

# Reinhold Environmental Ltd.

---



2008 NOx-Combustion Round  
Table & Expo Presentation

---

*February 4-5, 2008 in Richmond, VA*

Reinhold 2008 NOx Conference  
February 4 - 5, 2008  
Richmond, VA

Cindy Khalaf - Argillon  
Marilynn Martin - Evonik

ARGILLON



EVONIK  
INDUSTRIES

SCR Catalyst Testing – Comparison of Micro and Bench Scale  
Testing Methods

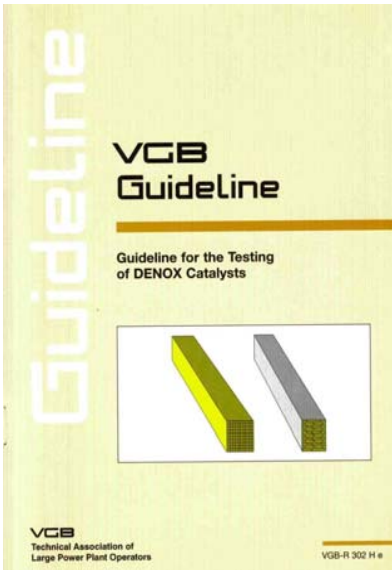
# Topics

1. Purpose of Catalyst Testing
2. Properties and Test Equipment
3. NO<sub>x</sub> Activity –  $k(\text{NO}_x)$
4. SO<sub>x</sub> Activity –  $k(\text{SO}_x)$
5. Micro vs. Bench Scale
6. Unresolved Issues
7. Summary

# Why Test? Benefits for the Owner

- Optimize SCR operation and catalyst utilization
- Increase SCR performance (NOx credits)
- Minimize operating costs (ash sale impacts, APH cleaning)
- Improve reliability
- Develop system-specific catalyst management plans to predict future catalyst needs, system maintenance and AIG tuning
- Link catalyst inventory management, catalyst manufacturing, regenerating and outage schedules
- Determine initial activity verification, current activity, deactivation rate and future budgeting strategy

## Testing Guideline Development



- Initial testing guidelines developed in 1987 by
  - Catalyst manufacturers (KWH, Siemens)
  - Power producers (STEAG, VKR)
  - SCR OEMs (AEE, Steinmüller)
  - Testing institutes (KEMA, TÜV)
  - Insurance companies (Germanischer Lloyd)
  - Technical Associations (VGB, FDBR)
- Testing methods based on industry
  - Standards, guidelines
  - Statutory requirements
  - Referenced to international literature
- Second revision published in 1998 including the English version VGB-R302He

# “VGB Certification” Round-Robin

- “Round-Robin Catalyst Experiments and Test Guidelines” were developed for certification of the bench scale reactors of all participating labs against a known standard
- VGB Round-Robin Testing done every 3 to 5 years
- Participation is voluntary – can take up to nine months to complete depending on number of participants
- Rigorous number of repetitive tests of the same sample by each participating lab
- Latest tests completed in summer 2005, 6 European participants, STEAG and E.ON are the only independent third party labs that passed and are currently “VGB certified”

# Catalyst Deactivation Factors

... determine the properties to be tested.

- Poisoning
- Deposition (masking by fly ash and ammonium sulfate or other compounds)
- Aging (change of the catalyst pores)

# Properties Tested

- Chemical composition of the catalytic material
- Change in catalytic properties (NO<sub>x</sub> and SO<sub>x</sub> activity)
- Change in external structure
- Change in inner surface and pore structure
- Change in mechanical strength properties
- Composition of accumulated deposits

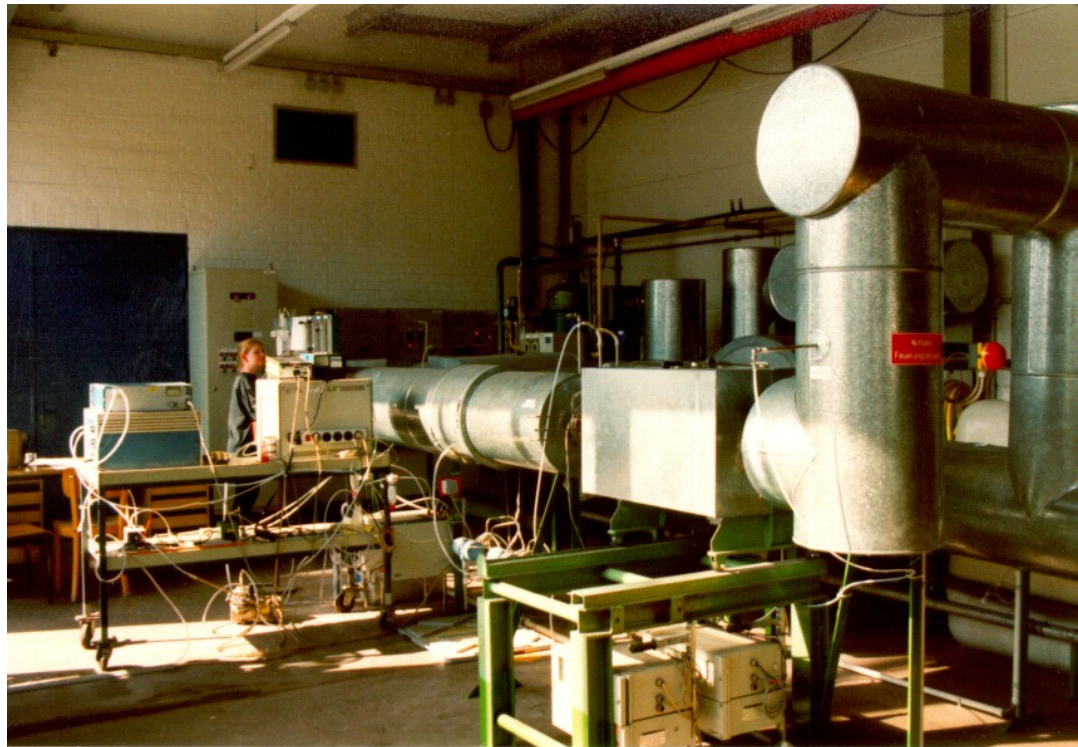
# Common Tests and Equipment used for testing

K value testing, SO<sub>2</sub> and Pressure drop testing - Performed by Micro scale reactor.



# Common Tests and Equipment used for testing

K value testing, SO<sub>2</sub> and Pressure drop testing - Performed by Bench Scale reactor

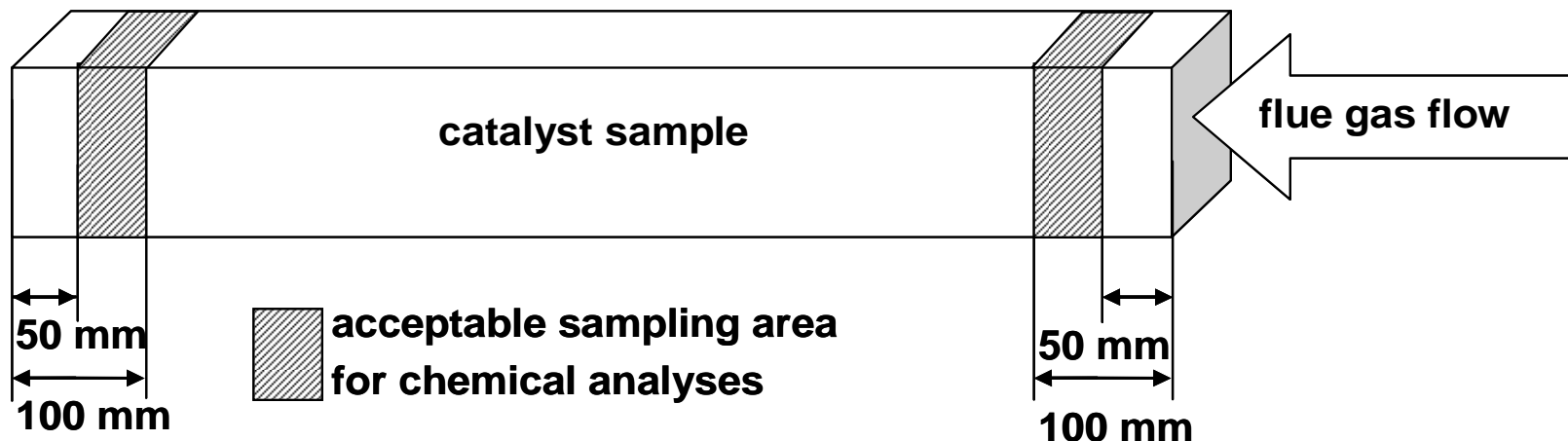


# Chemical Analysis

- Catalyst surface and bulk material chemistry are different because of a:
  - Quicker uptake of catalyst poisons on the surface
  - Slower changes in chemical composition of the catalyst bulk material
- Flue gas inlet and outlet side of a catalyst sample are different because of:
  - Highly turbulent flow conditions within the first 4 – 6 inches mass transfer by turbulence
  - Mostly laminar flow conditions downstream of 6 inches – mass transfer by diffusion
- Chemical analysis from inlet and outlet side as well as bulk material and catalyst surface needed

# Chemical Analysis

$\text{Al}_2\text{O}_3$   
 $\text{As}$   
 $\text{CaO}$   
 $\text{Fe}_2\text{O}_3$   
 $\text{K}_2\text{O}$   
 $\text{MgO}$   
 $\text{MoO}_3$   
 $\text{Na}_2\text{O}$   
 $\text{P}_2\text{O}_5$   
 $\text{SO}_3$   
 $\text{SiO}_2$   
 $\text{TiO}_2$   
 $\text{V}_2\text{O}_5$   
 $\text{WO}_3$



chemical analysis requirements for new and used catalyst				
flue gas		new, cleaned, rejuvenated and/or regenerated catalyst samples	used, deactivated catalyst samples	acceptable chemical analysis method
bulk material	inlet		x	AAS, EDX, XRF
	outlet	x	x	
catalyst surface	inlet		x	EDX, XRF
	outlet	x	x	

AAS – atomic absorption spectroscopy  
 EDX – energy dispersive X-ray  
 XRF – X-ray fluorescence

# Sample Information Needed

The following information should be provided to the test lab with the sample:

- Reactor level designation (1<sup>st</sup> layer, 2<sup>nd</sup> layer, etc.)
- Date and hours of exposure to flue gas
- Location from which sample was taken
- Flue gas flow direction
- Any changes to operation since last sample that could impact catalyst (fuel changes, additives)

# Sample Information Needed

- Volumetric flow rate
- Wall thickness
- Pitch
- Length of sample
- Volume of catalyst per module
- Boxes, logs per module

# NOx Activity – k(NOx)

k(NOx) is influenced by a number of factors:

- catalyst formulation
- geometry;
  - pitch, opening configuration, length, sample preparation
- operating conditions;
  - temperature, flowrate, NOx inlet concentration, ammonia concentration
- test set-up;
  - bench scale, semi-bench scale, micro-scale;
  - accuracy and repeatability of test instrumentation

# NOx Activity Defined

$$k(\text{NO}_x) = -A_v \ln(1-\eta) \quad m/hr$$

(For  $\text{NH}_3/\text{NO}_x = 1$ )

- **Area Velocity**

$$A_v = \frac{\text{flow rate}_{\text{FG}} (Nm^3/hr)}{\text{surface area}_{\text{CAT}} (m^2)} \quad m/hr$$

- **DeNOx Efficiency**

$$\eta = \frac{\text{Inlet NOx} - \text{Outlet NOx}}{\text{Inlet NOx}}$$

# NOx Activity Examples – Typical Bench Scale Test

$$k(\text{NO}_x) = -A_v \ln (1 - \eta) \quad m/hr$$

$$= - \frac{170}{8} * \ln (1 - 0.8) = 34 \text{ m/hr} \quad (\text{base})$$

$$= - \frac{170}{8} * \ln (1 - 0.64) = 22 \text{ m/hr} \quad (\eta -20\%)$$

$$= - \frac{204}{8} * \ln (1 - 0.8) = 41 \text{ m/hr} \quad (\text{Q}+20\%)$$

$$= - \frac{170}{9.6} * \ln (1 - 0.8) = 28.5 \text{ m/hr} \quad (\text{A}+20\%)$$

# SO<sub>x</sub> Activity – k(SO<sub>x</sub>)

k(SO<sub>x</sub>) is influenced by a number of factors:

- formulation
- geometry;
  - pitch, opening configuration, length
- operating conditions;
  - temperature, flowrate, SO<sub>2</sub> inlet concentration, oxygen concentration
- test set-up;
  - bench scale, semi-bench scale, micro-scale;
  - accuracy and repeatability of instrumentation

# SOx Activity Defined

$$k(\text{SO}_x) = -SV' \ln (1-\eta_{\text{so}_x}) \quad m/hr$$

- **Space Velocity**

$$SV' = \frac{SV}{1 - \varepsilon} \quad 1/hr$$

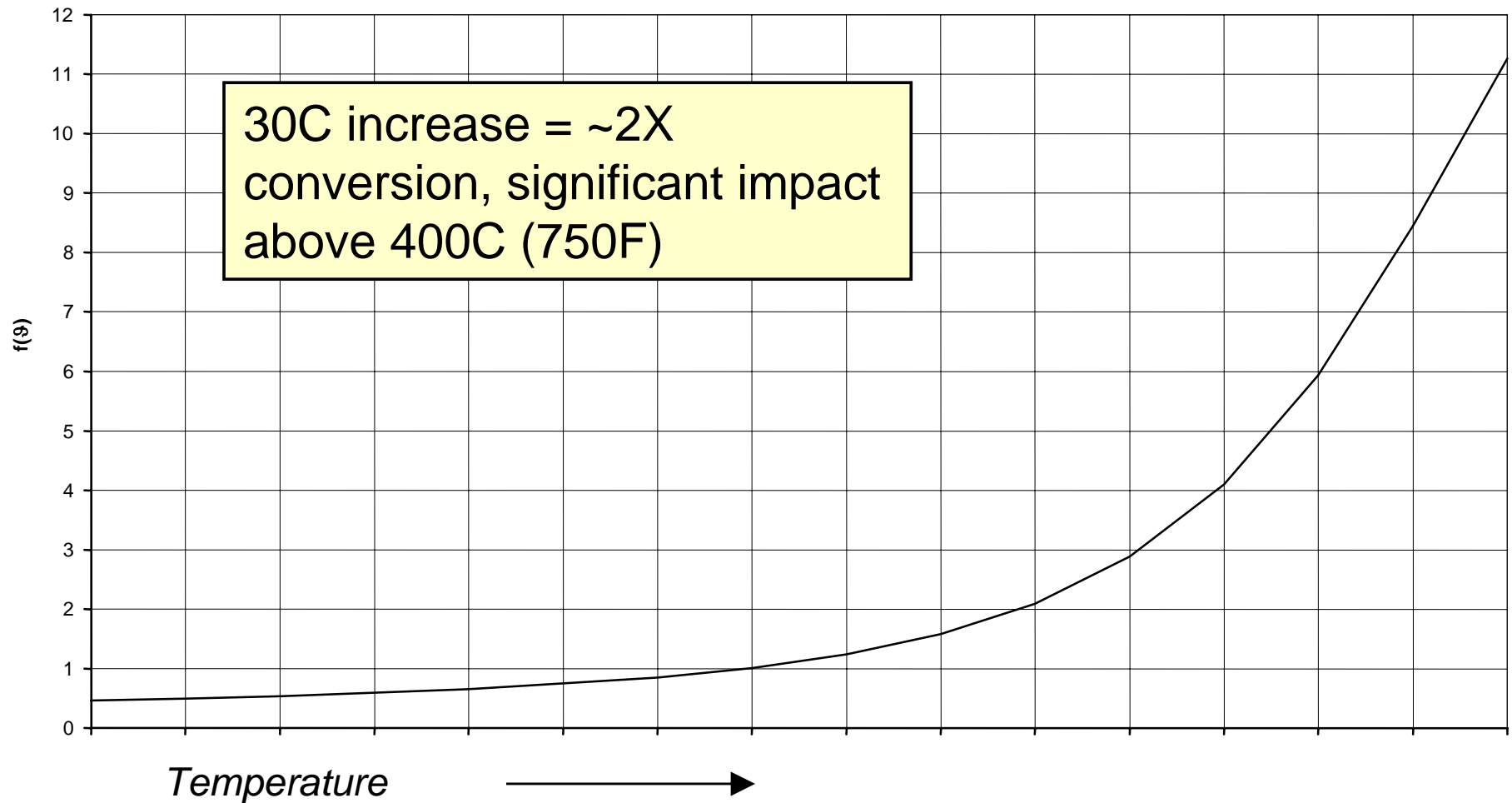
$$SV = \frac{\text{flow rate}_{\text{FG}} (Nm^3/hr)}{\text{volume}_{\text{CAT}} (m^3)} \quad 1/hr$$

- **SOx Efficiency**

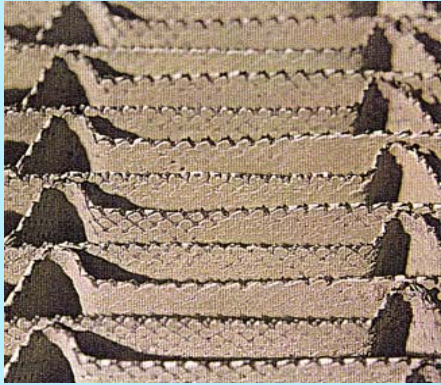
$$\eta = \frac{\text{Inlet SOx} - \text{Outlet SOx}}{\text{Inlet SOx}}$$

# Temperature has a non-linear impact on SO2 conversion

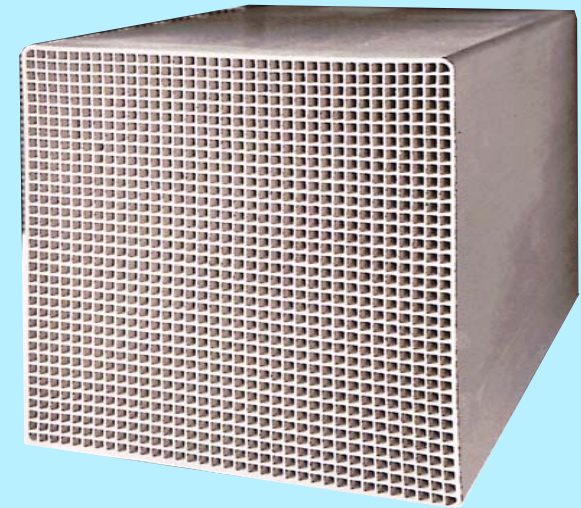
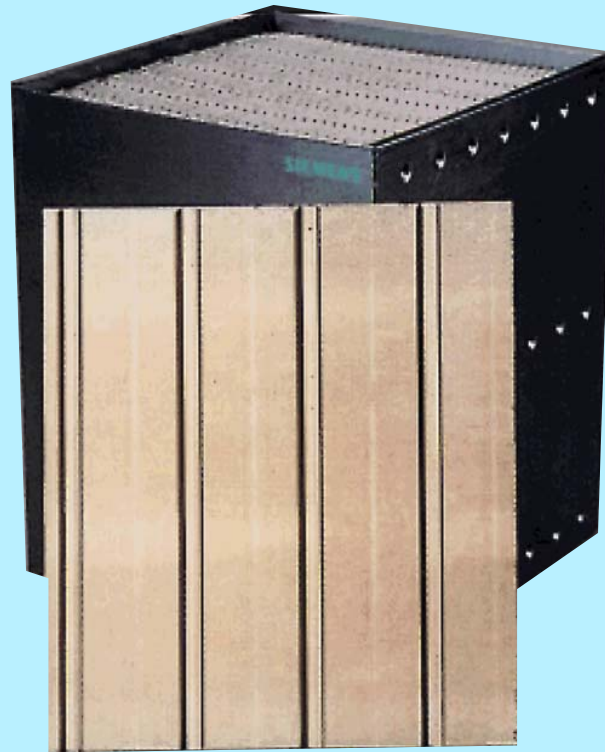
## Temperature- Correction for $k_{SOx}$



# Testing geometry is important



Plate



Extruded  
Honeycomb

The catalysts used for Power Plant SCR<sub>s</sub> are parallel-flow type.

# Test Reactor Sizes Defined

## Benchscale

- Full 6"X6"X (length) honeycomb block or plate catalyst cut to these dimensions. Plates stacked in test holder, usually without spacers. Plate notches used to preserve spacing.

## Semi-benchscale

- Honeycomb or plates cut to 3" X 3" X (length) sample. Plates usually flat, without notches, spacers used.

## Microscale

- Honeycomb or plates cut to 1" X 1" X (length) sample. Plates do not have notches. Spacers or slots separate plates.

# Test Reactor Sizes – Differences

## Benchscale & Semi-benchscale

- Less wall effect
- Plate geometry less controlled
- More expensive (larger equipment → less samples tested simultaneously)

## Microscale

- Greater wall effect
- Less expensive

## A Catalyst Manufacturer's Perspective

- Extremely large number of tests required for quality control during manufacturing, to support R&D activities, to support customer CMP activities thus testing per se is not performed primarily as revenue stream.
- Large number of tests required favor use of micro scale reactor – faster, less expensive results.
- Thousands of data points available from micro scale results
- Micro scale results can be adjusted to predict bench scale results.
- Results from different reactors vary. Typically test same catalyst on same reactor throughout life to achieve comparable results.
- For plate catalyst only, industry-wide agreement needed for geometry during testing and area used for calculations.
- Variability among bench scale test results – VGB round robin

# A Third-party Test Lab's Perspective

- VGB guidelines were adopted in Europe as standard for catalyst testing with Bench scale reactor accepted as standard test method.
- Team formed in US to adopt Bench scale test methodology from VGB guidelines and go further to define ambiguity
- Geometry for plates to be used was defined in latest revision
- Equilibrium time for new, dirty, and regenerated catalyst was defined along with number of samples and time between samples
- Testing for doing actual catalyst management plans as well as new K value should be done with bench scale reactor.
- QA/QC testing for regeneration and new formulation should be done by micro testing to save money.

# Unresolved Issues

SO<sub>3</sub> inlet concentration for testing

Plate-only

- Area to be used in calculation has differed among labs
- Sample geometry

# Summary

- There is a time and place to use bench scale and micro scale testing
- QA/QC for Catalyst Manufacturers and Regenerators should be done by micro-scale reactors in order to control cost
- K values in both before and after regeneration should be done on a bench scale reactor.
- Test results should be viewed comparatively: same conditions, same scale, same lab – same person?
- Variability exists even when same conditions and same scale are used (example: results from VGB round robin)

# Summary

- It is recognized that end users may be confused and concerned over the lack of consensus around every aspect of testing methods
- End users desire some confidence in data in order to compare different manufacturers and regenerators offerings
- The industry is making progress in working towards this goal but the final product has yet to be reached

Questions????????