

# Reinhold Environmental Ltd.

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2008 NO<sub>x</sub>-Combustion Round  
Table & Expo Presentation

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



**WorleyParsons**

resources & energy

POLLUTION CONTROL USERS GROUP 2008 CONFERENCE

# A NEW APPROACH FOR HYBRID SNCR/SCR FOR NO<sub>x</sub> REDUCTION

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- ▶ What is a “WorleyParsons”
- ▶ Location → world-wide company, but for the electric utility industry Reading, PA
- ▶ If you are old → Gilbert Associates or Gilbert/Commonwealth
- ▶ If you are middle age → Parsons → Parsons Energy & Chemicals (PEC)
- ▶ If you are young → an Australian engineering company specializing in the mining & oil industries brought PEC



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- ▶ Introduction
  - ▶ Background
  - ▶ NOx Reduction Technology Review
  - ▶ SCR Negative Impacts
  - ▶ Catalyst
  - ▶ Hybrid SNCR/SCR
  - ▶ Economics
  - ▶ Summary
  - ▶ Recommendation



- ▶ Approach for NO<sub>x</sub> control → CAIR
  - Phase 1 (2009) – 0.15 lb NO<sub>x</sub> / Mbtu → ~53% overall reduction
  - Phase 2 (2015) – 0.125 lb NO<sub>x</sub> / Mbtu → 60% overall reduction
- ▶ Present
  - Driver → lowest \$ per ton NO<sub>x</sub> removed
  - Large SCR reactors on large, base-load units → over-comply to achieve system average
- ▶ Future
  - Driver → easy, low-cost NO<sub>x</sub> removal already installed
  - SCR for smaller units



▶ NO<sub>x</sub> Formation mechanisms

- Fuel NO<sub>x</sub> → reaction of chemically-bound nitrogen (N<sub>2</sub>) in the coal with O<sub>2</sub> → ~70% of NO<sub>x</sub>
- Thermal NO<sub>x</sub> → reaction of N<sub>2</sub> in combustion with an excess of O<sub>2</sub> → 30% of NO<sub>x</sub>
- Prompt NO<sub>x</sub> → interaction of molecular nitrogen with hydrocarbons early in the combustion phase – minimal NO<sub>x</sub> increases with increasing temperature & O<sub>2</sub>

▶ NO<sub>x</sub> Composition

- NO → ~95%
- NO<sub>2</sub> → ~5%



- ▶ Ozone Season Only Operation
  - At 90% summer capacity factor → 3250 hours per ozone season, or ~6 year catalyst life
  - Most SCR units have completed 3 or 4 ozone seasons → over half-way to spare catalyst layer addition
  
- ▶ Year-round Operation
  - At 75% annual capacity factor → 6500 hours per year, or ~ 3 year catalyst life
  - 1<sup>st</sup> catalyst layer addition or replacement soon after year-round operation begins



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- ▶ Combustion Optimization
  - ▶ LNB – Low NOx Burners
  - ▶ OFA – Over-fired Air
  - ▶ SNCR – Selective Non-Catalytic Reduction
  - ▶ SCR - Selective Catalytic Reduction
  - Conventional approach for NOx reduction → LNB/OFA with SCR
  - ▶ Other
    - PRB significantly reduces NOx → lower flame temp
    - Reburning - Fuel staging using coal or gas as the reburn fuel, to burn fuel "rich" to reduce NOx formed below



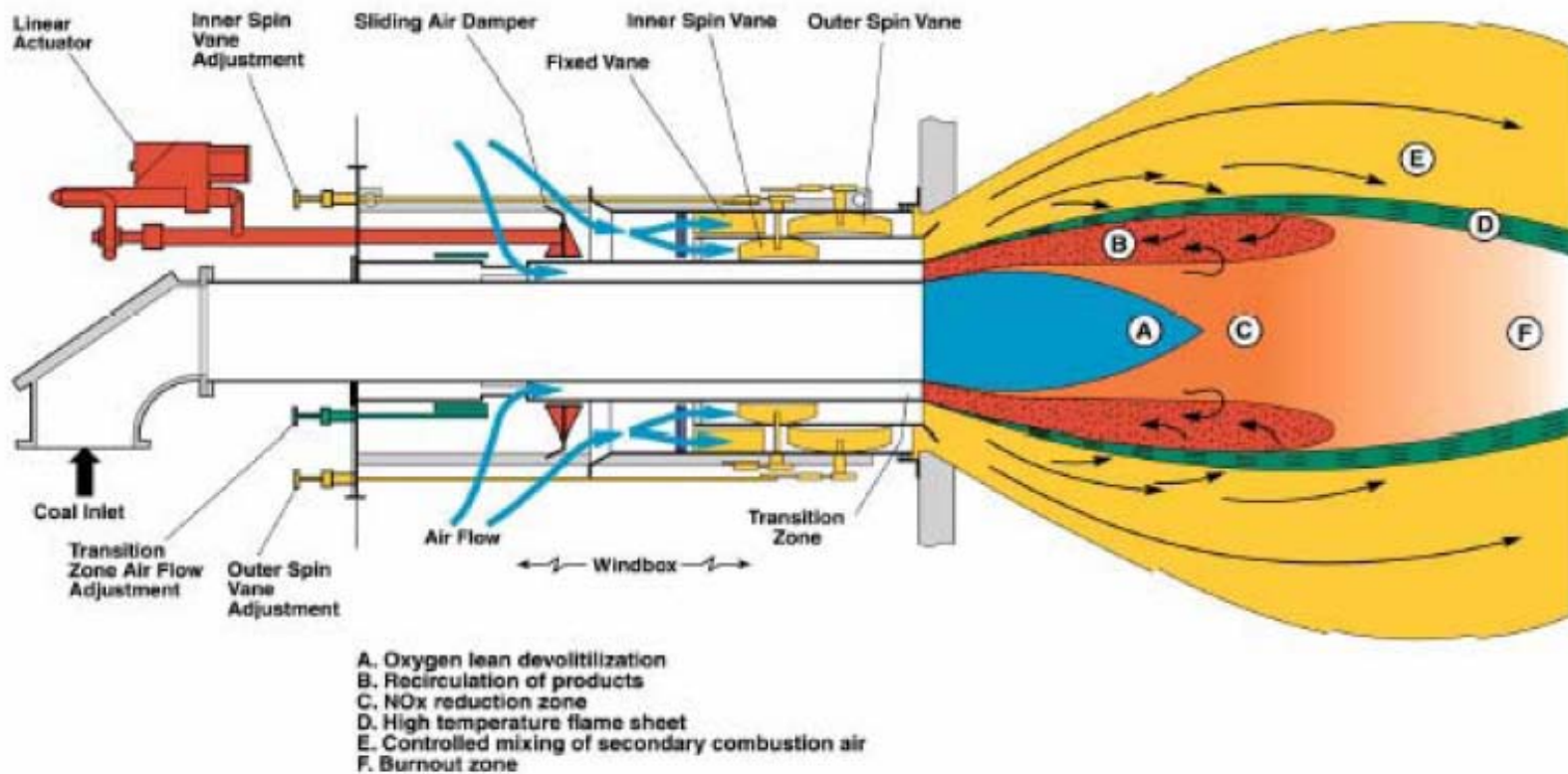
- ▶ Optimizing combustion
  - Stoichiometric balance of coal to air ratio → to each burner
  - Low NO<sub>x</sub>, CO, LOI
  - Low temperature gradient across furnace
- ▶ Non-optimized combustion
  - High coal flow & low air flow → high CO & LOI from incomplete combustion
  - Low coal flow & high air flow → high NO<sub>x</sub> from oxidation
- ▶ Results → varied, but back to original burner design



- ▶ Operating principal – air staging to manage the air /fuel in mixing in the flame
- ▶ Reduce the primary air to the coal burners
  - Reducing, fuel-rich atmosphere → coal-bound nitrogen converted to molecular N<sub>2</sub>, due to lower O<sub>2</sub>
  - Reducing atmosphere has lower temperature → further reducing NO<sub>x</sub>
- ▶ Secondary air combusts remainder of coal in a fuel-lean zone → at a lower temperature
- ▶ Results → NO<sub>x</sub> down to ~0.5 lb/Mbtu or less, regardless of inlet NO<sub>x</sub> (except for cyclone furnaces)



# Low NOx Burners (LNB) – Combustion NOx Control





- ▶ Further reduces total secondary air the burners
  - ▶ Part of increased secondary air (SA) to furnace ports above the burners for deeply staged combustion → 10% to 20% of SA
  - ▶ OFA Options
    - CC – closed coupled → uses top row of burners in windbox
    - SOFA – separated OFA → at SA pressure
    - BOFA – boosted OFA → uses separate air blower to increase OFA pressure
- BOFA has advantages in “short” furnaces with low residence time
- OFA is very furnace specific



- ▶ Negative impacts of LNB / OFA
  - Increased LOI (unburned carbon)
    - Due to incomplete combustion from reduced air/O<sub>2</sub> in combustion air
    - Impacts ESP operation & Fly Ash byproduct sales
  - Increased slagging → reducing ash temps different than oxidizing ash temps
  - Increased corrosion – water wall wastage
    - Due to the sub-stoichiometric (low O<sub>2</sub>) condition at the burner
    - Corrosive forms of sulfur & chlorine from reducing atmosphere
- ▶ Combination of LNB & OFA → NO<sub>x</sub> < 0.4 lb/Mbtu

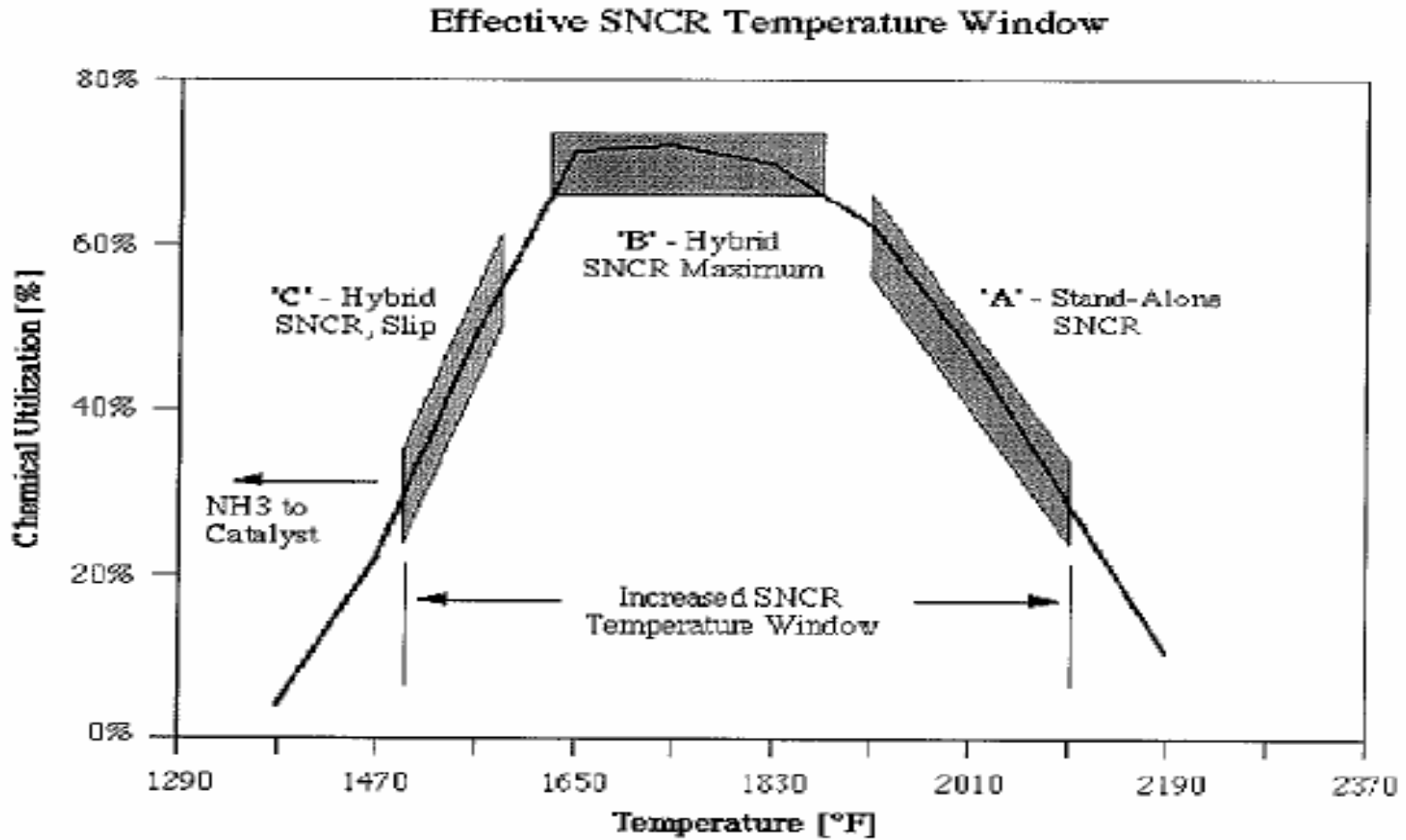


▶ SNCR Process

- Post-combustion, gas-phase reaction → no catalyst
- Complex reaction of ammonia ( $\text{NH}_3$ ) with NO
- Optimum gas temperature 1700 F to 1900 F
- In the upper furnace, before the convection sections, above OFA

▶ Trade-off between NOx removal &  $\text{NH}_3$  slip

- Below 1700 F → low NOx removal & high  $\text{NH}_3$  slip, due to limited decomposition of  $\text{NH}_3$  to  $\text{NH}_2$
- Above 1900 F → low NOx removal & low  $\text{NH}_3$  slip, due to oxidation of  $\text{NH}_3$  to NOx
- Conventional operation above optimum (> 2,000 F) to minimize  $\text{NH}_3$  slip → usually < 5 ppm



**Figure 1.** Hybrid SNCR/SCR yields improved performance.  
Total reagent utilization approaches 100 %



## ▶ NH<sub>3</sub> Injection

### – Chemical

- Anhydrous NH<sub>3</sub> → pure NH<sub>3</sub> ("hazardous"), vaporizes easily
- Aqueous NH<sub>3</sub> → ~20% NH<sub>3</sub> solution (to avoid being considered "hazardous")
- Urea → NH<sub>2</sub>CO NH<sub>2</sub> (2 moles of NH<sub>3</sub>), a solid which can be made into a solution

### – Equipment

- Liquid – low pressure lances, at multiple levels → optimum temperature shifts with load
  - Furnace → wall lances
  - Convective section → water-cooled retractable lances
- Gas → needs high energy to distribute gas across furnace



- ▶ NOx removal → for 5 ppm slip
  - Small boilers → up to 35%
  - Large boilers → up to 30%
  - NOx to < 0.3 lb/Mbtu → LNB / OFA + SNCR
  
- ▶ Design
  - Requires extensive physical & computer modeling to determine the optimum temperature region as a function of load
  - Stoichiometry → moles of NH<sub>3</sub> per mole of NOx
    - Up to 1.5 for urea
    - Up to 1.0 for NH<sub>3</sub>



- ▶ “Selective” – only removes  $\text{O}_2$  from nitrogen → not from carbon, sulfur or other oxygenated compounds
- ▶ Operation
  - ~650 °F with a vanadium/titanium catalyst → like a sulfuric acid catalyst, which oxidizes  $\text{SO}_2$  to  $\text{SO}_3$
  - Below ~600 °F, ABS formation in catalyst pores → depends on  $\text{SO}_3$  ppm
- ▶ SCR reactions
  - $\text{NH}_3$  diffuses to active sites in catalyst pore structure &  $\text{NH}_3$  is absorbed on active site
  - $\text{NO}$  reacts with  $\text{NH}_3$  on the catalyst surface → forms  $\text{N}_2$
  - Active site regenerated by oxidation



▶ SCR Types

- High dust → before ESP
- Low dust → after hot ESP

▶ SCR Design

- Typically 3 or 4 catalyst layers for 90% removal with < 2 ppm NH<sub>3</sub> slip (at end of catalyst life) → install 2 or 3 layers initially with space for spare layer
- NH<sub>3</sub> injection grid → multiple nozzles for precise distribution of NH<sub>3</sub> to match NO<sub>x</sub> concentrations
- As catalyst ages, NH<sub>3</sub> “breaks thru” → NH<sub>3</sub> slip
  - Very little NH<sub>3</sub> slip in first half of catalyst life
  - NH<sub>3</sub> slip increase significantly at ~90%



▶ Catalyst

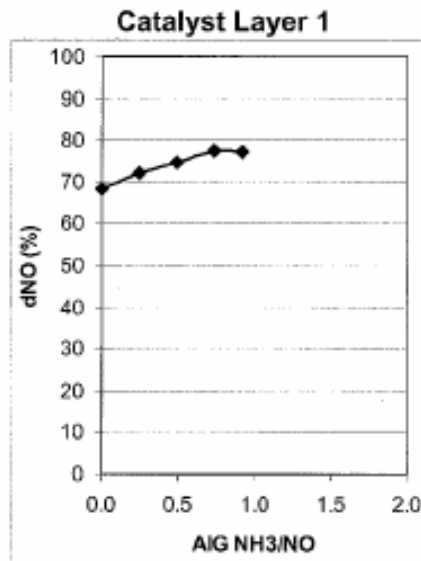
- Pitch (opening) – 6 to 7 mm → for fly ash to pass thru
  - Life - ~20,000 hrs
  - SO<sub>2</sub> Oxidation → 0.25% to 0.375% per layer
  - Higher catalyst activity (NO<sub>x</sub> removal) increases oxidation
  - Types
    - Honeycomb – homogeneous material, square openings with 1 mm wall thickness
    - Plate – catalyst coated metal plates, like air heater baskets
- Most SCR are due for addition of spare catalyst layer or replacement of first existing layer

▶ NO<sub>x</sub> Removal by layer (3 layers) → next slide

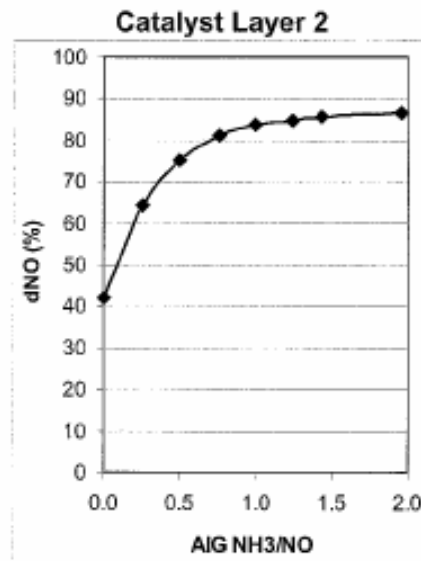


## In Situ Test Protocol and Typical Test Results

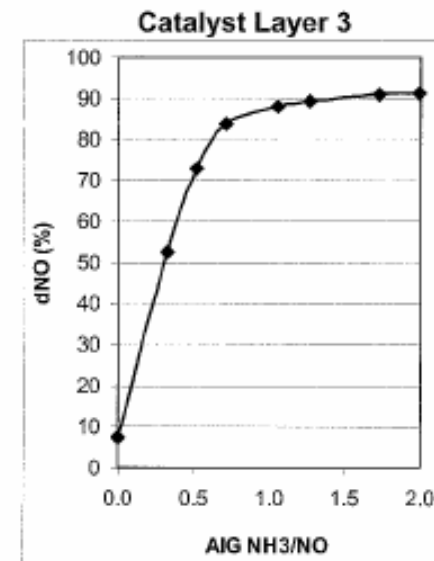
- Measure NO removal across test module without NH<sub>3</sub> injection
- Add NH<sub>3</sub> via test module AIG to point of maximum NO removal
- Calculate reactor potential from  $RP = -\ln(1 - \Delta NO)$



- dNO maximum = 77.3%



- dNO maximum = 86.6%



- dNO maximum = 91.3%



- ▶ Ammonia (NH<sub>3</sub>) slip → water soluble
  - ABS (ammonium bisulfate) formation on air heater surfaces
  - ABS condensing on ash → in air heater & ESP
  - NH<sub>3</sub> ad/absorbed on fly ash → in air heater & ESP
  - Remaining NH<sub>3</sub> absorbed in FGD solution
  - All have a wastewater discharge component → air heater wash water & leachate from dry ash disposal
  
- ▶ Increased SO<sub>3</sub> emissions → SCR doubles “boiler” SO<sub>3</sub>
  - Acid dew point (ADP) temperature increase → ductwork corrosion
    - Typically < 290 F with high sulfur coal (25 ppm SO<sub>3</sub>) – w/o SCR
    - With SCR > 300 F
  - Plume opacity increase → potential for visible “blue” plume



▶ ABS Formation

- Gas phase reaction of  $\text{SO}_3$  &  $\text{NH}_3 \rightarrow$  sticky solids formed in air heater
- Initial formation Temp (IFT)
  - IFT ranges from 330° F to 350° F
  - Lower IFT at lower  $\text{SO}_3$  ppm  $\rightarrow$  closer to exit of air heater
- With high-sulfur coals, measurable ABS deposits/pluggage in air heater above ~1.5 ppm  $\text{NH}_3$

▶  $\text{NH}_3$  ad/absorption on fly ash

- Ash sludge – 1ppm  $\text{NH}_3$  (absorbed from gas phase)  $\rightarrow$  ~0.5 ppm in sludge water
- Dry ash – 1 ppm  $\text{NH}_3 \rightarrow$  ~70 ppm on dry ash



- ▶ FGD (for 10% for the  $\text{NH}_3$ )
  - Open Loop → ~ 1 ppm
  - Closed Loop
    - Pond → ~2 ppm
    - Byproduct gypsum → up to 10 ppm
- ▶ Distribution of  $\text{NH}_3$  Slip - % Removal
  - Air Heater → depends on how close to ADP
  - ESP → 50 to 70% removal (from limited literature)
  - FGD → remaining  $\text{NH}_3$  slip
- ▶ Byproduct ash sales – limited to ~100 ppm  $\text{NH}_3$  → generic “rule of thumb”, but reality may be lower



- ▶ Acid Dew Point (ADP) temperature increase
  - Low-sulfur units switching to high-sulfur coals with FGD & SCR
    - 30+ F increase in ADP temperature
      - Low-sulfur coals, w/o SCR → ~5 ppm with ADP < 270 °F
      - High sulfur (3%) coals with SCR → up to 50 ppm with ADP of 305 °F
  - Corrosion of carbon steel ductwork
    - Additional insulation will not help → minimal temp loss along duct
    - Avoiding “cold” spots critical → wet insulation , no thermal breaks
  - Solution → Increase air heater outlet gas temperature
    - Add air preheat coils → maintains combustion air temps
    - Air heater bypass → decrease combustion air temp
    - Change speed of air heater → see Paragon presentation



- ▶ Plume opacity increase
  - Increased SO<sub>3</sub> may result in visible “blue” plume, esp for high-sulfur coals → ~ 10 ppm
  - Opacity limits may be exceeded → requiring SO<sub>3</sub> removal system
- ▶ Inherent SO<sub>3</sub> removal
  - Air Heater → up to 15 % (average), due to temp gradient across air heater
  - ESP → 5 to 10% (eastern bituminous)
  - FGD → 30 to 50%
  - Total → 50 to 70%
  - Stack can easily have > 10 ppm



- ▶ Ozone Season Only Operation
  - At 90% summer capacity factor → 3250 hours per ozone season, or ~6 year catalyst life
  - Most SCR units have completed the 3<sup>rd</sup> or 4<sup>th</sup> ozone season → over half-way to spare (top) catalyst layer addition
  
- ▶ Year-round Operation
  - At 75% annual capacity factor → 6500 hours per year, or ~ 3 year catalyst life
  - 1<sup>st</sup> catalyst layer addition / replacement soon after year-round operation begins

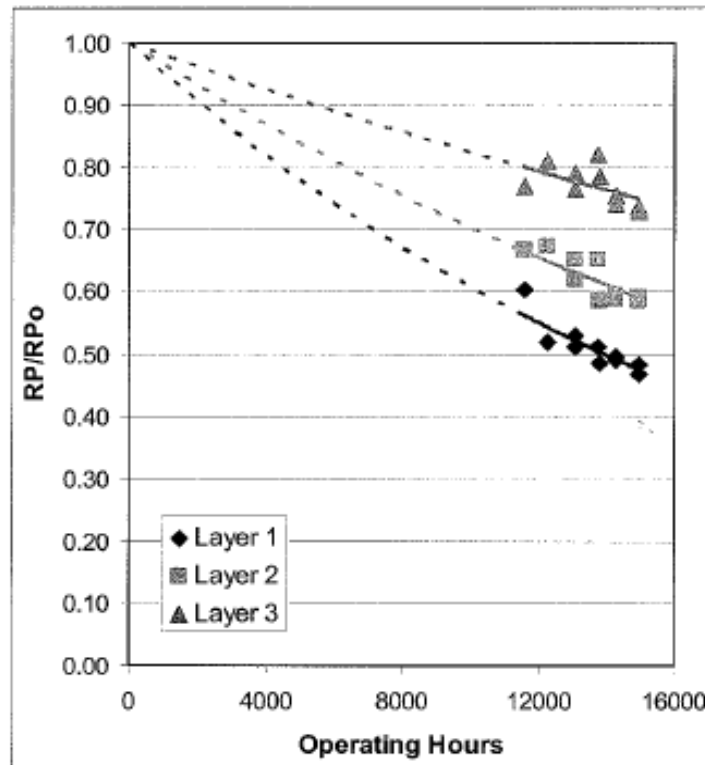


- ▶ Thermal – sintering > 750 F
- ▶ Fouling
  - Alkaline metals (Na, K) – water-soluble form is highly mobile, resulting in ion exchange with active sites → esp during shutdowns
  - Heavy metals (arsenic, lead, nickel, etc) – poisons active sites
- ▶ Pore Condensate
  - Alkali earth metals (Ca) – reacts with SO<sub>3</sub> → catalyst surface masking/blinding
  - Ammonia-sulfur compounds (ABS) – clogs pores, at low gas temperatures
  - Liquids – condensation in the pores acts as carrier of poisons & flashing during rapid thermal changes → cracking

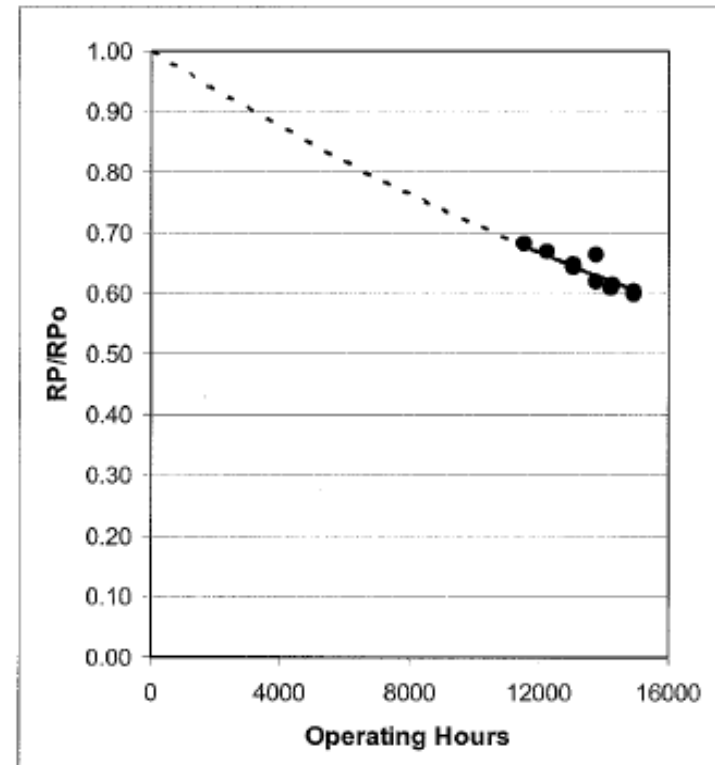


## In Situ Reactor Potential Results - 2005

Individual Layers



Overall Reactor





### ▶ Initial Operation

- 4 catalyst layer SCR, with initial fill of 3 lower levels → 3.0 total initial activity ( $K_i$ )
- 90+% NO<sub>x</sub> removal with no measurable NH<sub>3</sub> slip
- Top layer has most catalyst deactivation → assume 70% activity of  $K_i$  at end of catalyst life
- Other layers degrade at ~half the rate of top/most active layer

### ▶ Spare Layer Addition (top layer)

- At ~20,000 hours of operation
- Before addition of spare layer → ~2.4 catalyst activity with 2 ppm NH<sub>3</sub> slip
- After Addition → 3.4 activity with no measurable NH<sub>3</sub> slip



## Catalyst Replacement vs NH3 Slip

Layer	$K_i$ , Initial	$K_a$ , 20,000 hrs	Add Spare Layer
Top	0	0	1.0
	1.0	0.7	0.7
	1.0	0.8	0.8
Bottom	1.0	0.9	0.9
Total	3.0	2.4	3.4
NH3 Slip, ppm	0	2	0



- ▶ 1<sup>st</sup> Layer Replacement
  - May not necessarily be after 40,000 hours
  - 2<sup>nd</sup> layer from top – least  $K_a$
  - When top layer reaches 70% activity of  $K_i$  at end of catalyst life
- ▶ Before Replacement
  - 1.9 catalyst activity with > 2 ppm NH3 slip, based on condition of spare layer addition
- ▶ After Replacement
  - 2.6 catalyst activity with >1 pm NH3 slip



## Catalyst Replacement vs NH3 Slip

Layer	$K_i$ , Initial	$K_a$ , 20,000 hrs	Add Spare Layer	1 <sup>st</sup> Layer Replace ment	1 <sup>st</sup> Layer Replace ment	2 <sup>nd</sup> Layer Replace ment
Top	0	0	1.0	0.7	0.7	
	1.0	0.7	0.7	0.35	1.0	
	1.0	0.8	0.8	0.4	0.4	
Bottom	1.0	0.9	0.9	0.45	0.45	
Total	3.0	2.4	3.4	1.9	2.6	
NH3 Slip	0	2	0	>2	>1	



- ▶ Regardless of the deactivation rate assumptions, with the 1<sup>st</sup> layer replacement the NH<sub>3</sub> slip will:
  - Before replacement → exceed 2 ppm, for the nominal catalyst life
  - After replacement → start at > 1 ppm NH<sub>3</sub> slip
- Fly ash is in danger of always being “contaminated” for byproduct ash sales



- ▶ Conventional Hybrid
  - Conventional SNCR
  - In-duct SCR (single layer)
    - Located between economizer outlet & air heater inlet
    - Higher gas velocities, usually with horizontal gas flow → problem with fly ash deposition
  - Limited commercial application, to control NH<sub>3</sub> slip → very limited
- ▶ New Approach – “conceptual”
  - SNCR optimum NO<sub>x</sub> removal → ~ 50% with very high NH<sub>3</sub> slip (up to 40 ppm) to ~0.2 lb/Mbtu
  - Conventional, full size SCR with less catalyst layers with additional NH<sub>3</sub> added → 2 layers (with space for spare layer)
  - SCR removal ~70% → 0.05 lb with < 1 ppm slip
  - SCR’s SO<sub>3</sub> reduced with fewer catalyst layers



▶ HYBRID CUMULATIVE EFFECT

	<u>% Removal</u>	<u>Lb/Mbtu</u>
– LNB/OFA	Varies	< 0.4
– SNCR (Hybrid)	~50	< 0.2
– SCR	~70	~0.5
– TOTAL	~90	



▶ Capital (Removal vs \$/KW & vs \$/ton NOx removed)

	<u>Removal</u>	<u>\$/KW</u>	<u>\$/Ton NOx</u>
– LNB	20%	10	330
– LNB/OFA	30%	15	350
– SNCR	25/30%	20	250
– SCR	90%	120	850
– Hybrid	90%	140	1,000



▶ O&M

- Urea
  - SCR → \$350 per ton
  - Hybrid → \$400 per ton
- Replacement Power – up to 1" pressure drop per layer → ~\$25 per ton per layer
- Catalyst
  - Same catalyst as for SCR
  - Unknown cost savings, but expect longer catalyst life due to less removal
- Ash Disposal – for off-site disposal at ~\$20 per ton → \$260 per ton NOx



- ▶ Operating (\$ per ton NO<sub>x</sub> removed)
  - Ash disposal – off-site disposal of NH<sub>3</sub> contaminated ash → Hybrid credit of \$265 per ton
  - Replacement Power – lower pressure drop from less Hybrid catalyst layers → Hybrid credit of \$25 per ton (single layer)
  - Urea – higher urea consumption for Hybrid → Hybrid debit of \$50 per ton
  
- ▶ Net Cost → Hybrid (\$760) less than SCR (\$850), if off-site contaminated ash disposal is required



- ▶ NH<sub>3</sub> slip
  - ~1.5 ppm NH<sub>3</sub> slip in flue gas will eliminate byproduct fly ash sales
  - ~1.5 ppm NH<sub>3</sub> slip will result in air heater pluggage for high sulfur coals
  - Much over 1 ppm may be an operating concern
  
- ▶ SO<sub>3</sub> Emissions
  - 3 or 4 catalyst layers “doubles” the boiler SO<sub>3</sub>
  - Low-sulfur coal to high-sulfur coal with SCR+FGD → significant increase in ADP corrosion



▶ Capital

- New Hybrid SNCR/SCR has slightly higher capital cost than conventional SCR

▶ O&M

- Increased reagent usage is off-set by savings or avoided costs from lower NH<sub>3</sub> slip & SO<sub>3</sub> emissions than SCR



- ▶ Determine the “fate” of  $\text{NH}_3$  slip &  $\text{SO}_3 \rightarrow$  as the flue gas goes thru the air heater, ESP & FGD
- ▶ Measure the catalyst activity of each layer on a regular basis  $\rightarrow$  correlate total catalyst activity with  $\text{NH}_3$  slip as a function of time
- ▶ Determine the best method to off-set the increased ADP corrosion