

REINHOLD ENVIRONMENTAL Ltd.



## **2019 NO<sub>x</sub>-Combustion-CCR Round Table Presentation**

February 11 & 12, 2019, in Salt Lake City, Utah / Hosted by PacifiCorp

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# 4½ years of dual function catalyst performance at Wolf Hollow

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# Agenda

1. Who are Umicore again?
2. US Regulation
3. System design challenges
4. Dual function catalyst and its layout
5. Wolf Hollow the story updated
6. Questions



Who are Umicore again?

## Umicore Catalyst USA LLC

1. Late 2017 Umicore acquired Haldor Topsoe's Stationary and Automotive SCR businesses.
2. Umicore is a Belgian public traded company founded in 1989, but with roots dating back to 1805 in the mining industry.
3. Revenue of around 13.5 Billion USD and over 10,000 employees around the globe.
4. Three main business areas:
  1. Recycling
  2. Energy & Surface Technology
  3. Catalyst – this is where we are placed
5. Same good people, same good catalyst



# US Regulation on turbine emissions

Tough, Tougher, “Future”

## Regulations in the United States - “Tough”

Gas Turbine Emissions Standards (1995 – 2010)

- Average GT uncontrolled outlet NO<sub>x</sub>; 9 – 25 ppm
- NO<sub>x</sub> outlet range 2 – 8 ppm; 5 – >10 ppm NH<sub>3</sub> slip
- Average DeNO<sub>x</sub> removal efficiency; 77% - 90%
- No emission compliance requirements during start up
- Required NH<sub>3</sub> to NO<sub>x</sub> uniformity; 15% - 20% RMS
- Less than 1% gas bypass is acceptable
- Outlet CO emissions  $\leq$  2.0 ppm

## Regulations in the United States - “Tougher”

### Gas Turbine Emissions Standards (2010 – Current)

- Average GT outlet NO<sub>x</sub>; 20 – 35 ppm
- NO<sub>x</sub> outlet range 2 ppm; 2 – 5 ppm NH<sub>3</sub> slip
- Average DeNO<sub>x</sub> removal efficiency; 90% - 94%
- Emission compliance begins with starting of the GT
- Currently supplying units 92% - 96% DeNO<sub>x</sub> with some 2 ppm NH<sub>3</sub> slip
- Outlet CO and VOC emissions 1.0ppm in some cases

## Regulations in the United States – “Future”

Anticipate “newer” generation GT’s with up to 50 ppm outlet NOx

Anticipate more areas of the US to limit NH3 slip to 2 - 3 ppm

2 ppm NOx / 5 ppm NH3 slip or better will be the norm

California is moving from RECLAIM to “command and control”

Existing sources in CA will need to meet new lower limits

California making 2 ppm NOx and <5 ppm slip std for all sources requiring (BARCT)

CO & VOC emissions limited to 1ppm – 2ppm on most applications



# System design challenges

## Challenges OEM's Can't Ignore

Achieving >93% DeNOx and very low slip

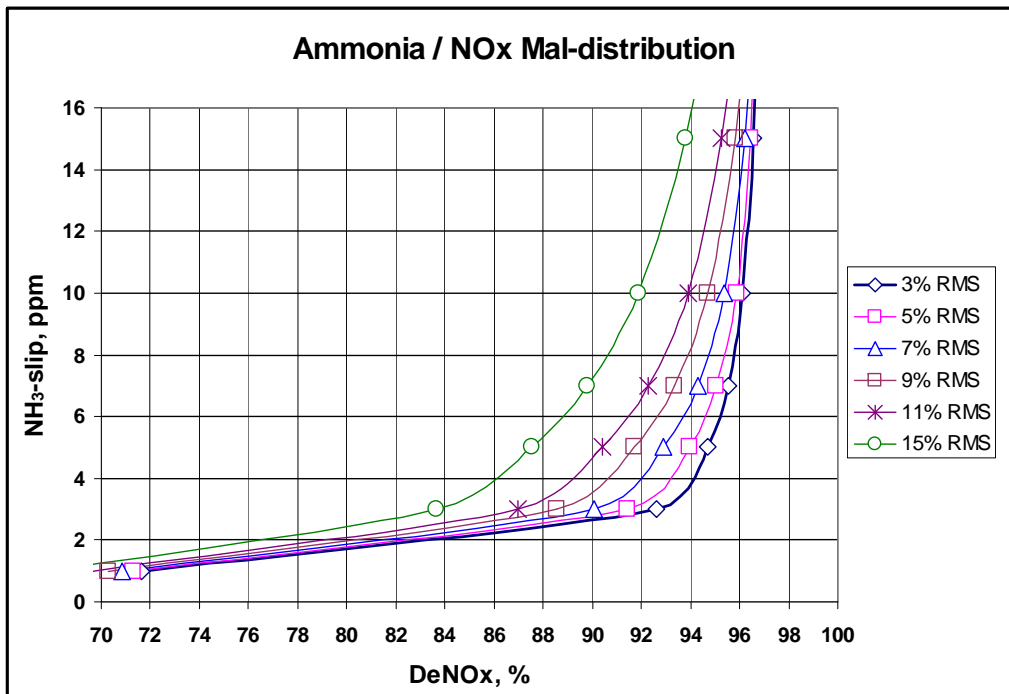
- Ammonia to NOx uniformity
  - ✓ New and better AIG design & tuneability (1, 2 or 3 zones; mult. zone)
  - ✓ Supplemental firing / duct burners – may require (2) AIG's
  - ✓ Permanent sample / test grid
  - ✓ Use static mixers at the AIG to improve mixing
  - ✓ Liquid reagent injection (ammonia or urea)
- Compliance through start-up
- Flue gas bypass, you can have none
- Improved / faster ammonia control systems
- Stack measurement multiple point (CEMS)

Catalyst is not the limiting factor, near 100% DeNOx removal

# Relationship of NH<sub>3</sub> to NO<sub>x</sub> Uniformity and NH<sub>3</sub> Slip

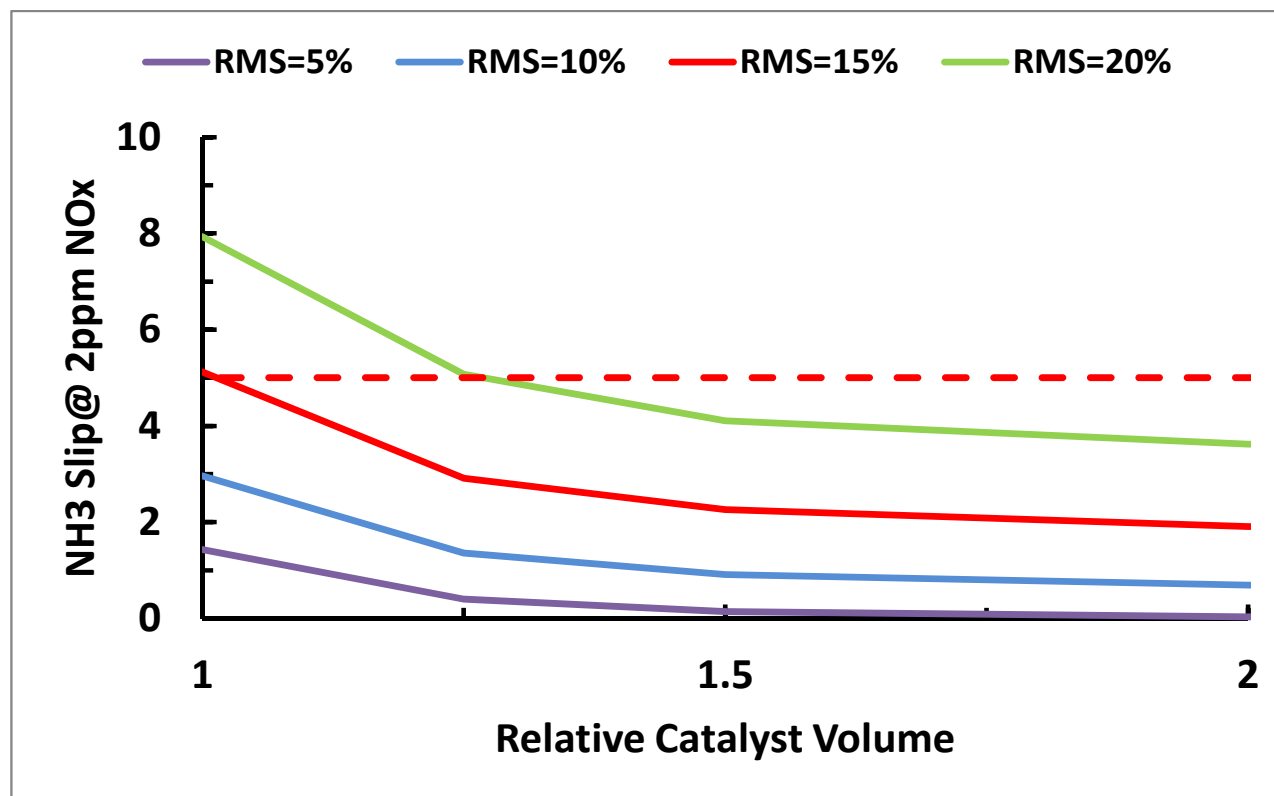


- Reagent Grade needed
- Ammonia slip given for end of guarantee period
- Ammonia slip will typically gradually increase over time due to loss of catalytic activity (except in high temp applications)
- Ammonia to NO<sub>x</sub> maldistribution is critical in high reduction low slip systems



# Impact of Catalyst Volume on NH<sub>3</sub> Slip

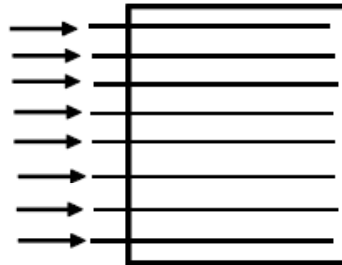
Based on 90% DeNO<sub>x</sub> design (20ppm-2ppm) & 5 ppm slip



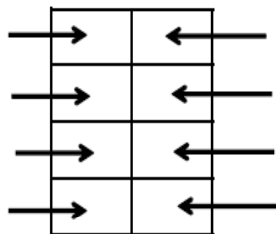
# AIG Design and Tunability

AIG Must Have Adjustment Valves

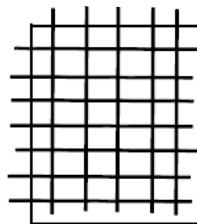
Single Zone - Common



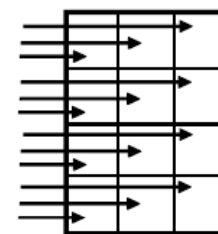
Double - Zone



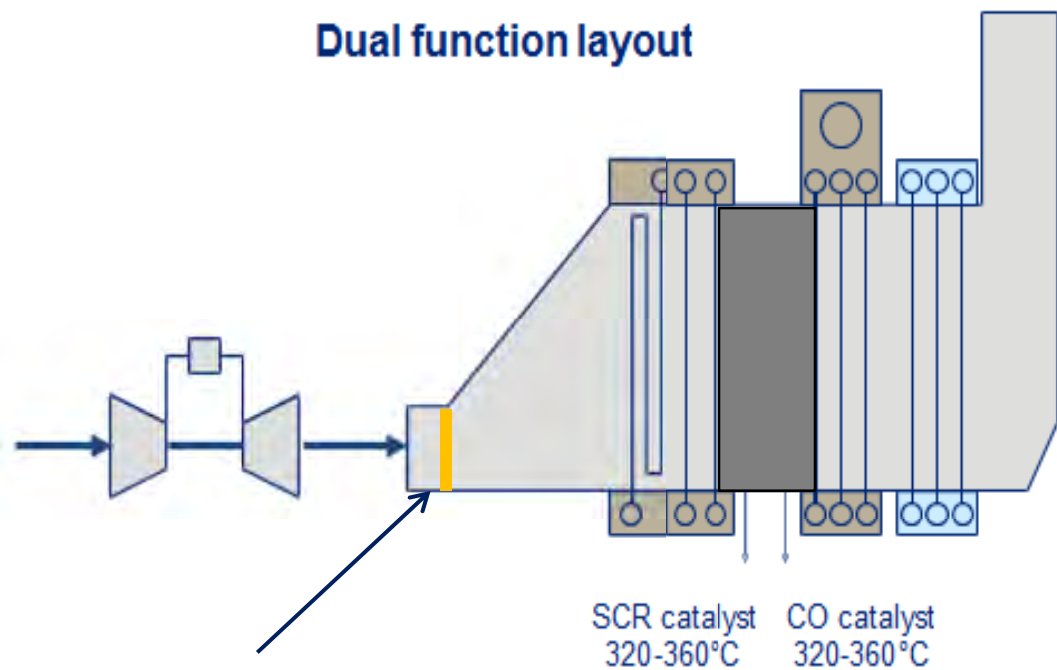
Multiple Zone



3 Zone – Vert. Adjustment



# Liquid Reagent Injection - HRSG



**Direct Injection of  
Aqueous Ammonia  
or a Urea Solution**



# The Dual Function Catalyst

What makes a good one

## What is a true dual function catalyst?

Beside NO<sub>x</sub> reduction it oxidize CO and VOC's, in one and same catalyst

Based on our DNX catalyst with the active component being Pd

Allows for high SO<sub>2</sub> tolerance and low SO<sub>2</sub> oxidation

Have been used in excess of 160+ plants in a divers range of applications such as

- Gas turbines
- Industrial plants
- Large NG fired Gas engines including landfill gas with siloxanes
- Diesel engines
- Chemical processing plants
- Refinery units

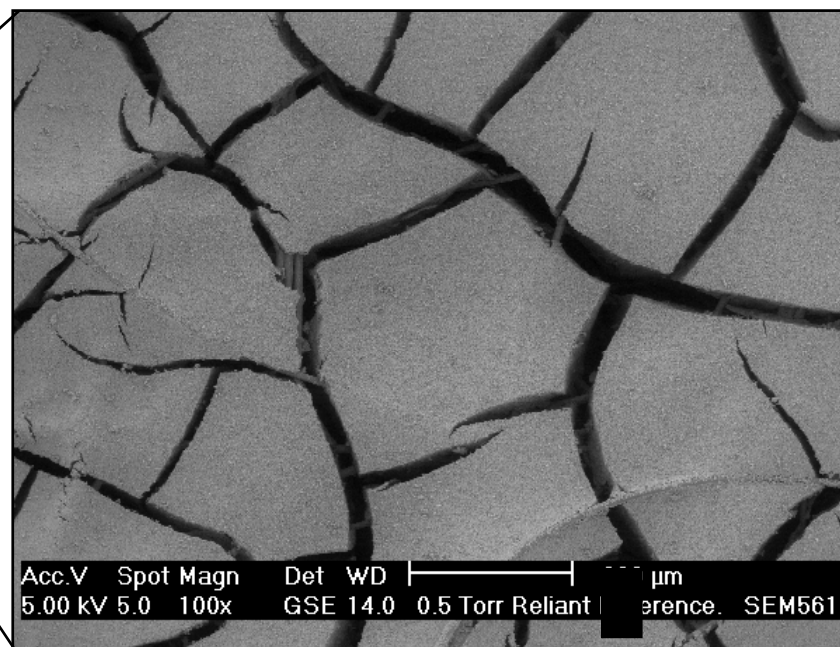
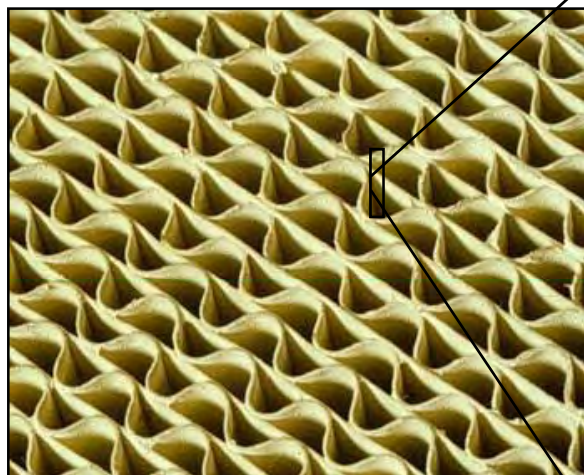
# Typical CCGT Catalyst Module



## Accessibility of active sites

DeNOx reaction is “Diffusion Limited”  
 more highways = higher diffusion rate = higher activity

**Tri-modal pore structure**



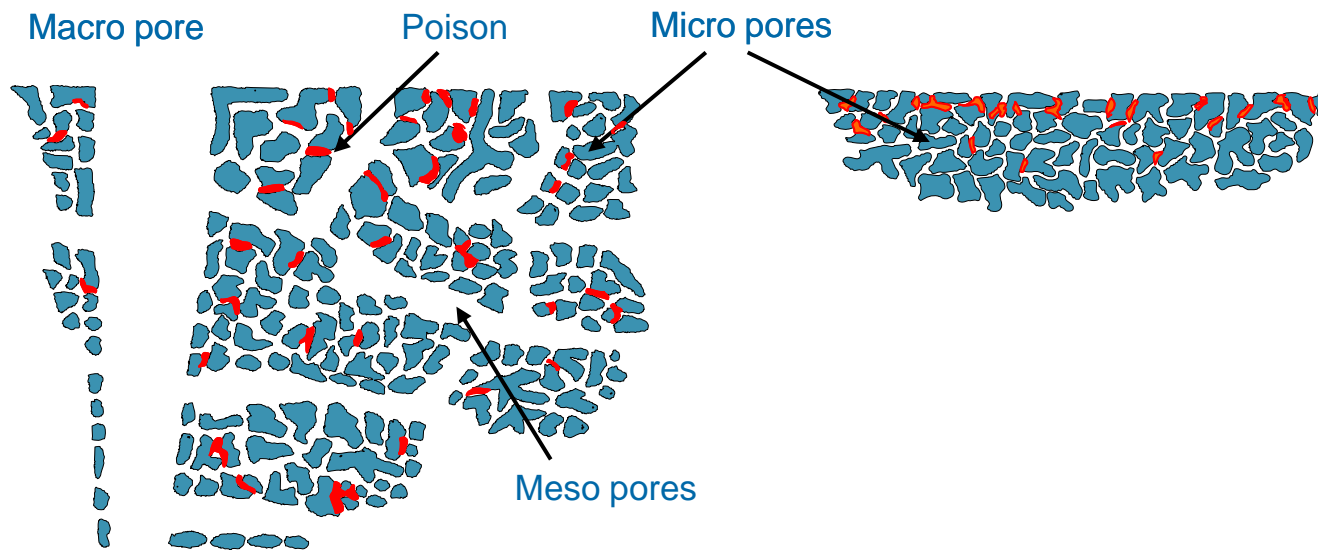
# Pore structures is key to fight catalyst poisons

DNX<sup>®</sup> type catalyst

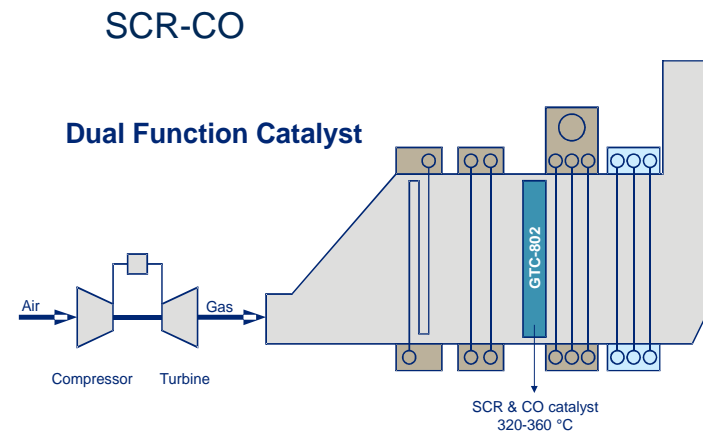
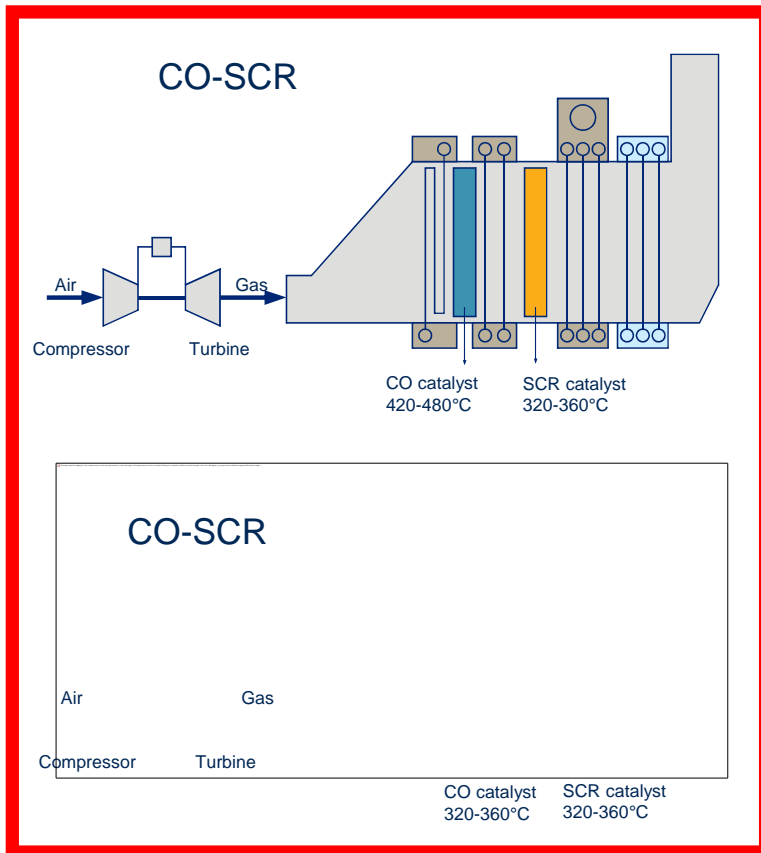
- Trimodal pore structure

Extruded & plate type catalyst

- Homogenous micro pore structure



# Basic HRSG Layouts

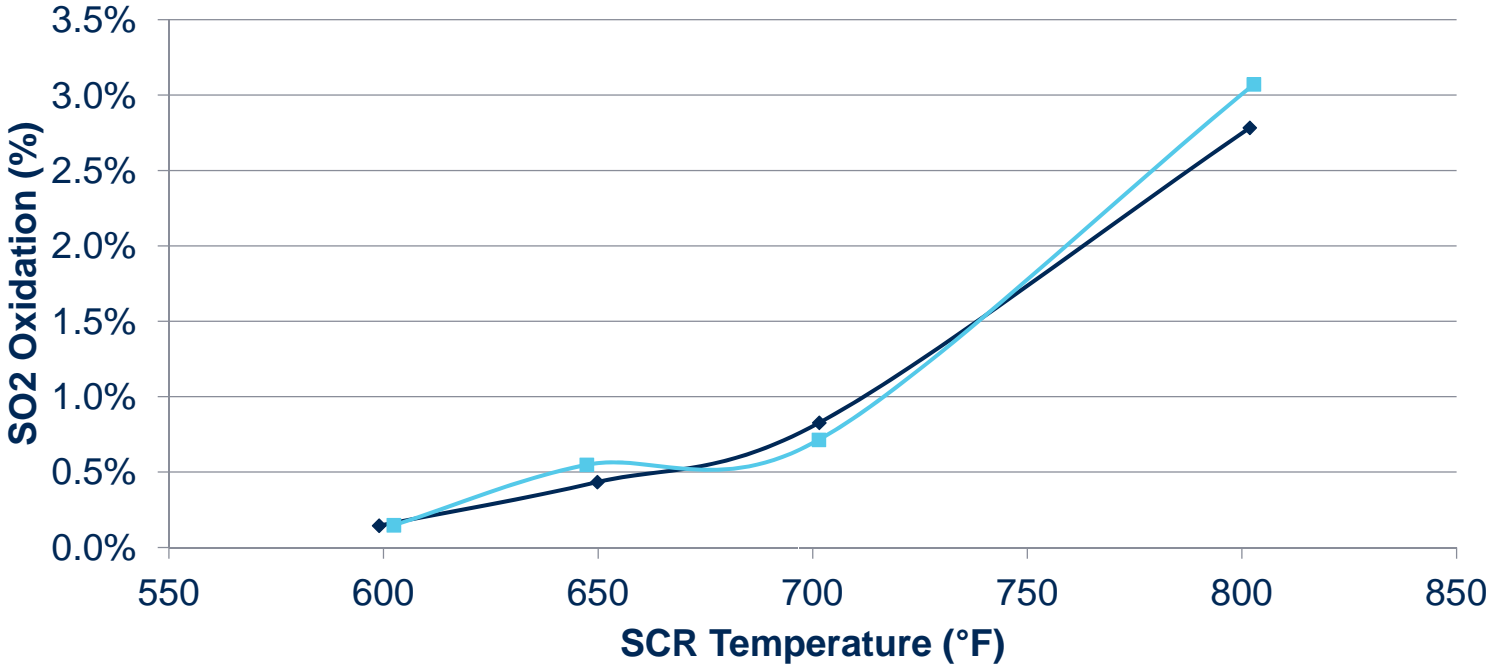


# SO<sub>2</sub> to SO<sub>3</sub> Oxidation Rate 10 - 30 times lower than Pt based oxidation catalyst



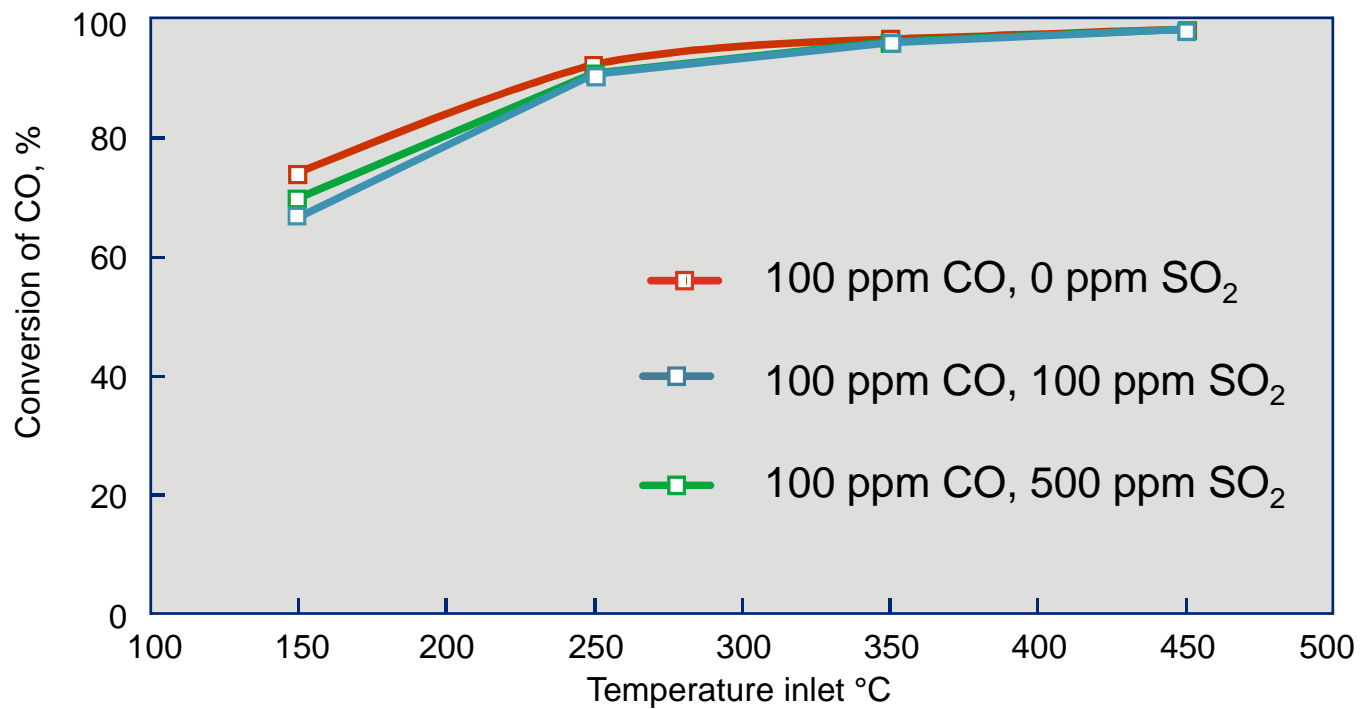
## GTC-802 SO<sub>2</sub> Oxidation

—◆— NH<sub>3</sub>/NO<sub>x</sub> = 0.9    —■— NH<sub>3</sub>/NO<sub>x</sub> = 0.0



# SO<sub>2</sub> tolerance

In operation since the mid 90'ies



## Development of a Dual Function Catalyst Performance Characteristics

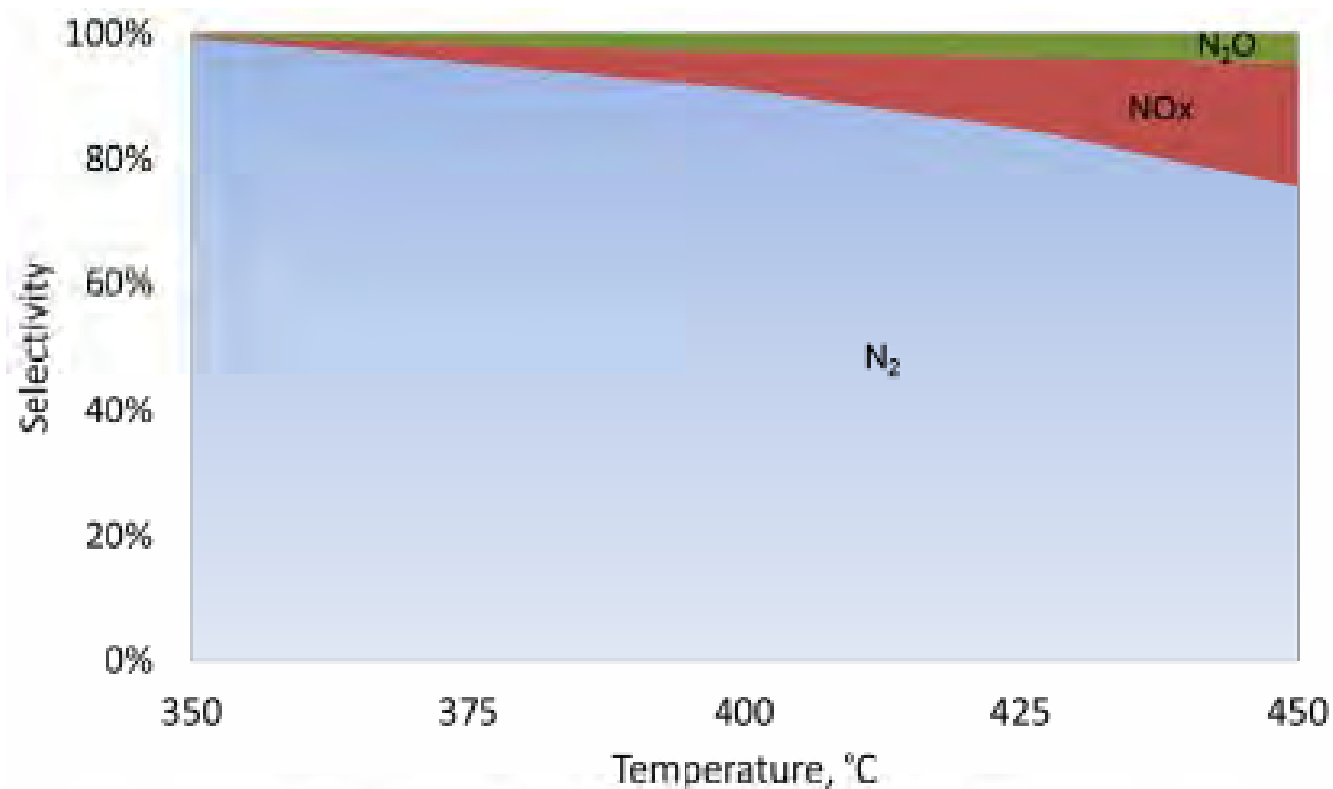
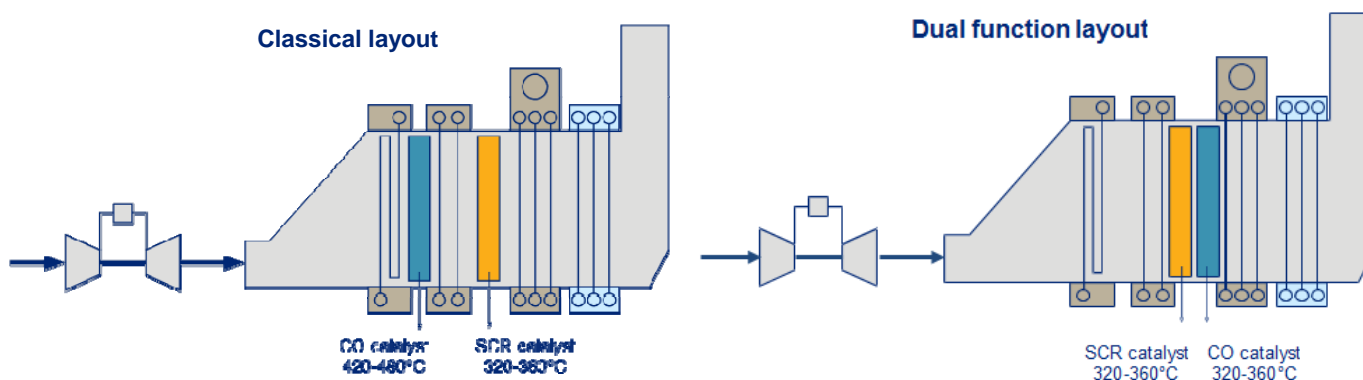


Figure 6 NH<sub>3</sub> oxidation selectivity on DNX® GTC-802

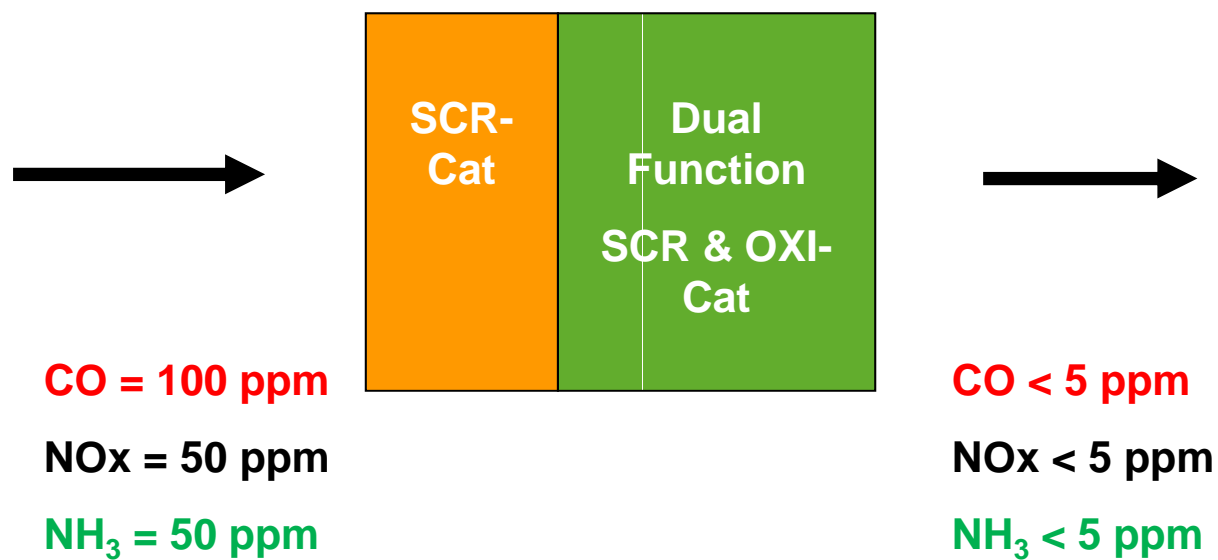
# Performance Comparison

## Advantages of a Pd based Dual Function Catalyst in a HRSG



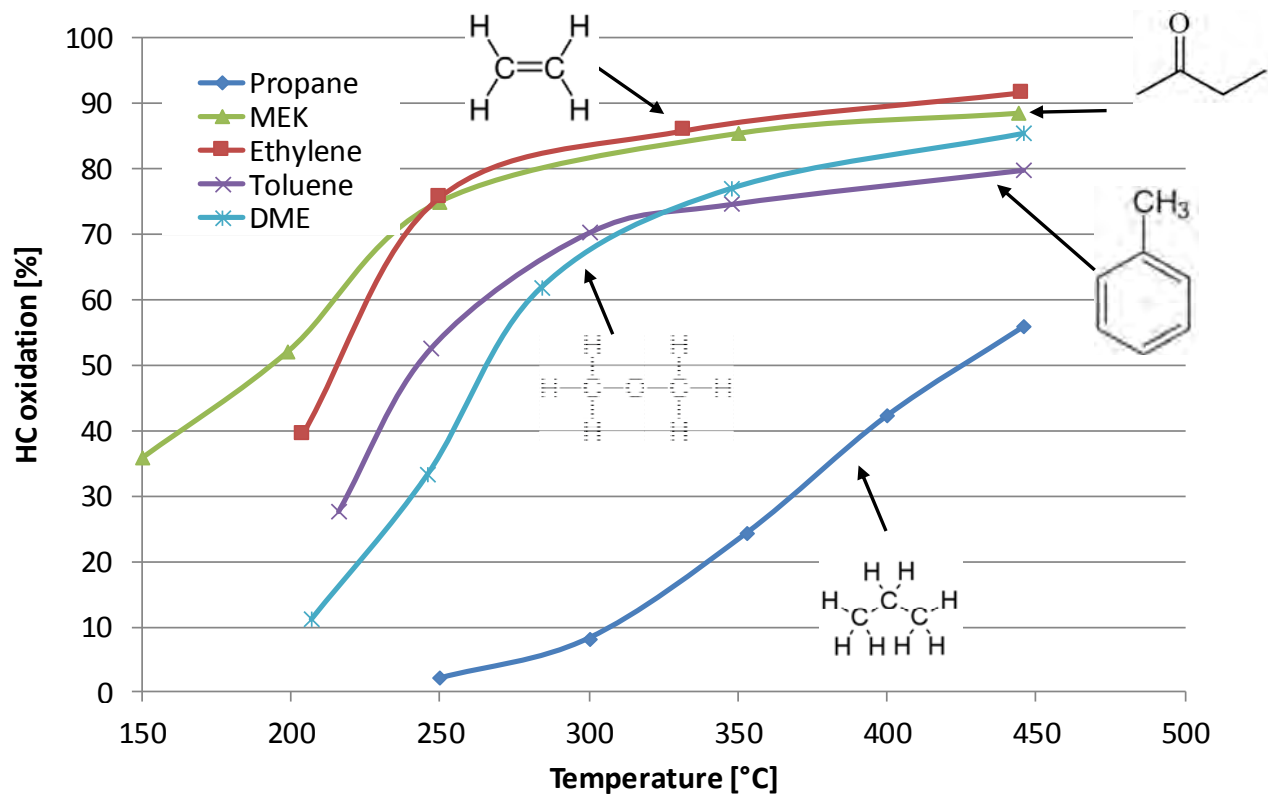
Classical Layout	Dual Function Layout
Lower CO-catalyst volumes	Lower specific pressure drop
Higher HC oxidation	Lower SO <sub>2</sub> oxidation
Can't be exposed to NH <sub>3</sub>	Not impacted by SO <sub>2</sub>
Very high SO <sub>2</sub> oxidation	Easier installation
CO catalyst impacted by SO <sub>2</sub>	Liquid ammonia injection

# The Dual Function Catalyst – Basic Principle



# The VOCs

## Propane, Ethylene, Toluene, MEK, DME





# Wolf Hollow

Performance update

## Story: Exelon, Wolf Hollow Plant

Left to Right:  
Exelon Generation,  
Wolf Hollow Unit 2 & 1  
725 MWe



# Background

## 2013-2014

1. In 2013 Umicore installed GT-201 at Wolf Hollow unit 1 & 2.
2. The plant operates under a CO emission permit.
3. Renewable energy causes the plant to sit at low load.
4. CO emission increases dramatically.
5. At this point in time Umicore's dual function catalyst haven't been utilized at a plant this size.
6. 3 options:
  1. Shut down the plant
  2. Insert a spool piece upstream the AIG for conventional CO catalyst
  3. Install Umicore's Dual Function catalyst

# So what was done?

1. In October 2014 the nearly brand new SCR catalyst were replaced with a similar volume of GTC-802 dual function catalyst in both units.
2. Performance test at SOR were carried out
3. Test samples been send to the same 3<sup>rd</sup> party laboratory for testing.
4. Latest sample were taken out November 2018



# Operating Performance - Wolf Hollow START-UP (Before vs. After)

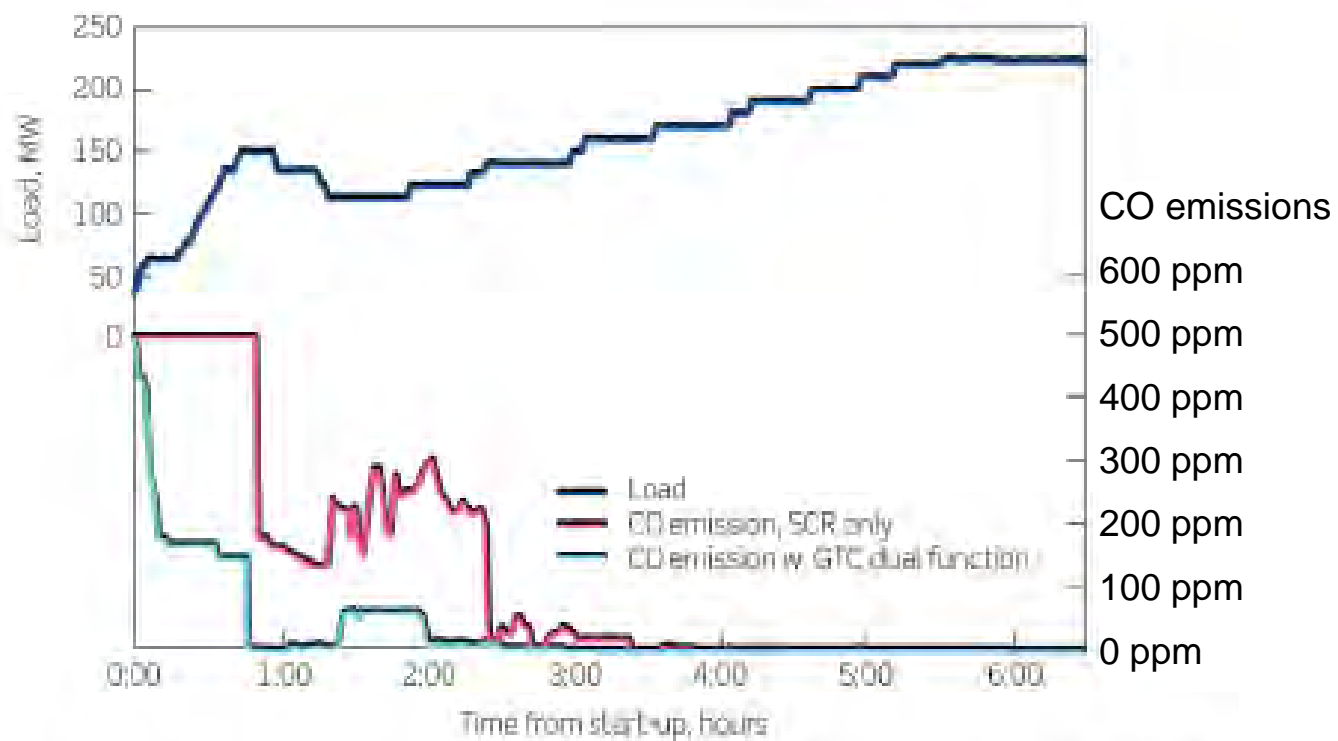


Figure 10 Comparison of performance between DNX® GTC-802 and DNX-828 SCR-only catalysts

## Operating Performance – SOR until May 2017



DeNOx Performance @ 662F / 350C & 0 ppm CO

Testing Performed on Bench Scale Reactor

Exelon, Wolf Hollow Units 1&2

Testing Performed by Same Third Party Lab

Sample Tested	Hours	Sample Length	Gas velocity Nm/s	NH3/NOx ratio	Relative k/k <sub>0</sub>
SOR, Oct. 2014	0	250mm	2.5	1.2	1.0
April 2015	4,000	500mm	2.5	1.2	1.0
March 2016	11,000	500mm	2.5	1.2	1.0
May 2017	20,000	500mm	2.5	1.2	0.98
November 2018	25,000	500mm	2.5	1.2	1.0

## Operating Performance – SOR until May 2017



- CO Oxidation Performance, with 70 ppm ammonia injection
- Testing Performed on Bench Scale Reactor
- Exelon, Wolf Hollow Units 1&2
- Testing Performed by Same Third Party Lab

Sample Tested	Hours	Sample Length	Gas Temperature F / C	Gas velocity Nm/s	NH3/NOx ratio	CO Oxidation %
SOR, Oct. 2014	0	500mm	700 / 371	3.2	1.0	98.7
April 2015	4,000	500mm	700 / 371	2.7	1.0	99.2
March 2016	11,000	500mm	700 / 371	2.7	1.0	99.6
May 2017	20,000	500mm	700 / 371	2.5	1.0	99.6
November 2018	25,000	500mm	700 / 371	2.5	1.0	99.5

# Thank you for your attention

## Any questions (left)?



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