REINHOLD ENVIRONMENTAL Ltd.

2011 NOx-Combustion Round Table & Expo Presentation

February 7-8, 2011, in Birmingham, AL / Hosted by Southern Company

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Meeting the World Energy Challenge.

Reinhold Environmental LTD.
2011 NOx-Combustion / PCUG Conference

SCR Catalyst Regeneration

February 7, 2011

Michael F. Mattes
Chief Operating Officer

Agenda

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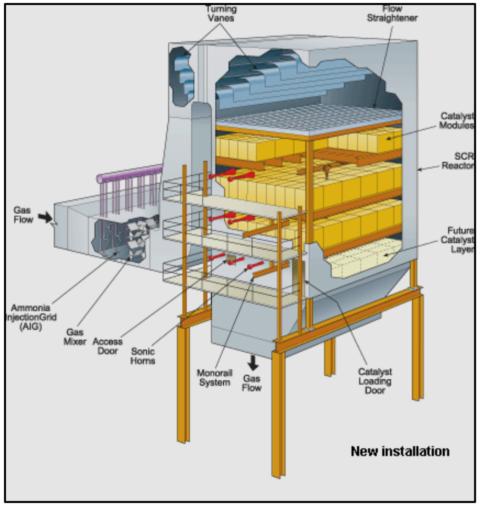
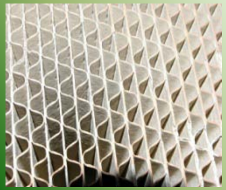
- Anatomy of SCR Catalyst
- Common Catalyst Processing Terms
- Deactivation Mechanisms
- How Regeneration Work?
- Regenerated Catalyst Performance
- Operating Experience with Regenerated Catalyst
- Factors to Consider When Purchasing SCR Catalyst



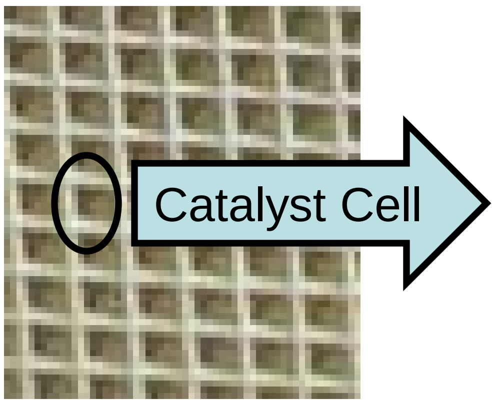


Anatomy of SCR Catalyst

Reaction Zones

Diffusion Controlled
DeNOx and Hg Region
0 to ~0.2 mm

Catalyst Pore



Honeycomb Element

Kinetically Controlled
SO_2 Oxidation Region
~0.2 - 1.0 mm.
"Low NH_3"

Flue Gas Residence Time ~ 0.15 seconds per Layer

Pore Size - Angstroms

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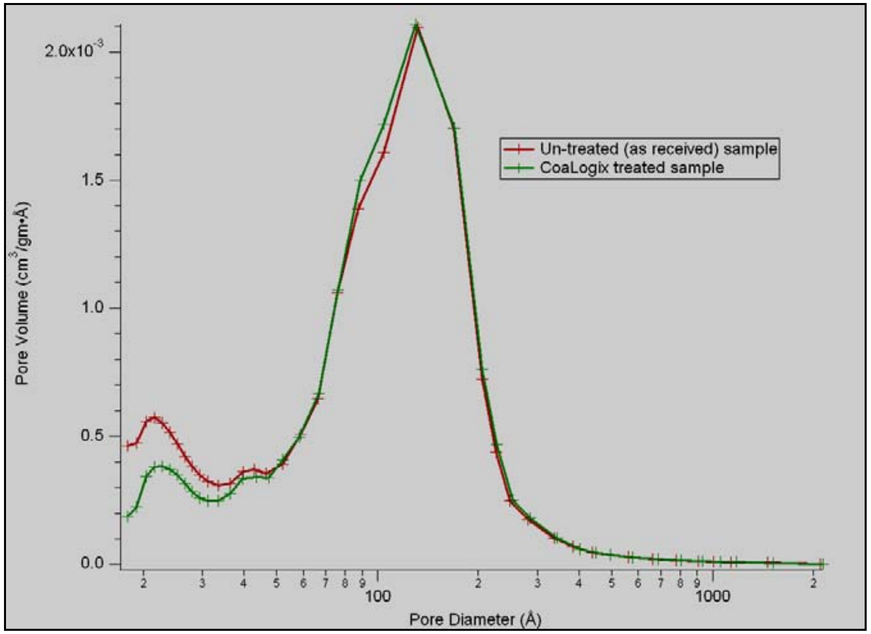

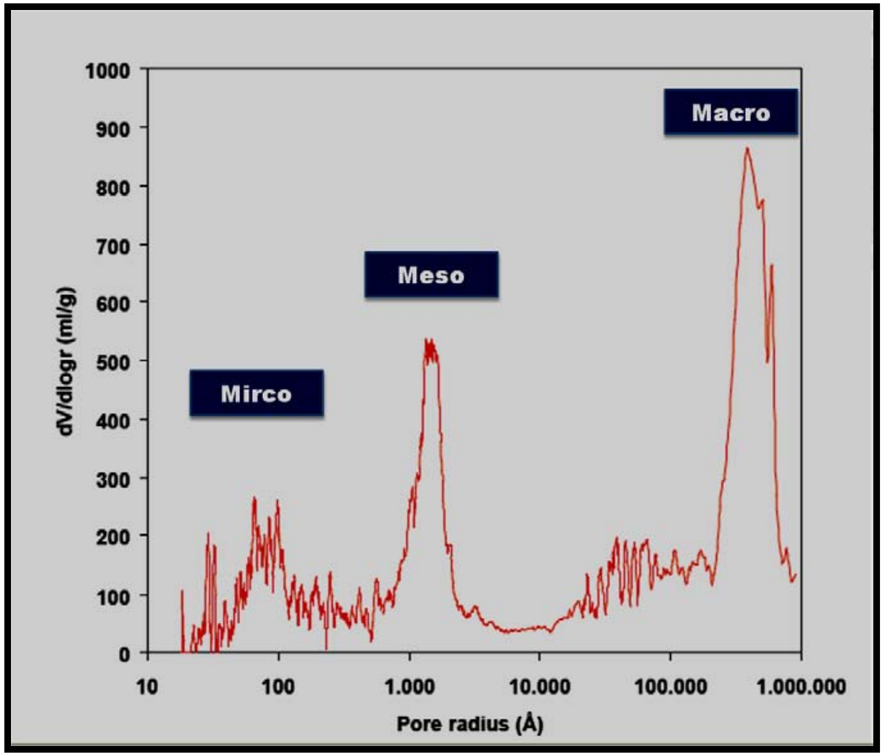

Varies by Manufacturer

Pore Sizes

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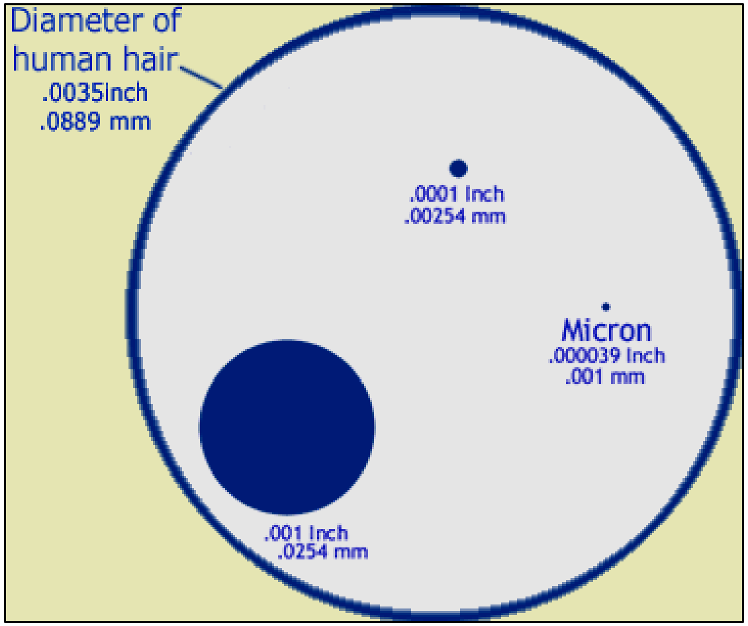
Pore Classification		Pore Size	
		Angstroms	Microns
Micro	Smallest	30	0.003
Meso	Medium	500	0.05
Macro	Largest	1,000	0.1
NO_x Molecule		8	0.0008



Human Hair ~ 900,000 Angstroms

Catalyst Surface Area

	Catalyst Surface Area	
Catalytic Surface Area	**65**	**Sq. Meters / Gram**
Visible Specific Area	**480**	**Sq. Meters / Cubic Meter**

Catalyst Surface Area

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	Catalyst Surface Area			
	Metric Units		English Units	
Catalytic Surface Area	65	Sq. Meters / Gram	19,845	Sq. Feet / Ounce
Visible Specific Area	480	Sq. Meters / Cubic Meter	45	Sq. Feet / Cubic Feet
Catalyst Volume	2.10	Cubic Meters / Module	74.2	Cubic Feet / Module
Catalyst Weight	680	Kilograms / Module	1,500	Lbs / Module
Visible Surface Area	1,008	Square Meters / Module	10,846	Sq. Feet / Module
Catalytic Surface Area	44,226,000	Sq. Meters / Module	476,291,400	Sq. Feet / Module
Ratio Catalytic to Visible Surface Area			~44,000 to 1	

650 Mw Unit has ~ 10,000 Sq. Miles of Catalytic Surface Area

10,000 Square Miles

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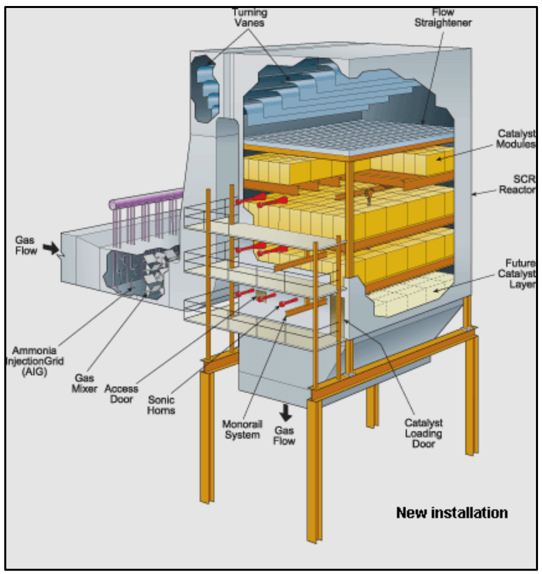
OEM Magic of Calcination

Common Catalyst Processing Terms



Common Terms

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Term	Definition
Dry Mechanical Cleaning	Utilizes compressed air and vacuum to removed loose fly ash.
Rejuvenation	Wet process to primarily remove “physical “ pluggage. No addition of active ingredient(s).
Regeneration	Wet process to remove desired compounds (decay chemicals and/or active ingredients). Followed by re-impregnation of active ingredient(s) .
Re-impregnation	Addition of active ingredient(s). May be one or more ingredients applied separately or simultaneously.
Drying	Removes free water. Normally at temperatures < 250 ^{o} F.
Heat Treatment	Removes the required bound water and properly activates the added active ingredient(s). Temperature varies by regeneration process used.
Calcination	One time event performed by catalyst OEM’s to produce its “catalytic” surface area, strength and performance properties.

Temperature Zones

Avoid OEM Calcination Temperatures

Common Terms

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Term	Symbol	Units	Definition
DeNOx Activity	K	m/hr	K = P*AV Analogy - Speed of a car
Area Velocity	AV	m/hr	AV = Flue Gas Flow / Visible Catalyst Surface Area Analogy - Inverse of residence time
Potential	P	Unitless	P = -ln (Fraction Nox Remaining) Analogy - Distance a car can travel Very useful tool in catalyst management Potential being a log function is additive Key to predicting SCR performance over time

Typical SCR Decay Curve

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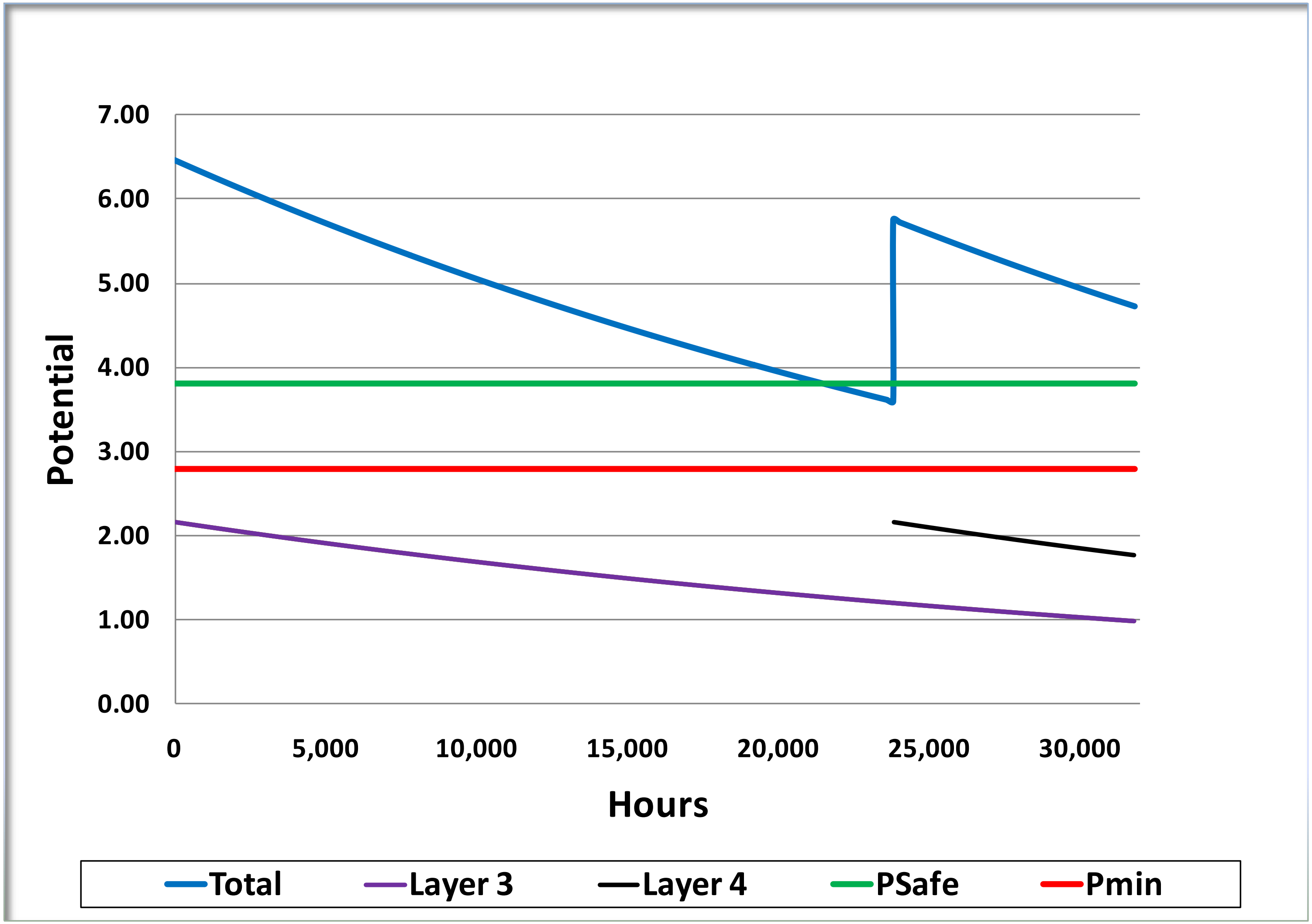

Area Velocity

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$$\underset{(m/hr)}{\text{Area Velocity (AV)}} = \underset{(Nm^3/hr)}{\text{Flue Gas Flow}} \div \underset{(m^2)}{\text{Catalyst Visible Surface Area}}$$

$$\underset{(m/hr)}{K} = \underset{(\text{unitless})}{P} * \underset{(m/hr)}{AV}$$

Area Velocity High – Residence Time in Catalyst Low

Potential

$$Potential = -\ln\left[1 - \left[\frac{NOx_{in} - NOx_{out}}{NOx_{in}}\right]\right]$$

$$Potential = -\ln\left[1 - \left[\begin{matrix}\text{Fraction} \\ \text{NOx Removed}\end{matrix}\right]\right]$$

$$Potential = -\ln\left[\begin{matrix}\text{Fraction} \\ \text{NOx Remaining}\end{matrix}\right]$$

Example Calculations

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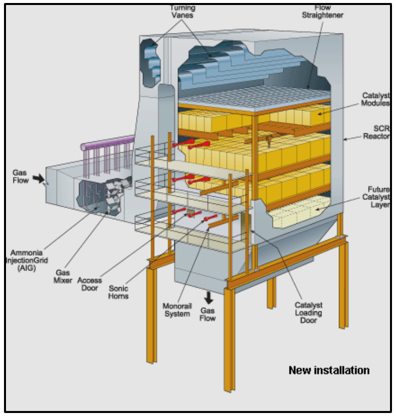
	Value	Units
Visible Surface Area	1,000	M^2 / Module
Modules	192	Per Layer
Visible Surface Area	192,000	M^2 / Layer
Flue Gas Flow	2,880,000	Nm^3 / hr
Area Velocity (AV)	12.0	m / hr



Measured		Calculated			
NOx_{in}	NOx_{out}	NOx Remaining	NOx Removed	Potential = -ln (Nox Remaining)	K = P * AV
ppmvd	ppmvd	Fraction	%	Unitless	m / hr
500	150	0.30	70%	1.20	14.4
500	100	0.20	80%	1.61	19.3
500	50	0.10	90%	2.30	27.6
500	25	0.05	95%	3.00	35.9
500	15	0.03	97%	3.51	42.1

Potential is a Better Measure of Catalyst Performance

Potential Vs % NOx Removal

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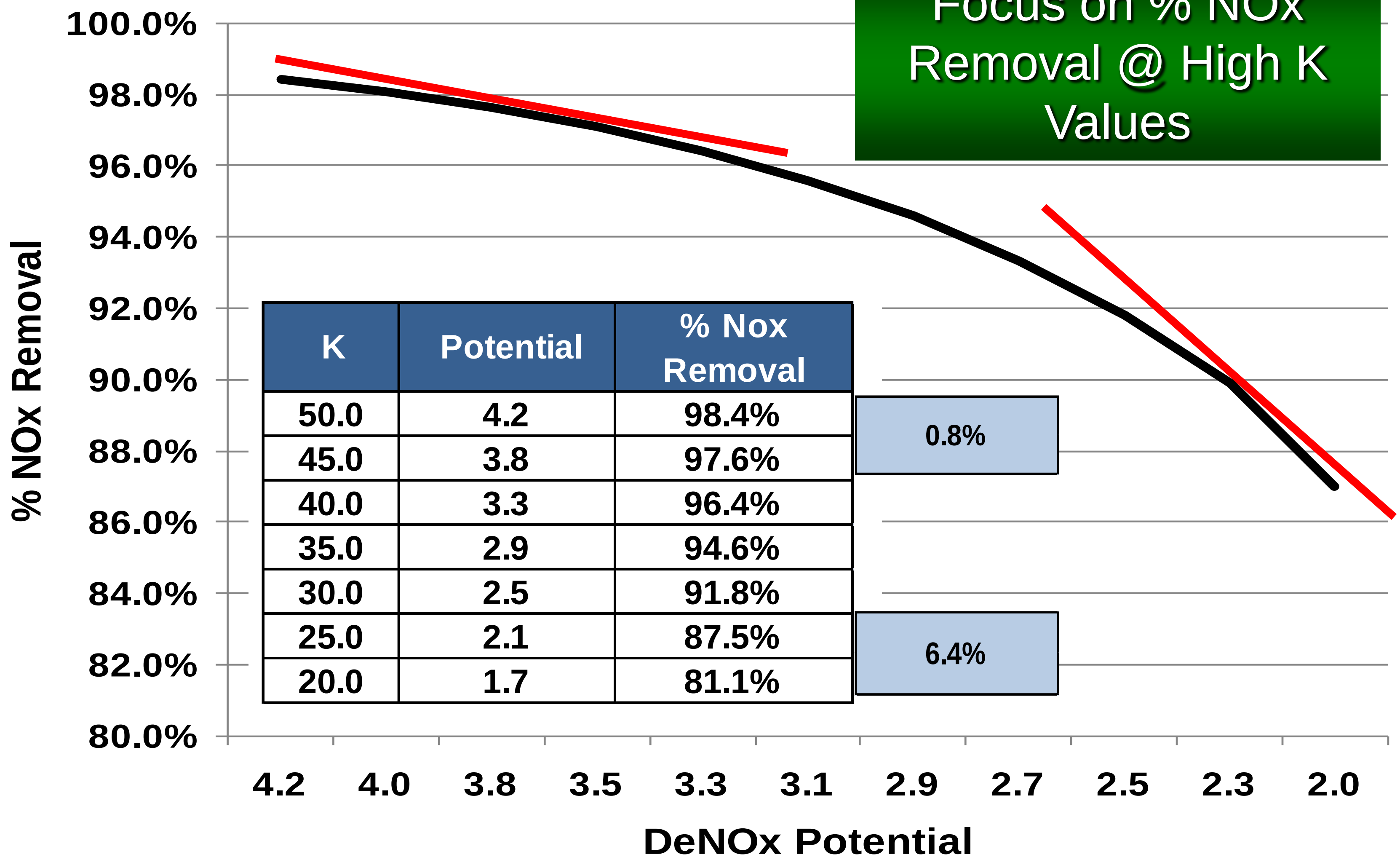
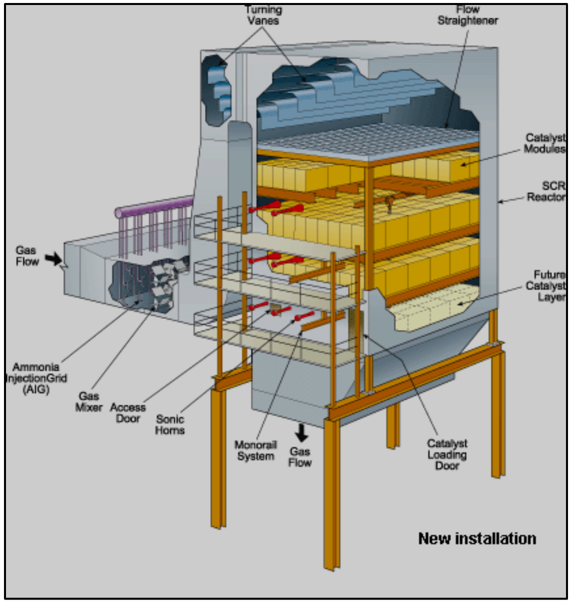
Focus on % NOx Removal @ High K Values



K	Potential	% Nox Removal
50.0	4.2	98.4%
45.0	3.8	97.6%
40.0	3.3	96.4%
35.0	2.9	94.6%
30.0	2.5	91.8%
25.0	2.1	87.5%
20.0	1.7	81.1%

Deactivation Mechanisms



SCR Prime Reactions

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Positive Reactions:

NO_x Reduction	$NO + NH_3 + 1/4\ O_2 \rightarrow N_2 + 3/2\ H_2O$
Hg Oxidation	$Hg + 2\ HCl + 1/2\ O_2 \rightarrow HgCl_2 + H_2O$

Negative Reactions:

SO_2 Oxidation	$SO_2 + 1/2O_2 \rightarrow SO_3$
$HgCl_2$ Reduction by NH_3	$HgCl_2 + NH3 + 1/4\ O_2 \rightarrow Hg + 2\ HCl + 1/2\ N2 + 1/2\ H_2O$
$HgCl_2$ Reduction by SO_3	$HgCl_2 + SO_2 + H_2O \rightarrow Hg + 2\ HCl + SO_3$

SCR Challenges

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	Parts per Million			Parts per Billion			Ratio to Hg $^{2+}$ Concentration		
	Inlet SCR	Exit SCR	FGD Outlet	Inlet SCR	Exit SCR	FGD Outlet	Inlet SCR	Exit SCR	FGD Outlet
SO_2	2,500	2,475	124	2,500,000	2,475,000	123,750	1,250,000	412,500	1,237,500
SO_3	25	50	30	25,000	50,000	30,000	12,500	8,333	300,000
NO_x	500	75	75	500,000	75,000	75,000	250,000	12,500	750,000
Hg^0	0.08	0.02	0.03	8	2	3	4	0	30
Hg2+	0.02	0.06	0.00	2	6	0.1	1	1	1
Hg Total	0.10	0.08	0.03	10	8	3	5	1	31

SCR's Performing Beyond Original Design

SCR Vs Catalyst Performance

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	Primarily Affected By		
SCR Performance	Catalyst Performance	Catalyst Decay Rate	Flue Gas Impurities
			Operating Conditions
		Temperature	
		Flue Gas Velocity	
		SO_3 Concentration - 0 to 10ppm	
		NH_3 Concentration < 1.0 Mole Ratio	
	% Catalyst Pluggage		
	% Flue Gas By-pass		

SCR Catalyst Deactivation: Physical

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- **Thermal sintering**
  - **Excessive temperature > 900 º F**
  - **Leads to loss in catalytic surface area**
  - **Not common in coal fired units**

- **Mechanical erosion**
  - **< 30% pluggage - Minor**
  - **> 30% to 50% pluggage - Significant**
  - **>50% pluggage – Very Severe**

Irreversible

SCR Catalyst Deactivation: Physical

- **Catalyst plugging**
  - **Fly ash near inlet wall**
  - **LPA / "popcorn ash"**
  - **Often the controlling decay mechanism**
  - **Easily detected**

- **Pore mouth blinding**
  - **Silica & aluminum-silicate**
  - ***$CaSO_4$***
  - ***$CaCO_3$***
  - **A common form of activity loss**

Reversible

SCR Catalyst Deactivation: Poisons

- Alkaline metal (Na, K)

- Phosphorous
  - High phosphorous coals fired in "reducing environment" (low NOx burners) generated PX_3 species that actively poison V_2O_5 V-P complex

- Arsenic – 2 mechanisms
  - Gaseous arsenic (As_2O_3) condenses in catalyst pore
  - Further oxidation to solid As_2O_5 to permanently plugs pore mouth
  - Combines with vanadium to form inactive V-As species

Reversible

SCR Catalyst Pluggage

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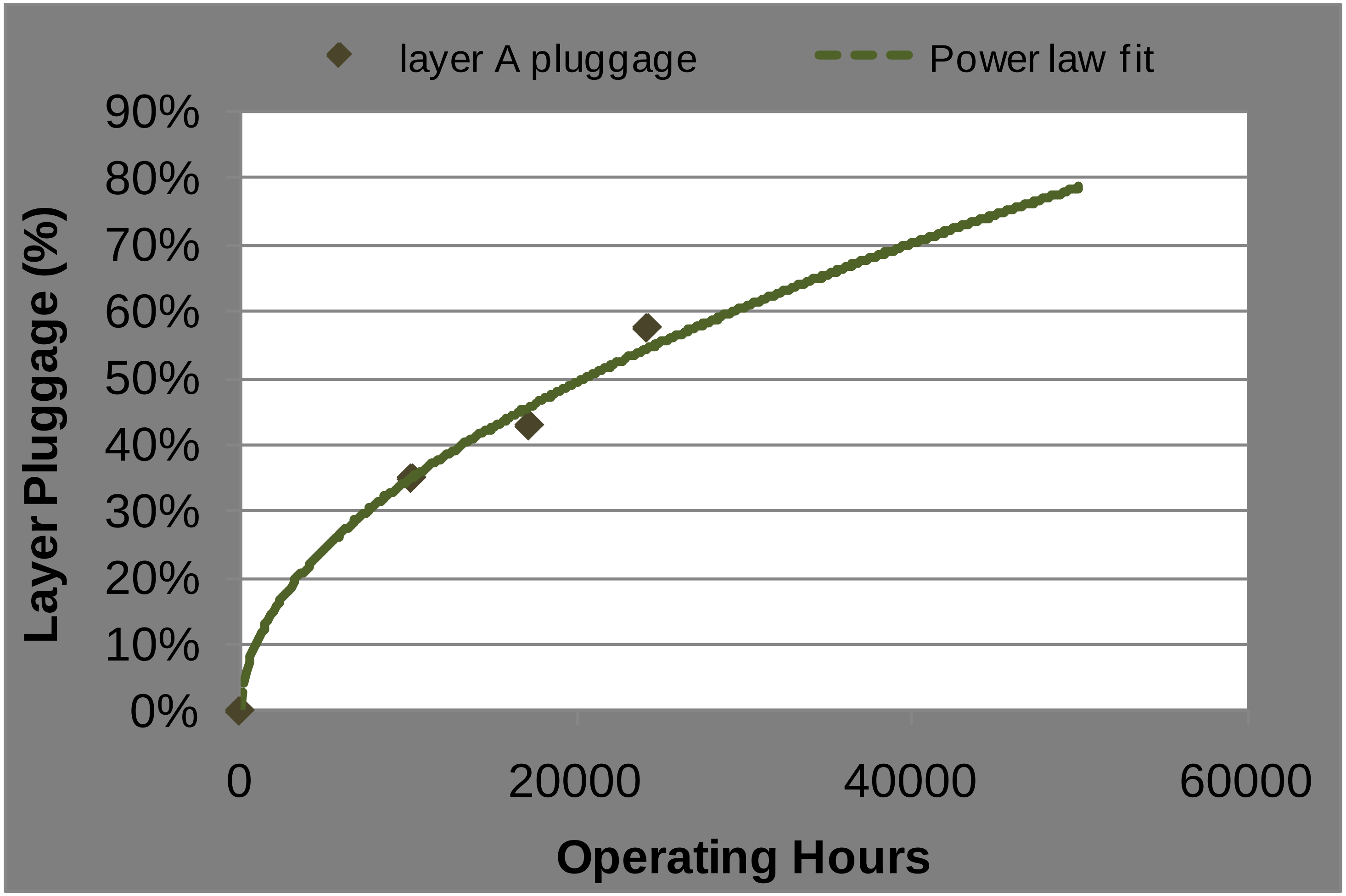

Pluggage – Increases erosion

Affect of SCR Pluggage

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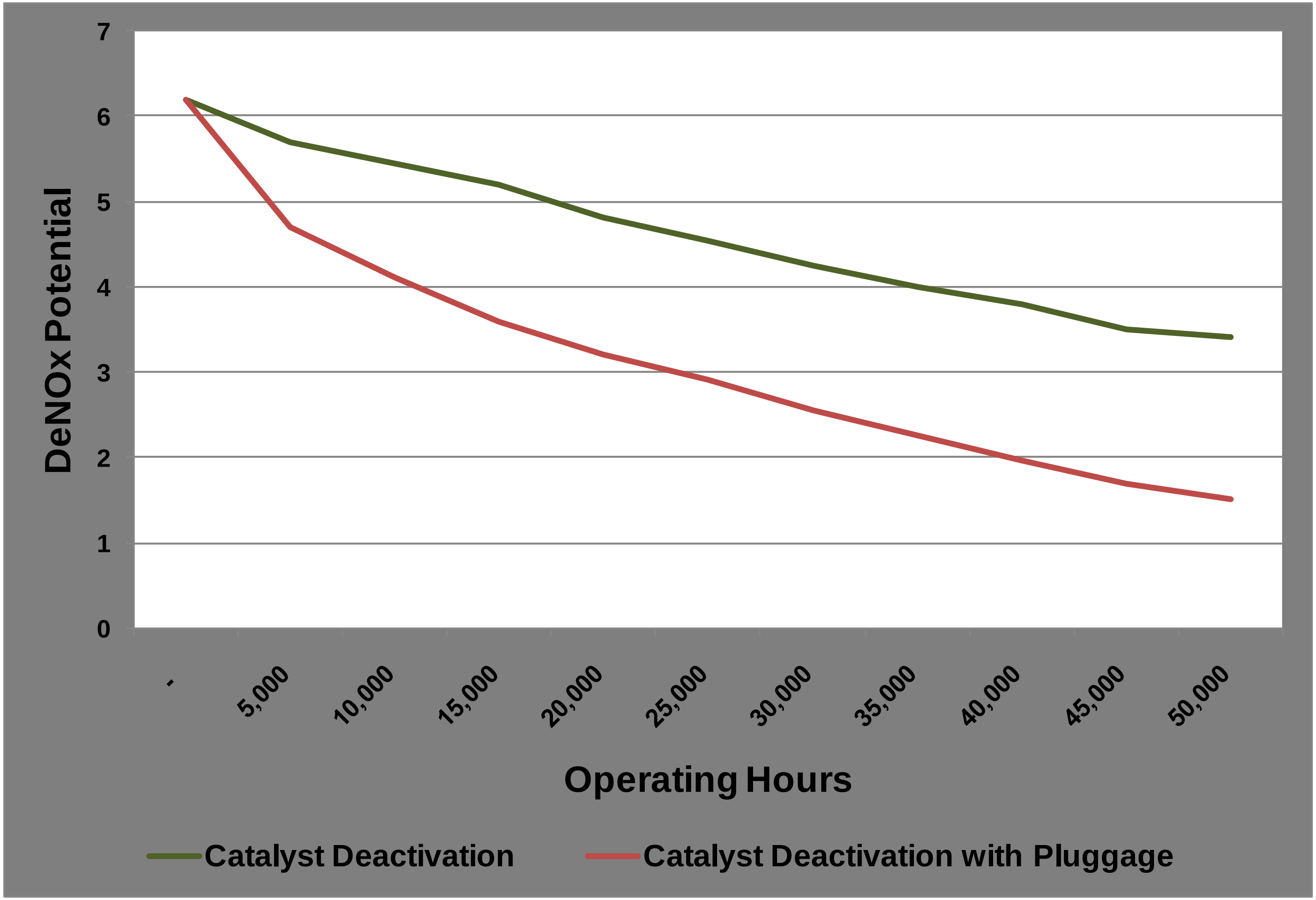

Affect of SCR Pluggage

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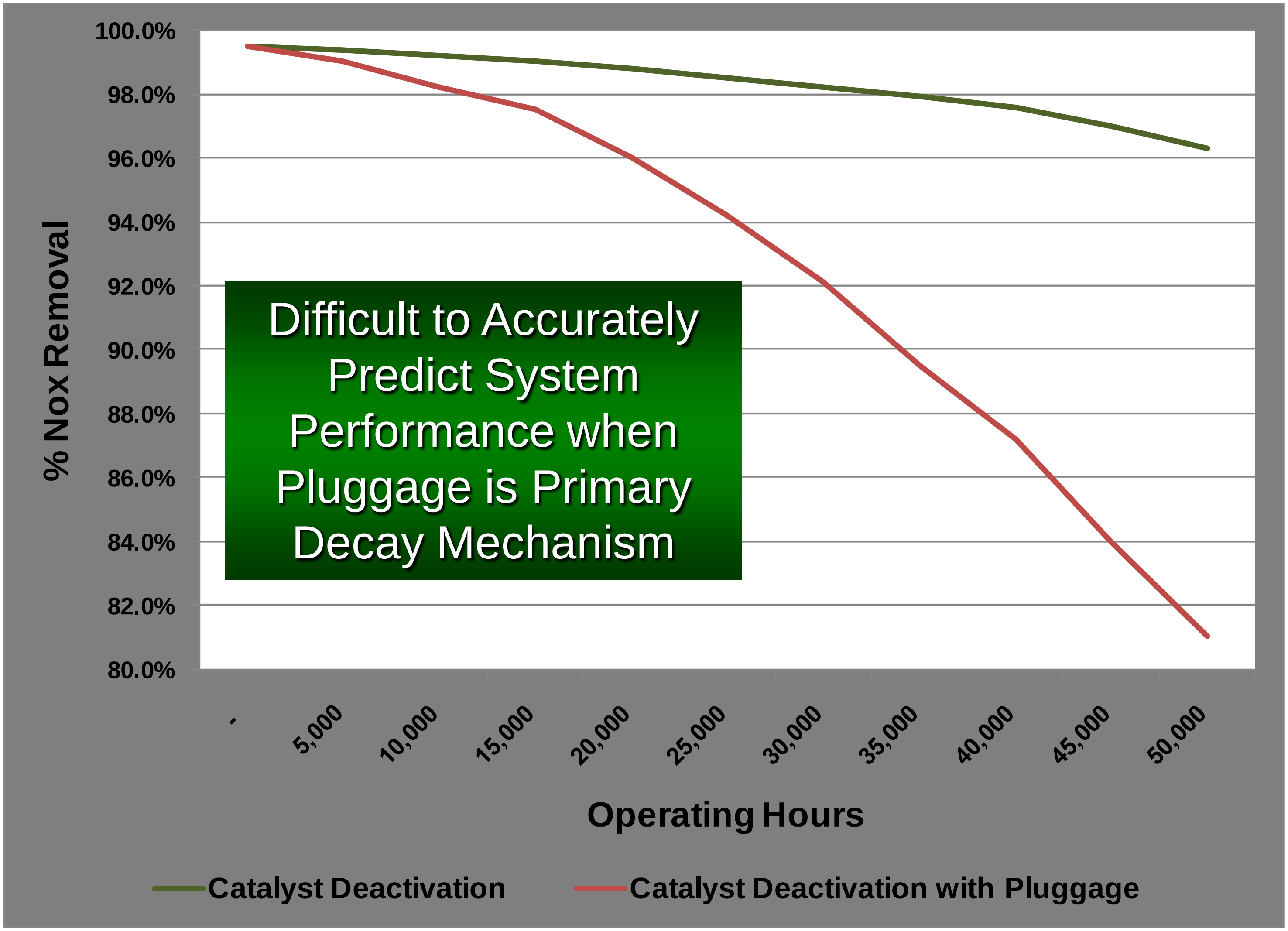

Affect of NH_3 Imbalance

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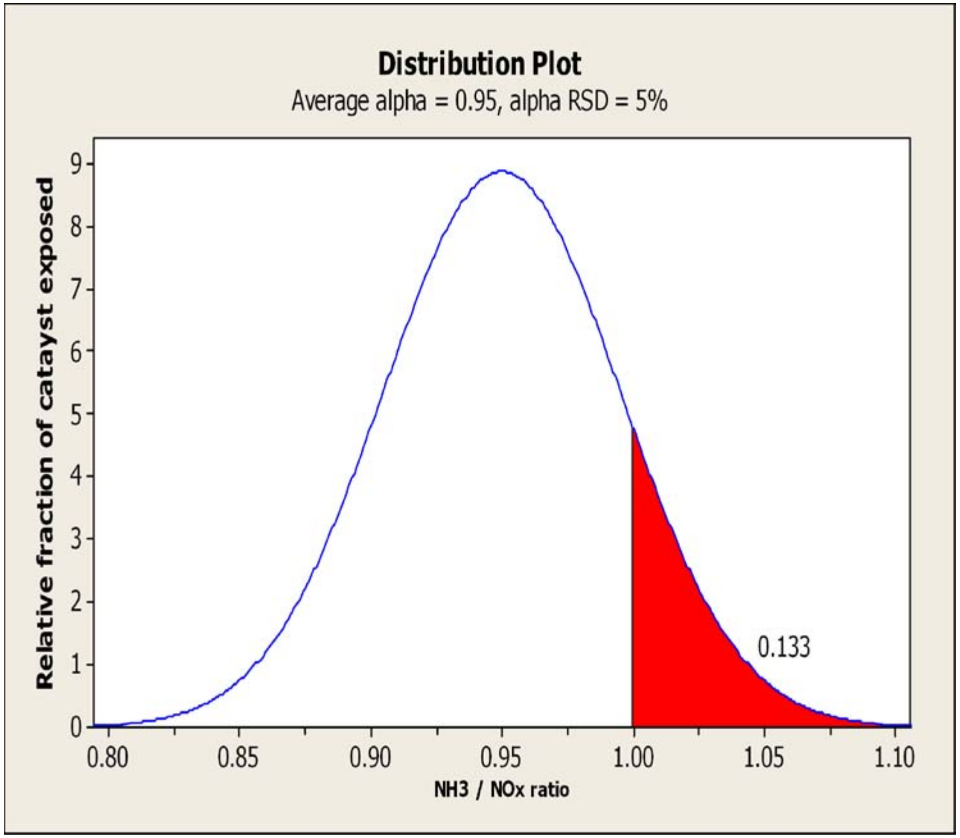
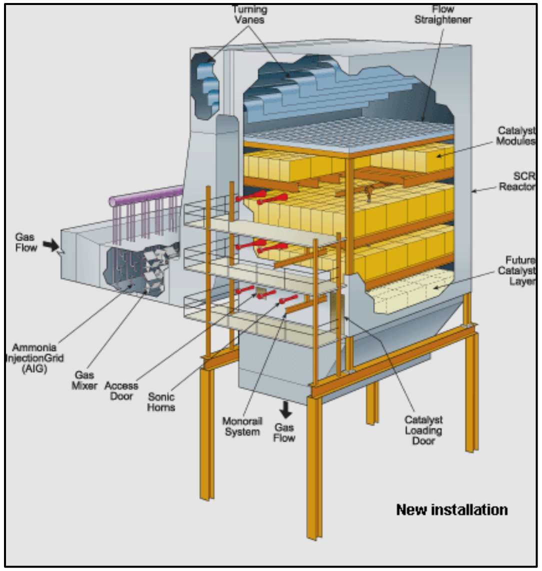


% NH3 Imbalance	Actual % Nox Removal	
0%	90%	
5%	90%	Normal Range
10%	88%	
15%	86%	
20%	83%	
25%	81%	
30%	78%	
35%	76%	
Base Efficiency	95%	
NH_3 Flow at 0.95 molar ratio		

NH3 Imbalance Affects DeNOx and NH3 Slip

How Does Regeneration Work?



How Does Regeneration Work?

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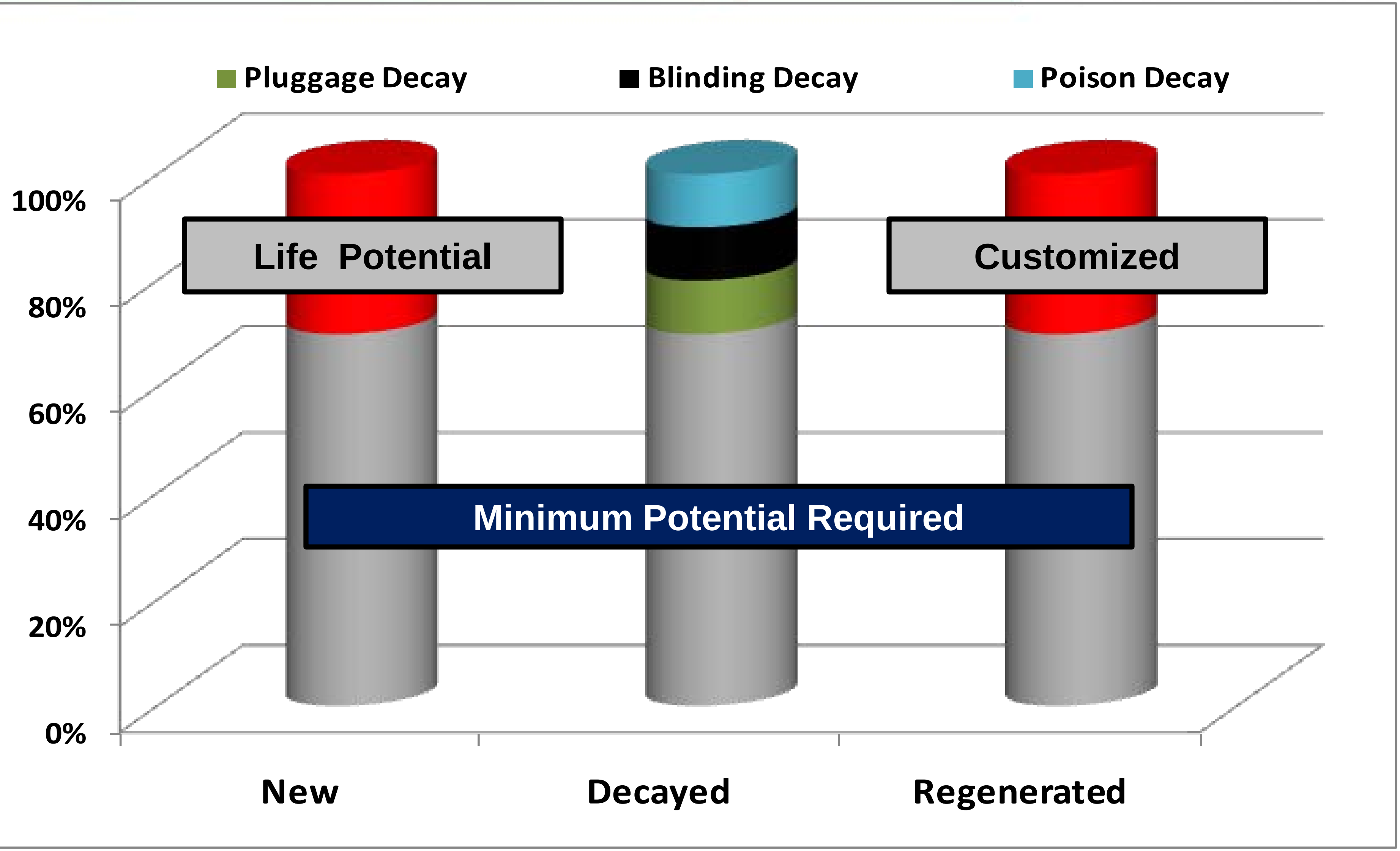

Regeneration Process

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Dry Mechanical Cleaning	**Plate catalyst disassembled. Can hold > 2,000 lbs. of fly ash**
Wet Chemical Treatment	**Precise control, mild chemicals, removes remaining physical pluggage**
Ultrasonic Treatment	**Utilized as required. Allows removal of difficult contaminants with mild chemicals.**
Pre-Drying	**Removal of all cleaning compounds and impurities. Critical to catalyst performance. Especially SO_2 conversion.**
Drying	**Removal of free water. Amount varies by catalyst type and size. Can be > 100 gallons per module.**

Regeneration Process

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Drying — Continuation

Re-impregnation — Customized to meet requested performance. Primarily places chemicals in the $DeNO_x$ and Hg oxidation vs. SO_2 Conversion zone.

Final Heat Treatment — Removes bound water, properly activates the added ingredient(s) and strengthens catalyst. Temperature varies by regeneration process used.

Repairs — Module casings and catalyst elements or cassettes.

Storage — Weather controlled. Capacity for > 12,000 modules.

Process Results

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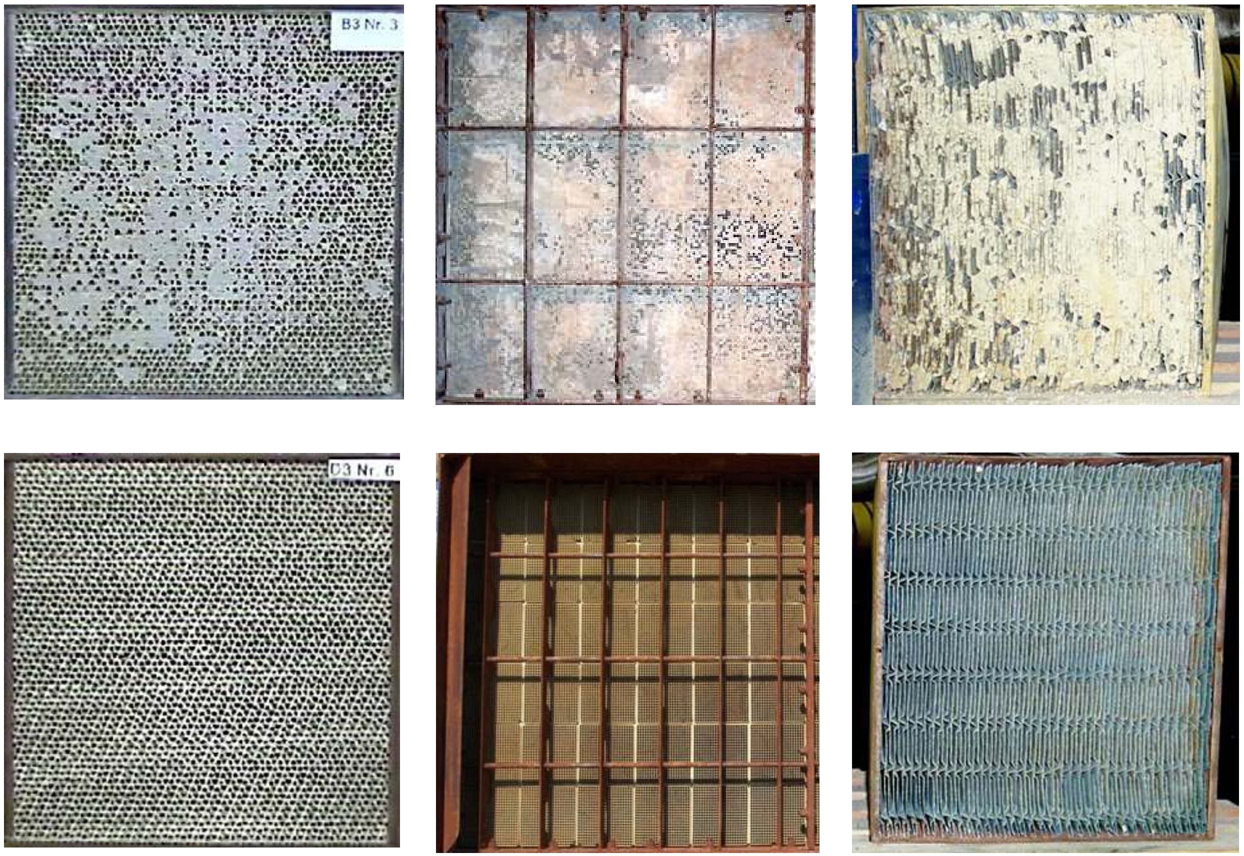
	Corrugated	Honeycomb	Plate
Before			
After			



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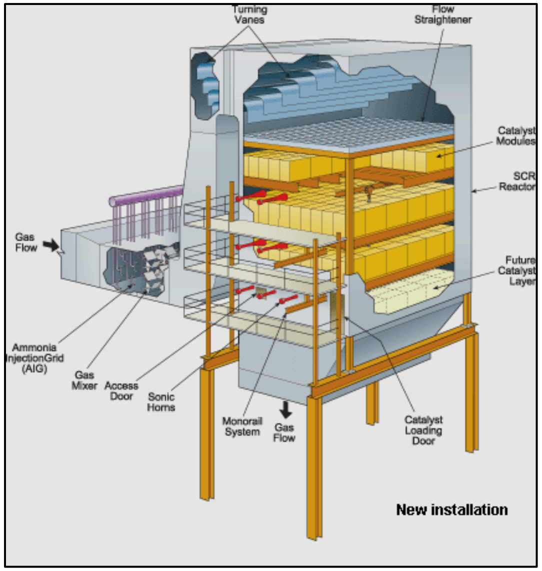
Regenerated Catalyst Performance



What to Expect?

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Performance equal to the original catalyst

- $DeNO_x$ Potential
- SO_2 conversion
- Hg oxidation – Need more data!
- Pressure drop - % pluggage < 5% per layer

Customized Performance

- Adjust active ingredient(s) for proposed operating conditions
- Can normally improve performance by placing active ingredient(s) in preferred reaction zone.

Re-impregnate catalyst based on where it is going

Mechanical Integrity

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- **Crush tests have significant variances**
  - **Sensitive to micro cracks**
  - **More important to guarantee condition of catalyst returned to customer**
- **Erosion tests more useful**
  - **Method very important**
  - **Good relative test**

°F	Ratio of Mass Removed			Average	Std. Dev.
	1	2	3		
400	0.89	1.07	0.93	0.96	0.09
600	0.92	0.83	0.98	0.91	0.08
800	1.07	1.02	0.87	0.99	0.10
Ratio is to a new control sample tested at the same time.					

What to Expect?

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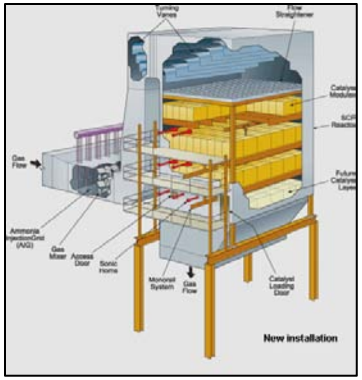
- **Same decay rates as original catalyst**
- **Testing capability**
- **Hot Regeneration - Ability to regenerate catalyst during your outage**



- **Brokering of catalyst**
- **Assist in disposal options**
- **Catalyst availability – Weeks with NOxAssure**
- **Storage**

Decay Rates vs. New

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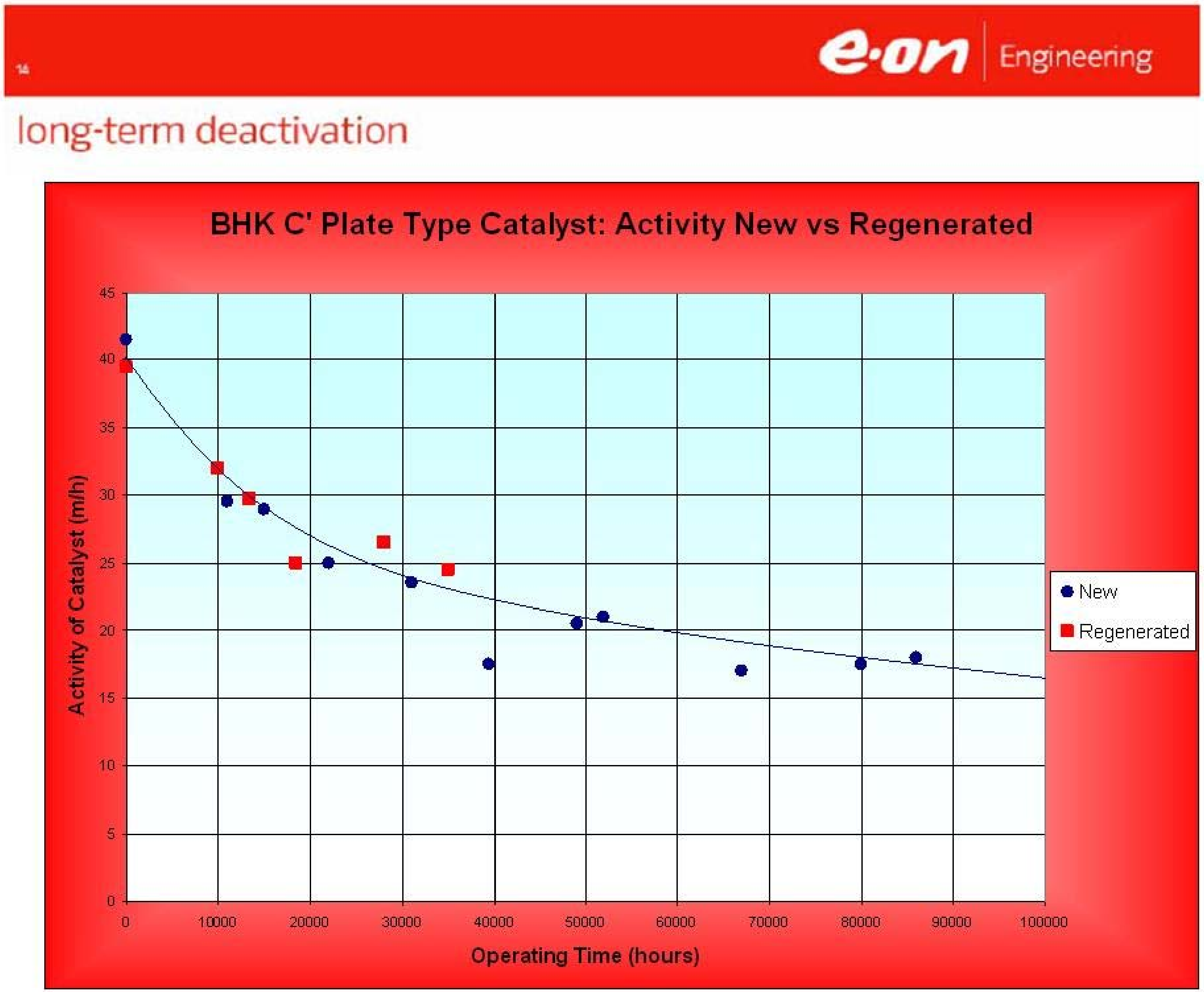

How Many Times for Regeneration?

- **Depends on:**
  - **% pluggage**
  - **Exposure to moisture**
  - **Handling - removal and installation**
  - **Location in SCR**

- **Ability to regenerate can be determine with annual inspections**

- **Bottom cassette layers will likely last longer**

Normally Assume 3 Regenerations for Budgets

Variations in Regeneration

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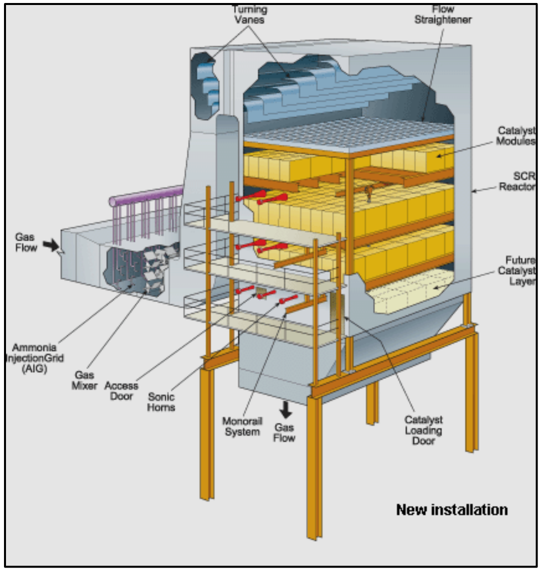
	Significance	Comments
Original Manufacturing	Low	OEM's have good AC/QC procedures
Exposure to Flue Gas	Low to High	% and rate of pluggage
Exposure to Moisture	Low to High	Air and tube leaks
		Shutdown and storage procedures
		Especially important for plate catalyst where "rusted iron" can be an issue for SO2 conversion
Catalyst Testing	Medium to High	Full bench vs. micro
		Extrapolation from standard operating conditions
		Stability of catalyst
		Inlet SO3 concentration - Can be very significant
		Molar ratio NH3 to NOx
		Sampling method, etc.

Operating Experience with Regenerated Catalyst



Regeneration Market Share

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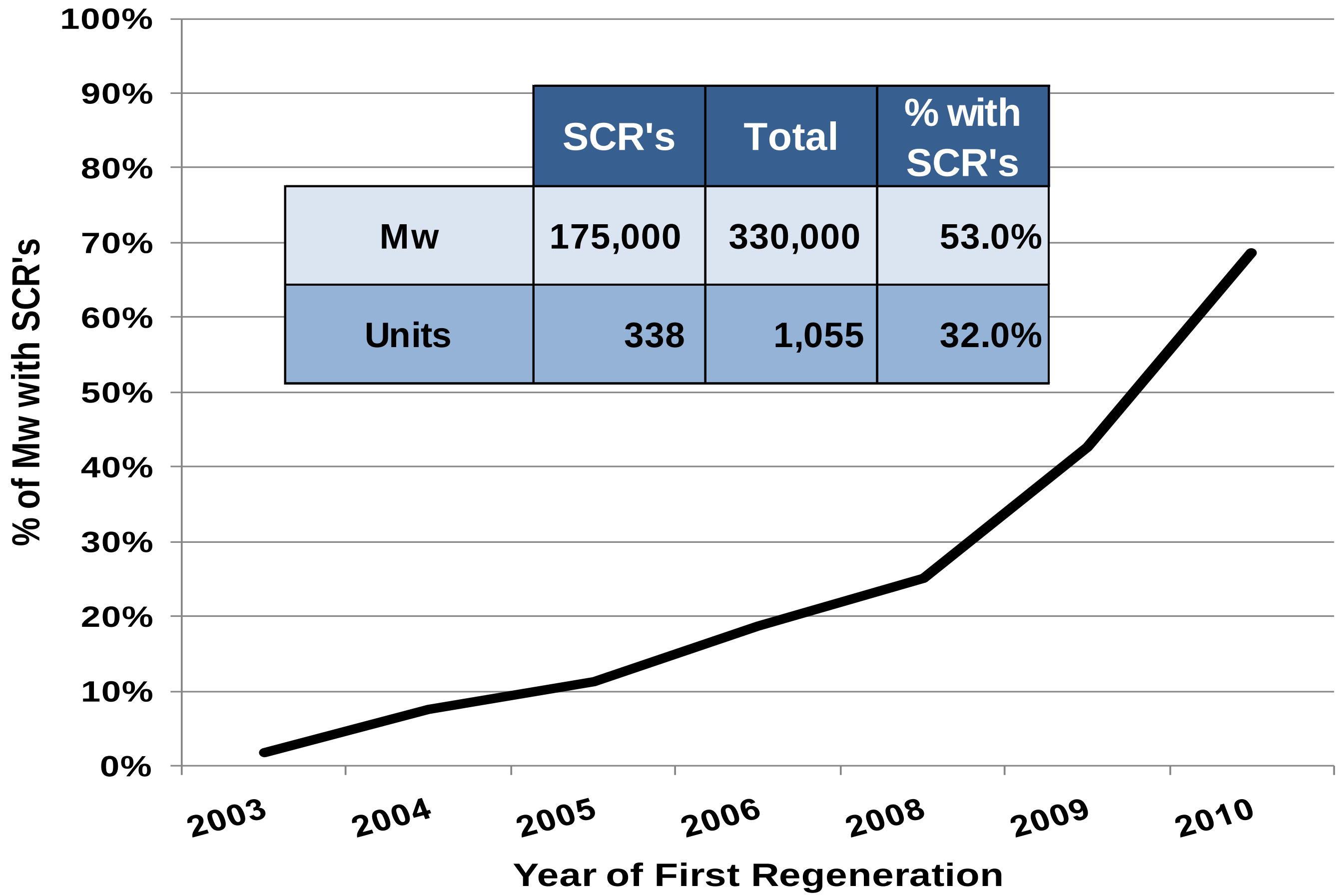

	SCR's	Total	% with SCR's
Mw	175,000	330,000	53.0%
Units	338	1,055	32.0%

70% of the Utilities with SCR's have Regenerated Catalyst

SCR-Tech Experience

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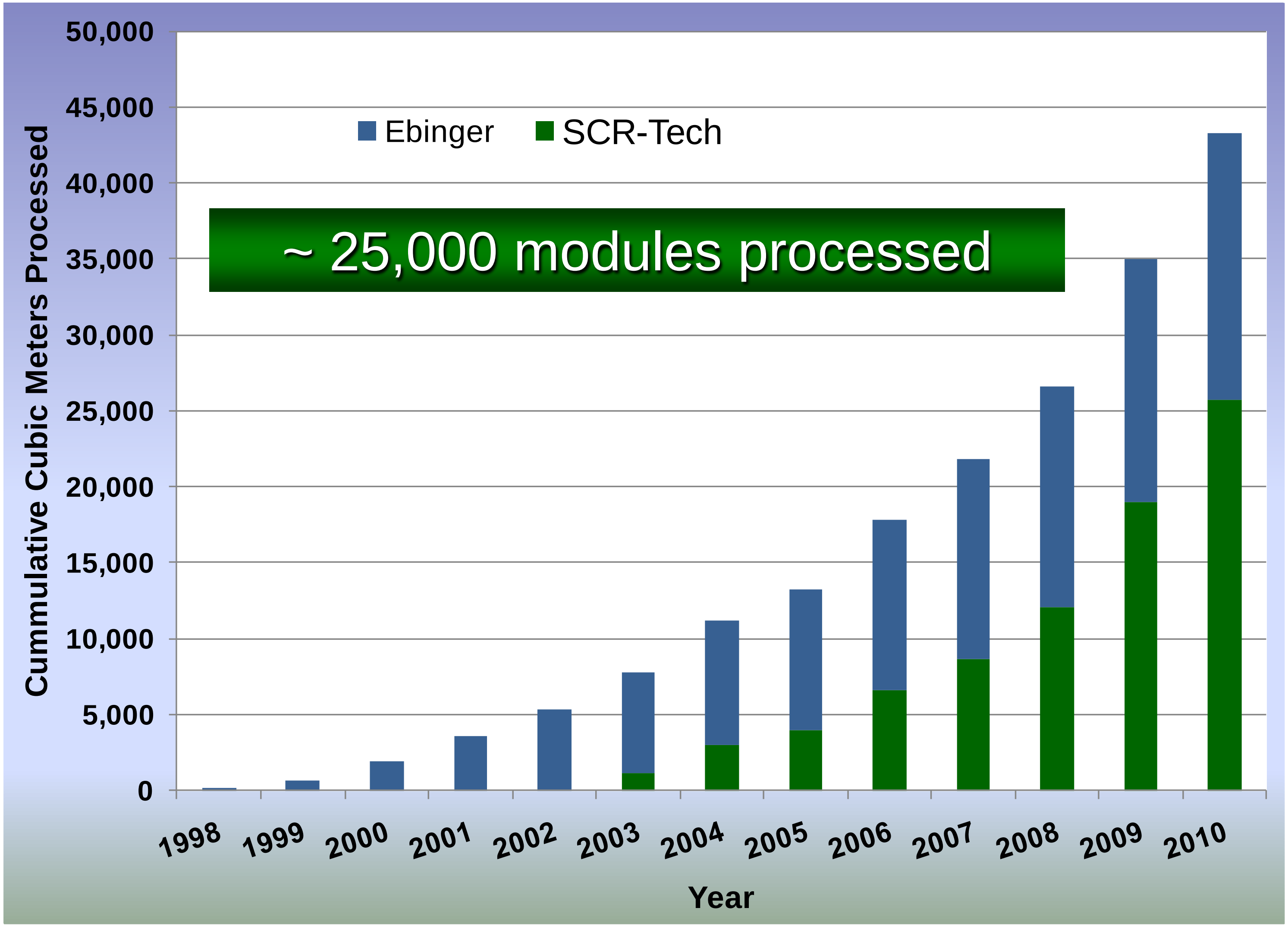

SCR-Tech Experience

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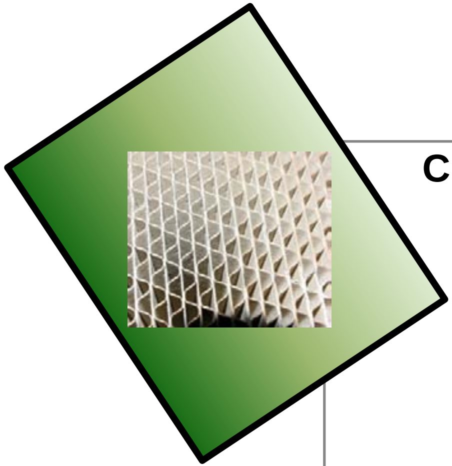
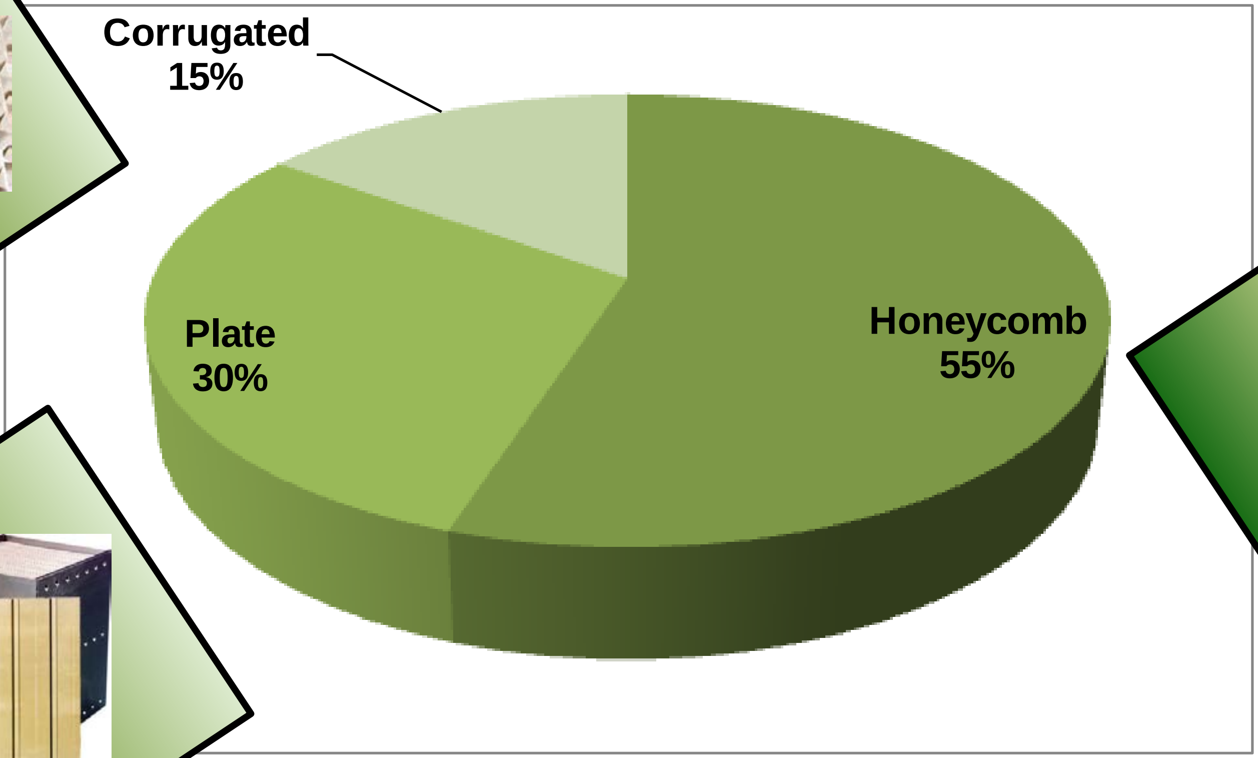
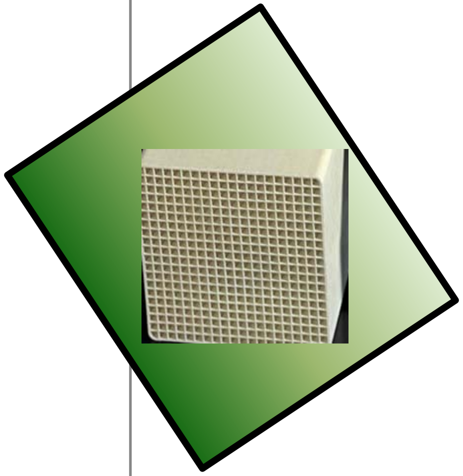
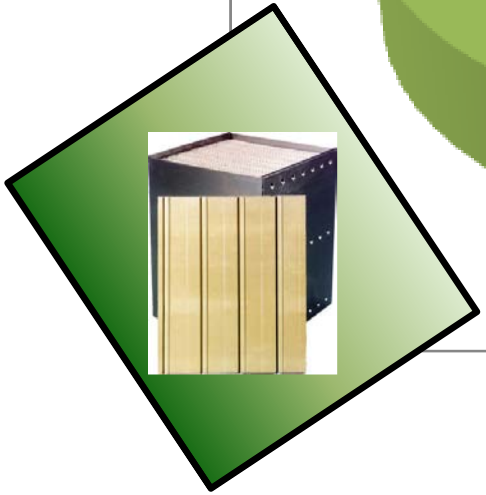
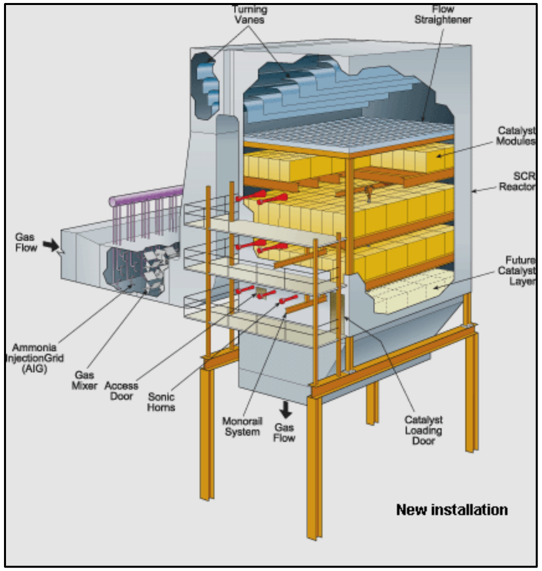








Factors to Consider When Purchasing SCR Catalyst



Factors to Consider

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Item	Comments
Pitch	Number one item
	Insure that pluggage will be <15%
Screen Size	Normally slightly smaller then "free opening" (pitch - wall thickness) of catalyst
	Screen pluggage can lead to catalyst erosion
Value	$ / potential, not $ per layer or $ / cubic meter
	Balance of performance - DeNOx, SO2 conversion, Hg oxidation, pressure drop, life
	Support, experience and technical expertise
Plate Catalyst	Know the quality of the mesh - 400 vs. 300 series stainless steel
	Can lead to future SO2 conversion issues

Summary

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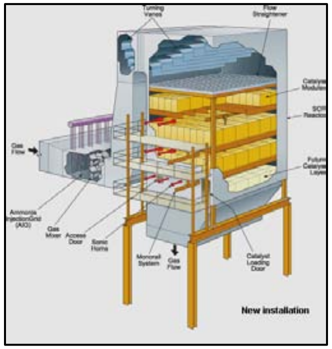
- **Regeneration is a proven technology**



- **Should be part of your overall catalyst management strategy**

- **Customized regeneration available to assist in catalyst management flexibility**

- **Brokering (selling or purchasing) previously owned catalyst may be a helpful option**

- **Regenerated catalyst can be available in weeks**

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Thank-you

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Michael F. Mattes
Chief Operating Officer