CATALYST TESTING

Overview, Methodology, Reporting, and Full-Scale Application

Sean A. Bogseth, P.E.
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’
LABORATORY TESTS

- SCR Activity ‘K’
  \[ K = -A_v \ln(1 - dNO_x) \]

- NO\textsubscript{x} Reduction @ NH\textsubscript{3} Slip
  \[ RP = K / A_v = -\ln(1 - dNO_x) \]

- CO Oxidation

- SO\textsubscript{2} Oxidation

- VOC Oxidation

- Chemical Analysis
  - Usually surface & bulk x-ray flourescence (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\textsubscript{X} reduction, NH\textsubscript{3} slip, CO oxidation, and SO\textsubscript{2} oxidation
  - Coal and gas-turbine catalyst

- **Semi-Bench**
  - Less than 6” by 6”, up to 1 m long catalyst
  - NO\textsubscript{X} reduction, NH\textsubscript{3} slip, CO oxidation, and SO\textsubscript{2} oxidation
  - Coal and gas-turbine catalyst

- **Micro-Scale**
  - Nominally 1.25” diameter, 6” long core catalyst sample
  - NO\textsubscript{X} reduction, CO oxidation
  - SO\textsubscript{2} oxidation, NH\textsubscript{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
**METHODOLOGIES**

- **VGB Guidelines (VGB-R 302 He)**
  - Early testing document, 1\textsuperscript{st} edition produced in 1988, 2\textsuperscript{nd} 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
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
• 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\textsubscript{x} reduction at NH\textsubscript{3} slip limit
MEASUREMENT UNCERTAINTY

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

- Calculation Uncertainty
  - The activity measurement itself is prone to uncertainties
  - Example below assuming $K = 85 \text{ m/hr}$, $\text{NO}_x\text{-in}=100 \text{ ppm}$, $\text{Av}=20\text{--}45 \text{ m/hr}$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow</td>
<td>Q</td>
</tr>
<tr>
<td>Sample X-Section Dimension</td>
<td>d</td>
</tr>
<tr>
<td>Sample Length</td>
<td>L</td>
</tr>
<tr>
<td>Specific Surface Area</td>
<td>Asp</td>
</tr>
<tr>
<td>Inlet $\text{NO}_x$</td>
<td>$\text{NO}_x\text{in}$</td>
</tr>
<tr>
<td>Outlet $\text{NO}_x$</td>
<td>$\text{NO}_x\text{out}$</td>
</tr>
<tr>
<td>Uncertainty</td>
<td>$K$</td>
</tr>
</tbody>
</table>

- $2\%$  
- $1 \text{ mm}$  
- $1 \text{ mm}$  
- $0 \text{ m}^2/\text{m}^3 \ (a)$  
- $0.5 \text{ ppm}$  
- $0.1 \text{ ppm}$  
- $2.3 \text{ m/hr}$  
- $2.7\%$
TECHNICAL CONSIDERATIONS

- Inlet NO\textsubscript{x}
  - Low inlet NOX effects SCR activity

\[ y = 0.1077 \ln(x) + 0.5288 \]
\[ R^2 = 0.9895 \]
**TECHNICAL CONSIDERATIONS**

- **NO₂/NOₓ**
  - Ratio not only effects NOₓ reduction, but also stoichiometry of reaction equations
  - What NH₃/NOₓ?
  - Held ≤ 5% during testing

---

\[
\text{NO} + \text{NH}_3 + \frac{1}{4} \text{O}_2 \rightarrow \text{N}_2 + \frac{3}{2} \text{H}_2\text{O}
\]

\[
6\text{NO}_2 + 8\text{NH}_3 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O}
\]

\[
\text{NO}_2 + 2\text{NH}_3 + \frac{1}{2} \text{O}_2 \rightarrow \frac{3}{2} \text{N}_2 + 3\text{H}_2\text{O}
\]

\[
\text{NO} + \text{NO}_2 + 2\text{NH}_3 \rightarrow 2\text{N}_2 + 2\text{H}_2\text{O}
\]
TECHNICAL CONSIDERATIONS

- \( \text{NH}_3/\text{NO}_x \)
  - 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\textsubscript{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\textsubscript{X} may lead to minute outlet NO\textsubscript{X} measurements, even as the catalyst begins to age!
  - For GT catalysts with ≥ 95% NO\textsubscript{X} reduction, test at A\textsubscript{V} = 35 Nm/hr

![Graph showing Reactor Potential vs. Outlet NO\textsubscript{X} ppm @3% O\textsubscript{2} dry. The graph illustrates a trend where the Reactor Potential (RP\textsubscript{min}) is approximately 2.3 (RMS<10%).]
TECHNICAL CONSIDERATIONS

- Moisture Level
  - Difference between lab and field H$_2$O concentration can make a large difference in activity and full-scale projections

![Graph showing the relationship between H$_2$O concentration and K/K@10% H$_2$O.](image)
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
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 temperature range
TECHNICAL CONSIDERATIONS

- **VOC Oxidation Tests**
  - Oxidation varies with temperature for usual species of interest
Testing methodology is dependent on:

1. **Catalyst Source**
   - Coal / Natural-Gas

2. **Catalyst type**
   - SCR / CO

3. **Size**
   - Core / Cube / Button
RESULTS & REPORTING

- **NO\textsubscript{x} Reduction**
  - Activity, ‘K’, or NO\textsubscript{x} reduction at NH\textsubscript{3} slip
  - Can be used for full-scale projections (reactor potential, RP)
  - Catalyst life estimates if starting activity/\Delta NO\textsubscript{x} and end-of-life conditions are known
  - Track deactivation over time with regular testing (often yearly or bi-yearly)

- **CO, SO\textsubscript{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
- NH3 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?

Minimum Total RP = \( f(\text{NO}_{x}, \Delta \text{NO}_{x}, \text{NH}_3\text{ Slip}) \)

Starting total RP (all three layers) after one layer replaced

When do I get from here to here?

Operating Hours
“End of Life” Prediction After 1 Year

![Graph showing the relationship between operating hours and reactor potential, indicating the minimum total RP at 1st annual sample.]
Catalyst Samples After 1 & 2 Years

Operating Hours

Reactor Potential

Minimum Total RP

2 annual samples
FULL-SCALE APPLICATION

- Layer-by-Layer Deactivation Tracking

![Graph showing deactivation tracking over operating hours]

- $K/K_0$ vs. Operating Hours for Layer 1 (Top), Layer 2 (Mid), and Layer 3 (Bottom)
FULL-SCALE APPLICATION

- Life Projections

Monitoring NH₃ slip also critical!
FULL-SCALE APPLICATION

- NH₃ 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

![Diagram of reactor and in-situ test setup](image-url)
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\textsubscript{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.
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
Volume of Data: Laboratory vs. In Situ

**Annual Laboratory Analysis**

![Graph showing Laboratory Relative Activity (K/Ko) vs. Operating Hours for Layer 2 and Layer 3.](image)

**On-Demand CatalysTrak™ Measurements**

![Graph showing Relative Reactor Potential (RP/RPo) vs. Operating Hours for Layer 2 and Layer 3.](image)
IN-SITU MEASUREMENT

Graph showing Reactor Potential vs. Operating Hours for different layers:
- All Layers
- Layer 1
- Layer 2
- Layer 3

Key features:
- Minimum Total RP
- Sum of Individual Layer RP Results

Operating Hours range from 0 to 24,000.
Reactors Potential range from 0 to 8.0.

Graph indicates trends and test results for layers over operating hours.
CATREACT™

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

**Unit Data**

<table>
<thead>
<tr>
<th>Unit Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size (MW)</td>
<td>400</td>
</tr>
<tr>
<td>Heat Rate (HHV), Btu/kW-hr</td>
<td>9,500</td>
</tr>
<tr>
<td>Flue Gas Flowrate, lb/hr</td>
<td>5,386,614</td>
</tr>
</tbody>
</table>

**Allowable Range**

<table>
<thead>
<tr>
<th>Coal Type</th>
<th>Low</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>HS Bit</td>
<td>0</td>
<td>1,300</td>
</tr>
<tr>
<td>LS Bit</td>
<td>0</td>
<td>14,000</td>
</tr>
<tr>
<td>PRB</td>
<td>0</td>
<td>456,000</td>
</tr>
<tr>
<td>Sub Bit</td>
<td>0</td>
<td>16,000</td>
</tr>
<tr>
<td>Lignite</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coal Sulfur (wt%)</th>
<th>Low</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coal Arsenic (wt ppm)</th>
<th>Low</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Boiler Produced SO3 (ppm)</th>
<th>Low</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fan Efficiency (%)</th>
<th>Low</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>85</td>
<td>50</td>
<td>100</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Motor Efficiency (%)</th>
<th>Low</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>95</td>
<td>50</td>
<td>100</td>
</tr>
</tbody>
</table>

**Flue Gas Flowrate Converter**

<table>
<thead>
<tr>
<th>Volumetric Flowrate (scfm)</th>
<th>Mass Flowrate (lb/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>964916</td>
<td>450000</td>
</tr>
</tbody>
</table>

scfm: MW=29.5 lb/ft³-mole, T=70°F, P=14.7 psia

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.)
Thank You!

Questions? Comments?

Sean A. Bogseth, P.E.
Fossil Energy Research Corp.
sbogseth@ferco.com
(949) 859-4466
www.ferco.com