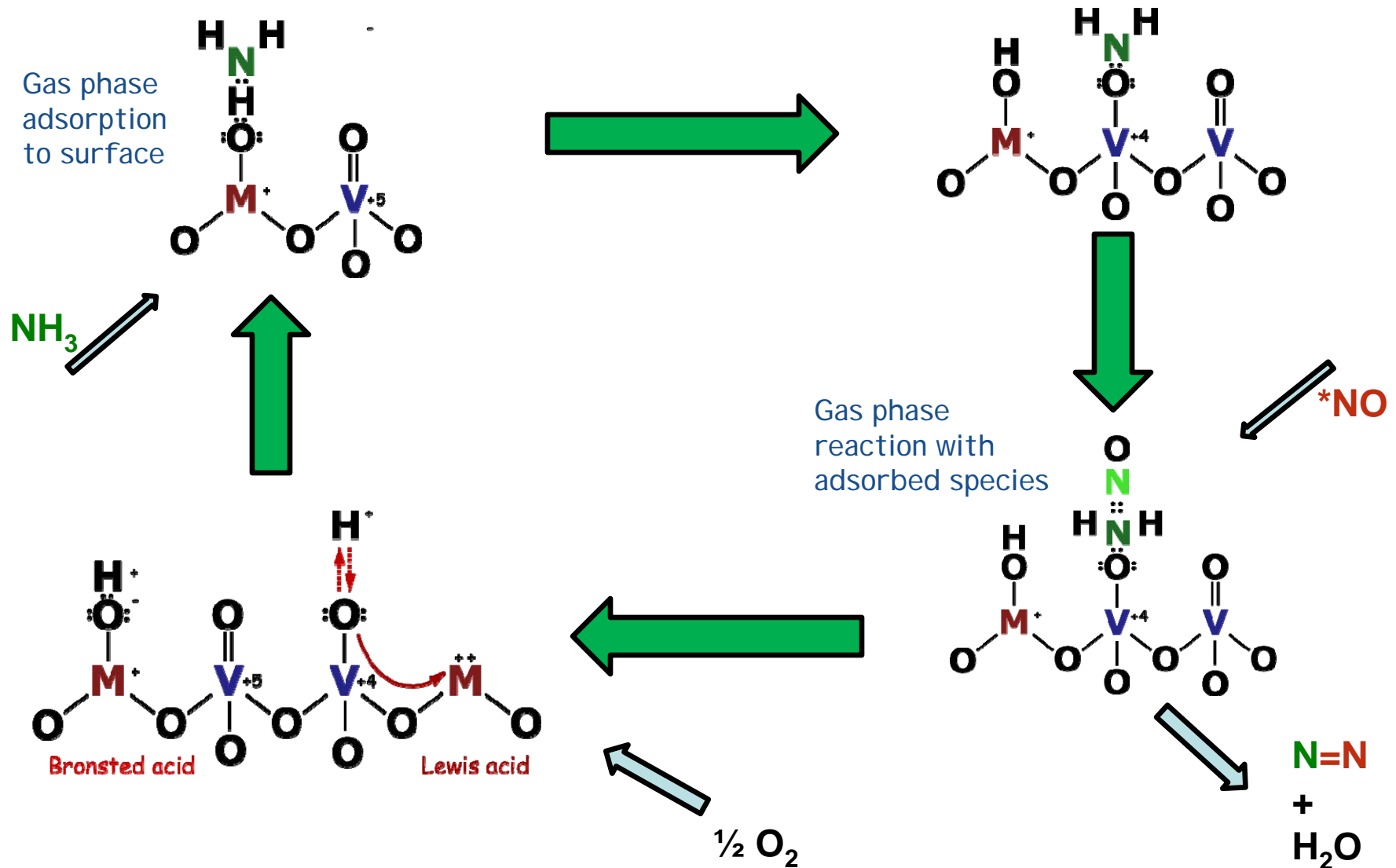
$$r_{NO} = k_c C_{NO} \theta_{NH_3}$$

K_c = rate constant; C_{NO} = gas phase NO concentration; θ_{NH_3} = ammonia coverage

Kinetic Model Practical Implications

- All homogeneous gas phase models teach NOx reduction is ~1st order in NO and ~0 order in NH₃
 - Reaction rate directly dependent on NOx concentration – *independent of NH₃ concentration*
 - *Reaction extent is dependent on NH₃ concentration*
- For gas / surface models (Eley-Rideal) reaction order less defined
 - 1st order in NOx / dependent on *extent of surface coverage* θ of NH₃
 - Reaction rate 0 order in NH₃ -- *NH₃ concentration independent at NH₃:NO ≥ 1*
 - DeNOx rates measured at $\alpha \geq 1$ “still hold” at typical commercial $\alpha < 1$!
- Water and ammonia “compete” for coverage on surface sites
 - $\theta_{\text{NH}_3} \gg \theta_{\text{H}_2\text{O}}$ *but having correct [H₂O] in test flue gas critical!*
- DeNOx reaction rate independent of O₂ at concentration $> \sim 2\%$

Eley-Rideal Gas / Surface Reaction Mechanism



Hybrid Test Reactor

- **Simultaneous testing on up to six samples**
- **Combustion generated flue gas**
- **Operated at exact plant conditions**
- **Sample size**
 - Typical ~30mm x 30mm at the face by 300mm long
 - Maximum - 50mm x 50mm at the face by 500mm long
- **State of the art FTIR analyzers for NO_x, NH₃, H₂O and SO₂**
- **SO₃ by controlled condensation**



Catalyst Testing Options

Parameter	Full Bench Reactor	Typical Micro-reactor	Hybrid Test Reactor
Sample Size Cross Section	150mm X 150mm	~ 30mm X 30mm	~ Up to 50mm X 50mm
Sample Length	Full Layer / cassette	~ 300 mm or less	Up to 500mm
Flue Gas Generation	Combustion System	Bottled compressed gas	Combustion system
Gas flow: in Channel Linear Velocity	Same as plant reactor	Less than plant reactor	Same as plant reactor
Tested at Actual Plant Operating Conditions?	Varies by vendor	Normally no	Yes
Sample Capacity per Day	Normally 1 per day	Varies by vendor	12 per day
Information Generated	Integrated $K\alpha$ (m/hr) of entire element or cassette length	$K\alpha$ (m/hr)	First order rate constant and $K\alpha$ (m/hr)

Full Bench Vs Micro/Hybrid

- **Full bench (element or cassette - half layer) sample**
 - Best integrated measure of NO_x reduction from catalyst inlet to outlet
 - Averages out axial / radial variations in element DeNO_x activity and/or SO₂ conversion rates
 - More difficult to generate catalyst kinetic rate model
 - **Independent testing recommended for guarantee verification**

- **Micro/ Hybrid reactor sample**
 - All active sites work at maximum turnover frequency – gas phase NO_x concentration equivalent for all sites axially
 - Requires more samples to average out axial / radial variations in DeNO_x activity or SO₂ conversion
 - More sensitive to variation in sample geometry or gas flow
 - **Recommended for production QA/QC**

Hybrid Test Reactor Example

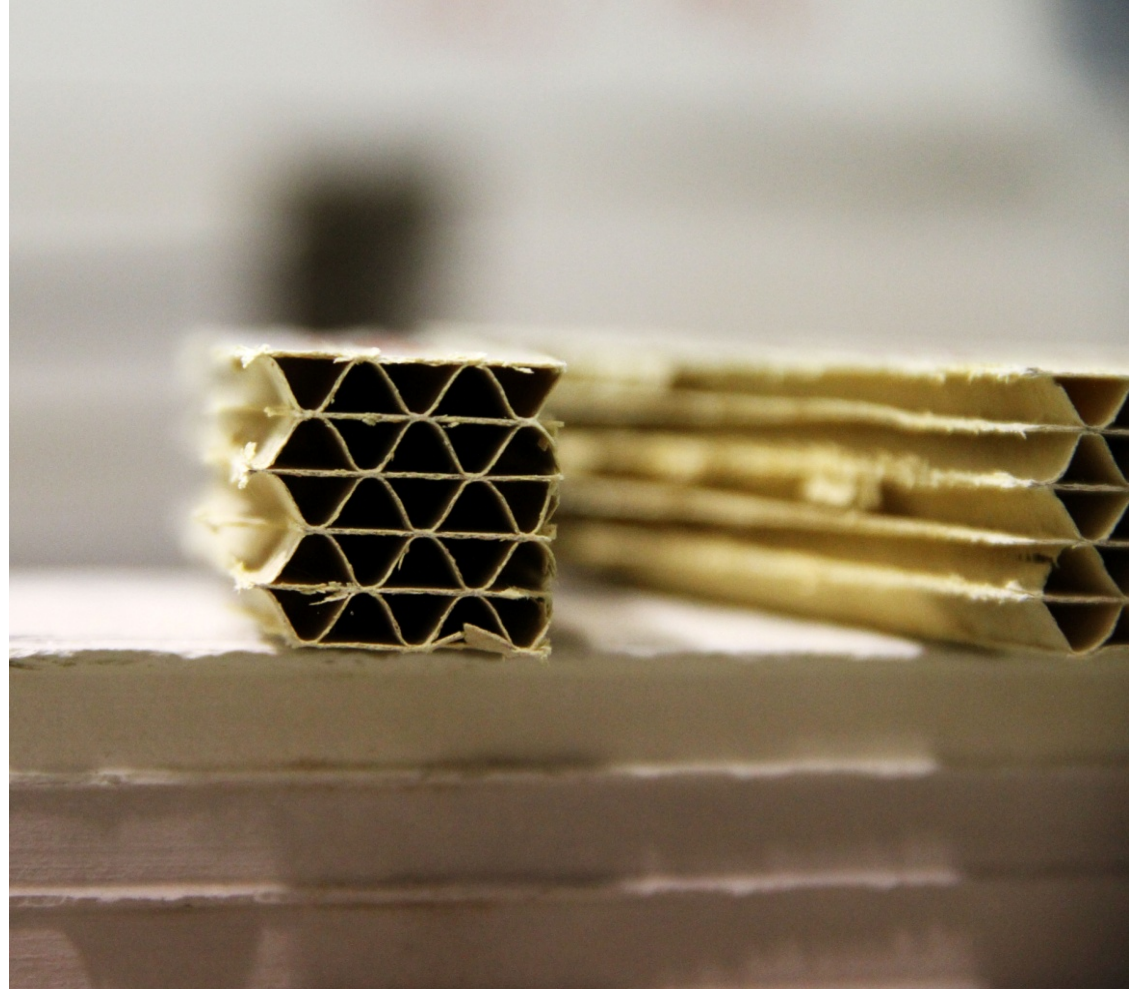
- ❑ Tested SCR catalyst samples for DeNO_x activity

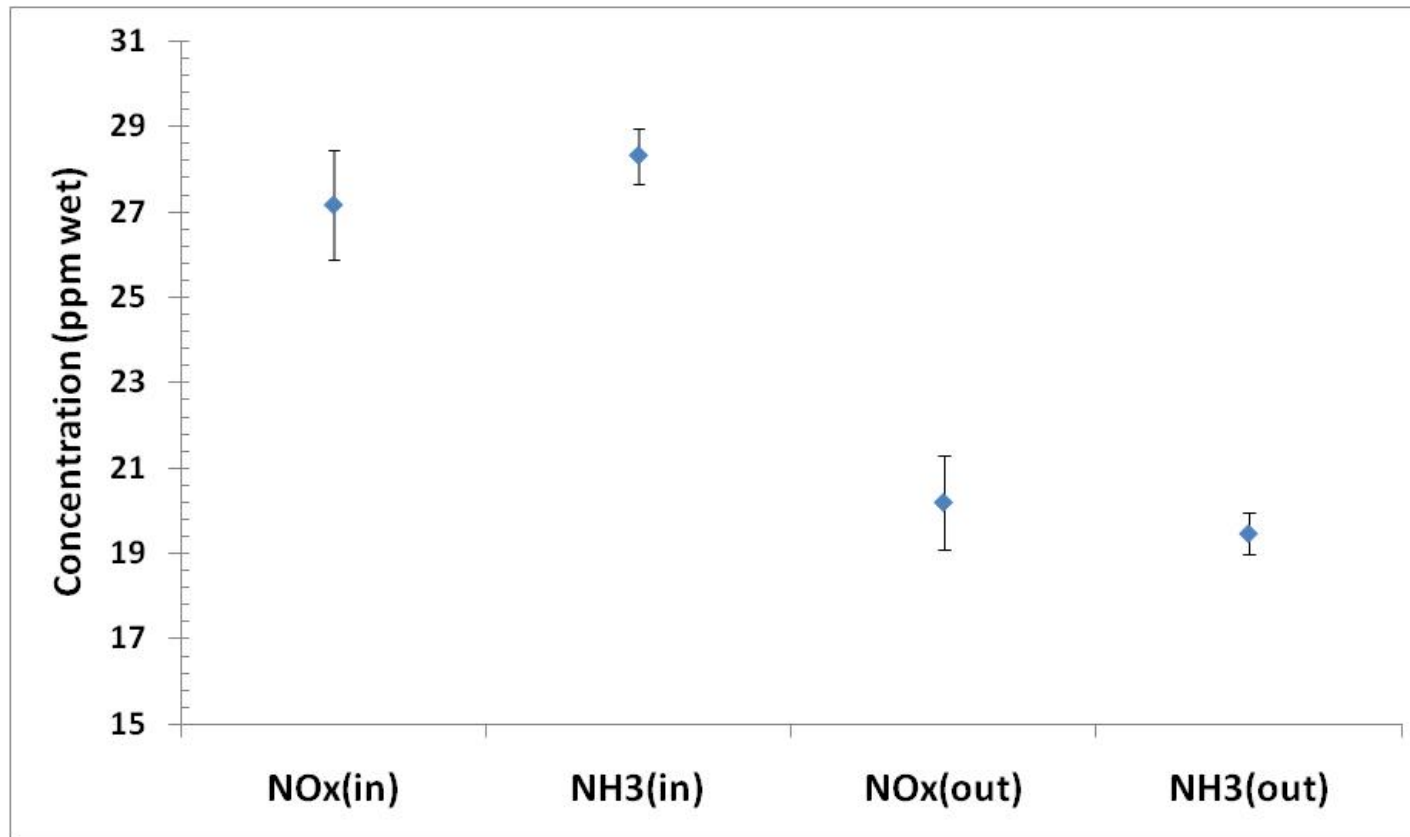
- ❖ Five from unit A and five from unit B

- ❑ Flue gas compositions, reaction temperatures, gas flows (in channel linear velocities) identical to plant conditions

- ❑ Measure NO_x and NH₃ concentrations at catalyst inlet and outlet

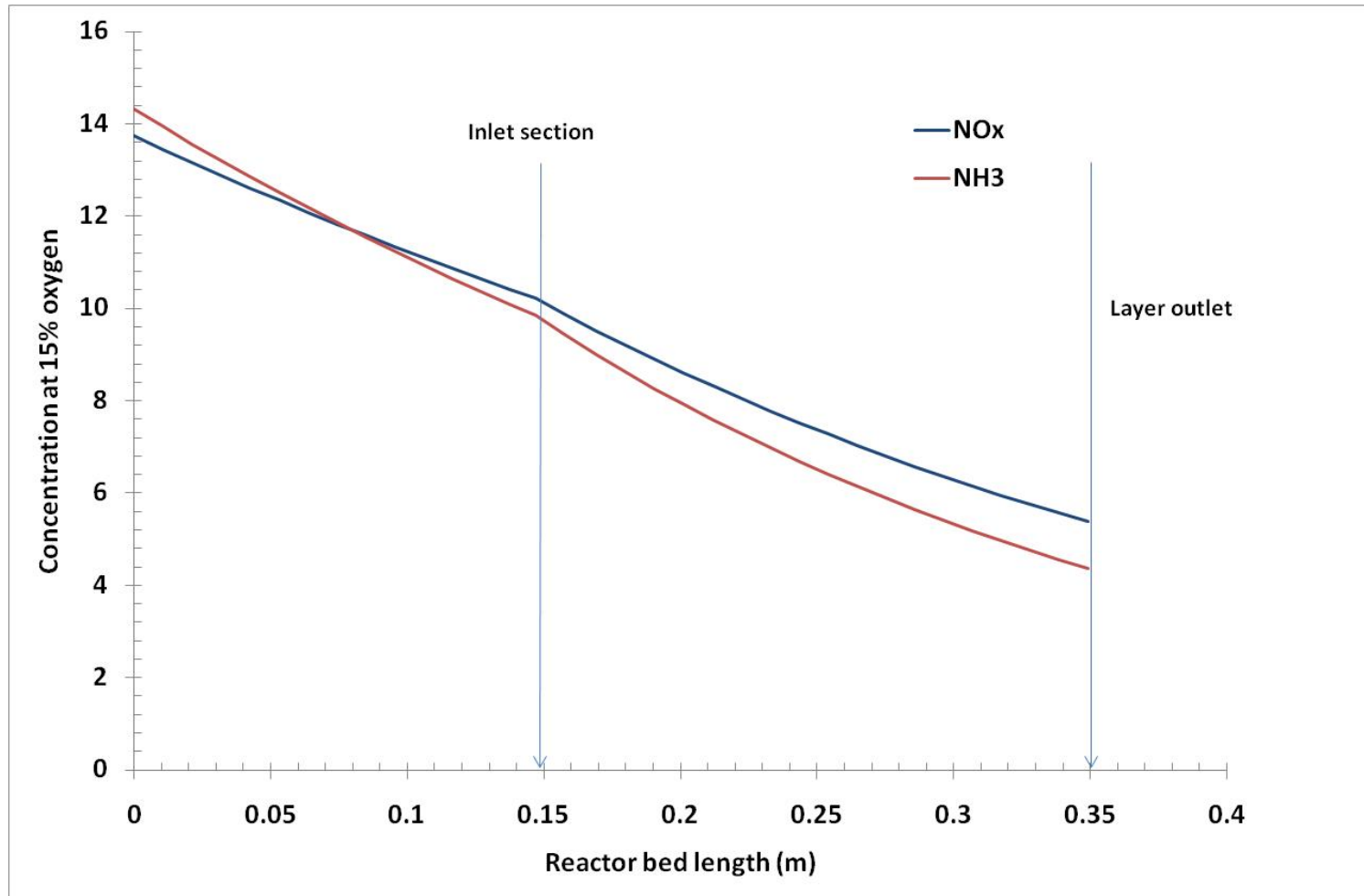
- ❖ Three 20 min sample periods separated by 1 hour each insures “steady state”



Data Workup: 1st Order Rate Constant

Inlet / outlet NOx and NH₃ used to calculate 1st order rate constant: $k \text{ sec}^{-1}$

$$NOx_{outlet} = NOx_{inlet} \times e^{-k \cdot time}$$



Reaction rate constants allow determination of NOx and NH₃ concentrations at any point (axially) in SCR reactor

Test Results Summary

Sample	k (sec-1)	K (m/hr)
UA 1	18.1	46.2
UA 2	21.3	53.1
UA 3	21.7	50.2
UA 4	21.0	48.7
UA 5	21.8	50.6
Mean:	20.8	49.8
Stdev:	1.6	2.5
95% conf:	1.1	1.9

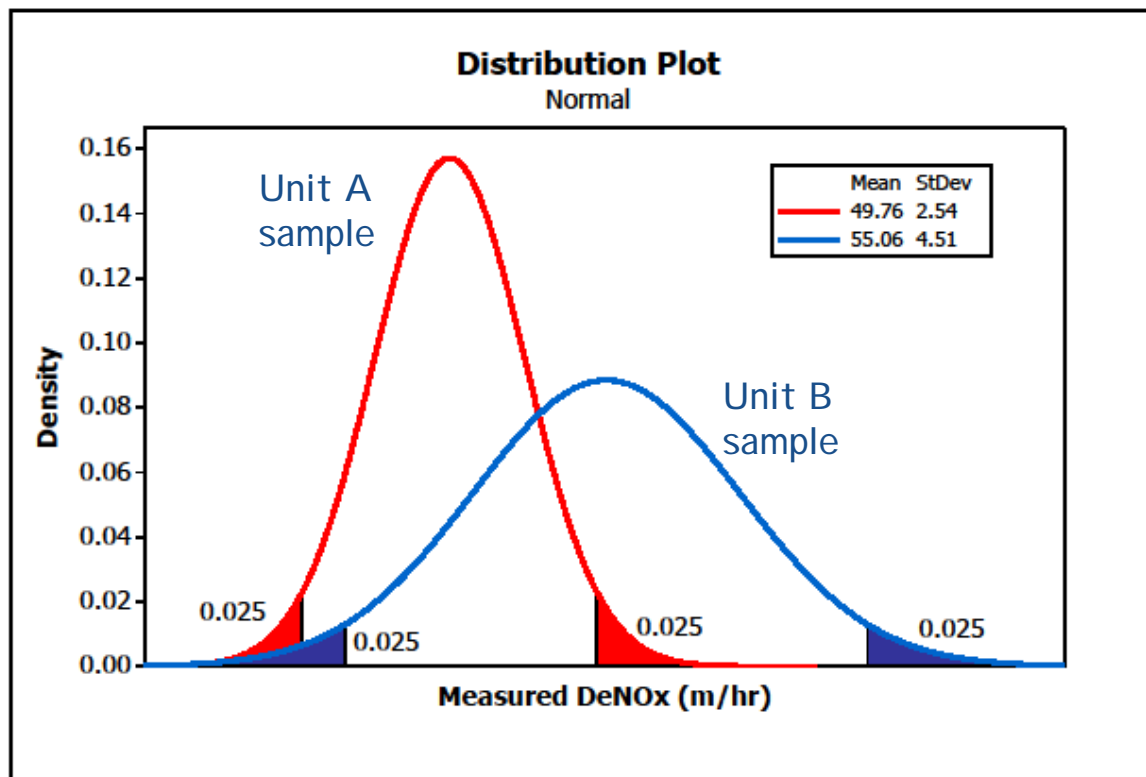
Sample	k (sec-1)	K (m/hr)
UB 1	22.3	55.5
UB 2	27.1	62.7
UB 3	22.9	53.1
UB 4	20.6	51.8
UB 5	22.5	52.2
Mean:	23.1	55.1
Stdev:	2.4	4.5
95% conf:	1.8	3.3

Sample standard deviations with error band allow inference about differences in populations that are otherwise impossible

Error bands around single measurements are infinite!

Difference Between Sample Sets

Unit A and unit B samples fully described and modeled by mean and sample standard deviation



Pared T test results:

Probability that unit A and unit B samples come from same population: 3.7%

Summary

- **Intelligent SCR sampling and testing strategy improves the value of predictive models**
- **All inferences (“estimates”) derived from sample data have a measurable probability of being wrong**
- **Rational methods for determining ideal number of samples and interval between samples exist**
 - Too few samples gives weak model – too many increases cost only
- **Value of catalyst testing data depends on DeNOx reaction kinetic assumptions**
 - Rate directly dependent on NOx concentration but not NH₃ ($\alpha \geq 1$) or O₂ (> 2% by volume)
- **SCR catalyst testing options: full bench; micro-reactor; hybrid reactor all play a role**