Meeting the World Energy Challenge.

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Fuel Impacts on SCR Catalysts is "Hot Topic" on June 30, 2011

THE McILVAINE COMPANY

www.mcilvainecompany.com

Brian Adair
Director of Technology Development
SCR-Tech, LLC, a CoaLogix Company

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Initial Considerations

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- **Coal is the largest operating expense for a power plant**
  - SCR catalyst is often considered the sacrificial expense for burning less expensive or not the original designed coal
- **For SCR System Performance**
  - Fly-ash loading
  - Pressure drop
  - DeNOx performance
  - Ammonia slip
  - Plugging
  - Flue gas temperature
  - Sulfur content in coal & SO_2 conversion
  - Poisons & blinding agents (e.g. As, Ca, Na, K, P …)
  - Next planned outage

SCR Catalyst Overview

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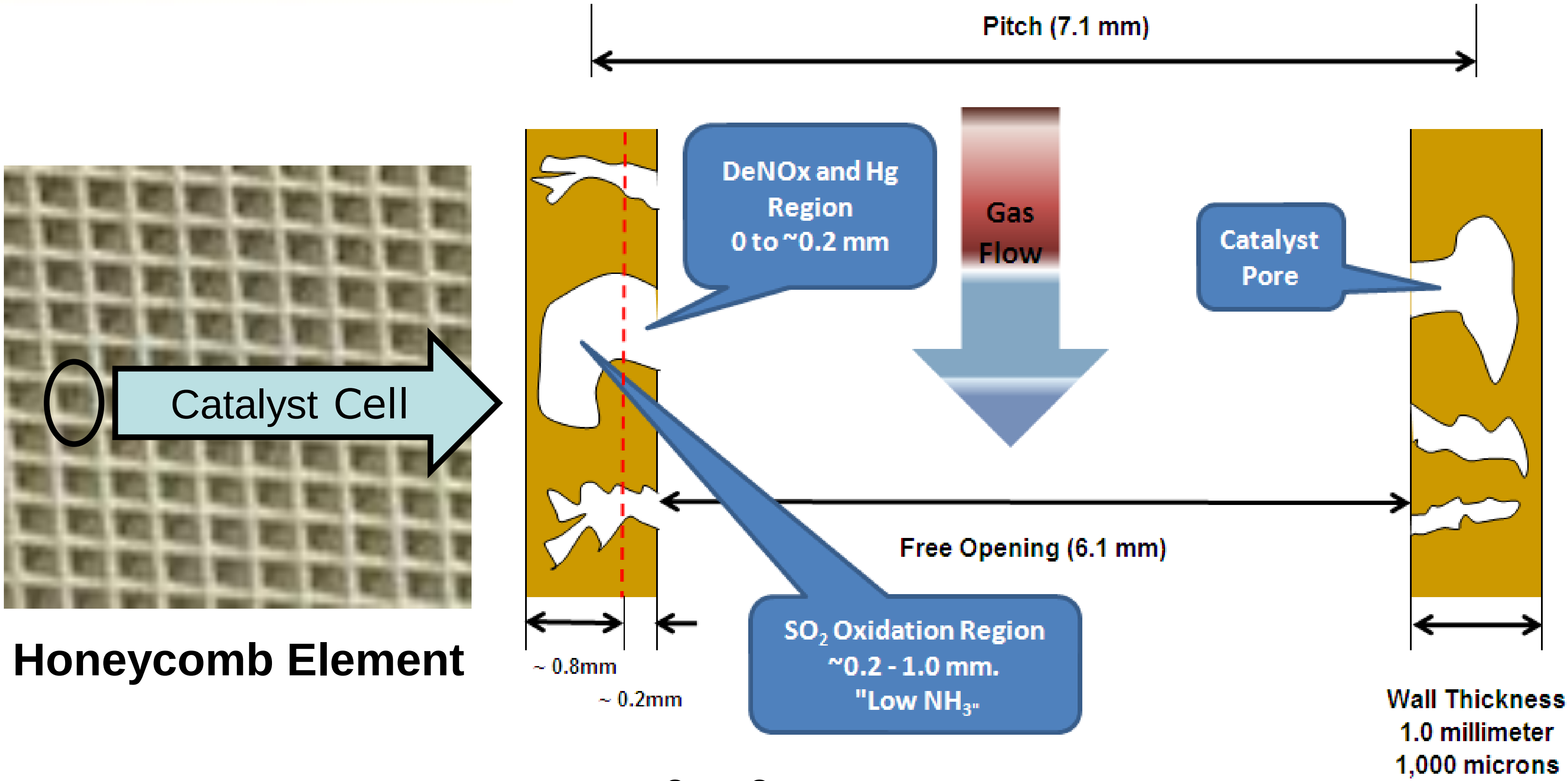
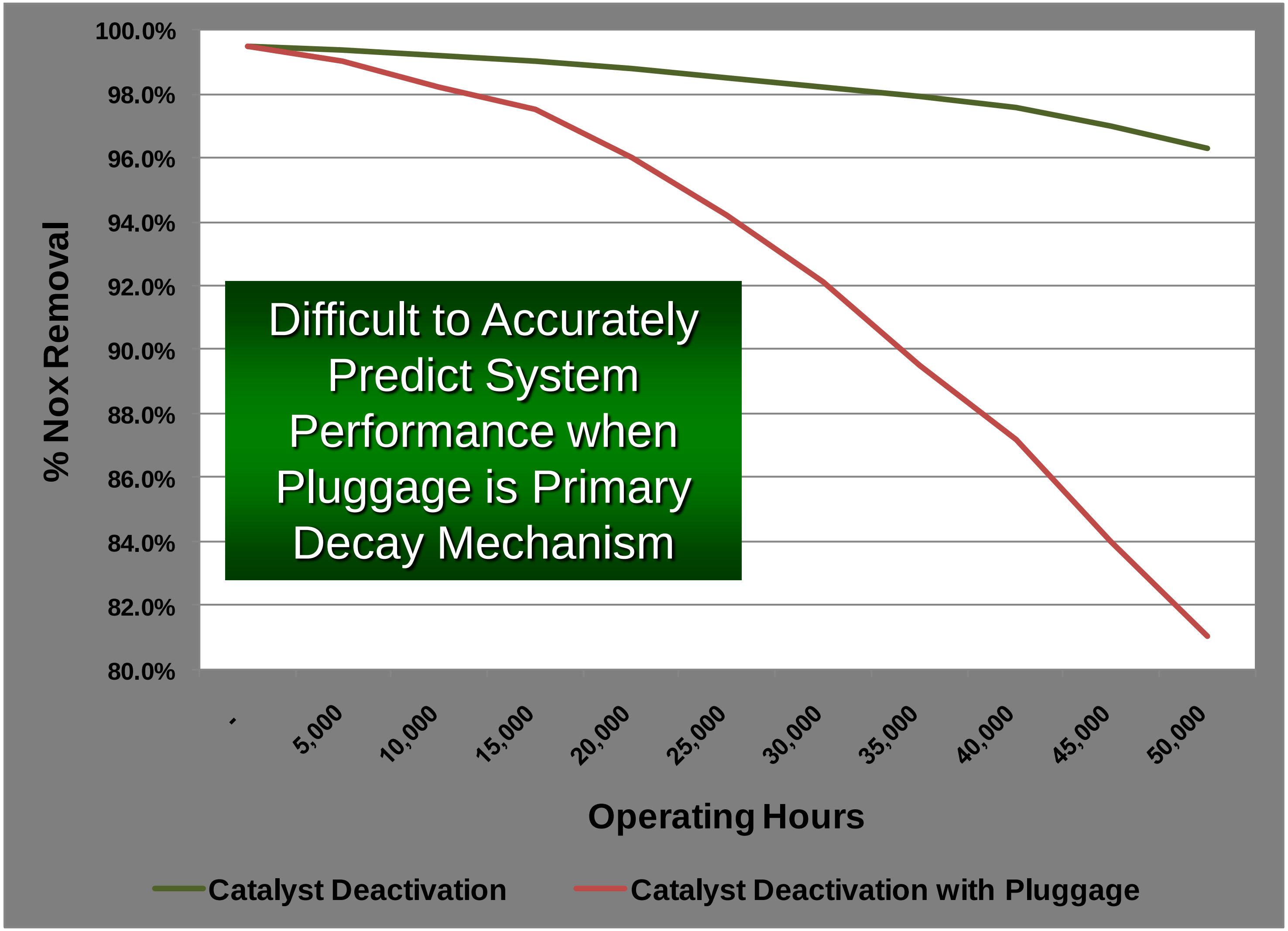


- Visible surface ~ 400 m^2/m^3
- Catalytic surface at 65 m^2/g
- 30 million m^2/m^3

Fuel Related Catalyst Deactivation Mechanism: Physical

- **Catalyst plugging**
  - Alkali and alkaline earth metals act as “flux” to reduce ash fusion temperature → large particle ash or LPA
  - LPA build-up cuts flow through catalyst channels
  - Fly-ash also can build up to block channels
  - Direct reduction in available catalyst surface
  - Easily detected (reversible *via* regeneration process)

Effect of SCR Pluggage



Plugging is Reversible

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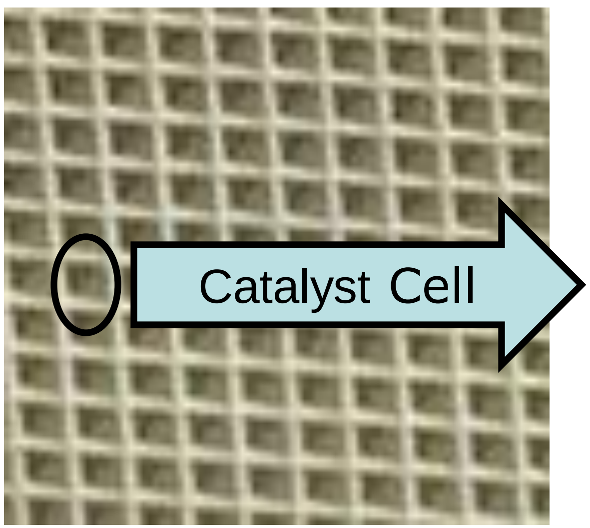
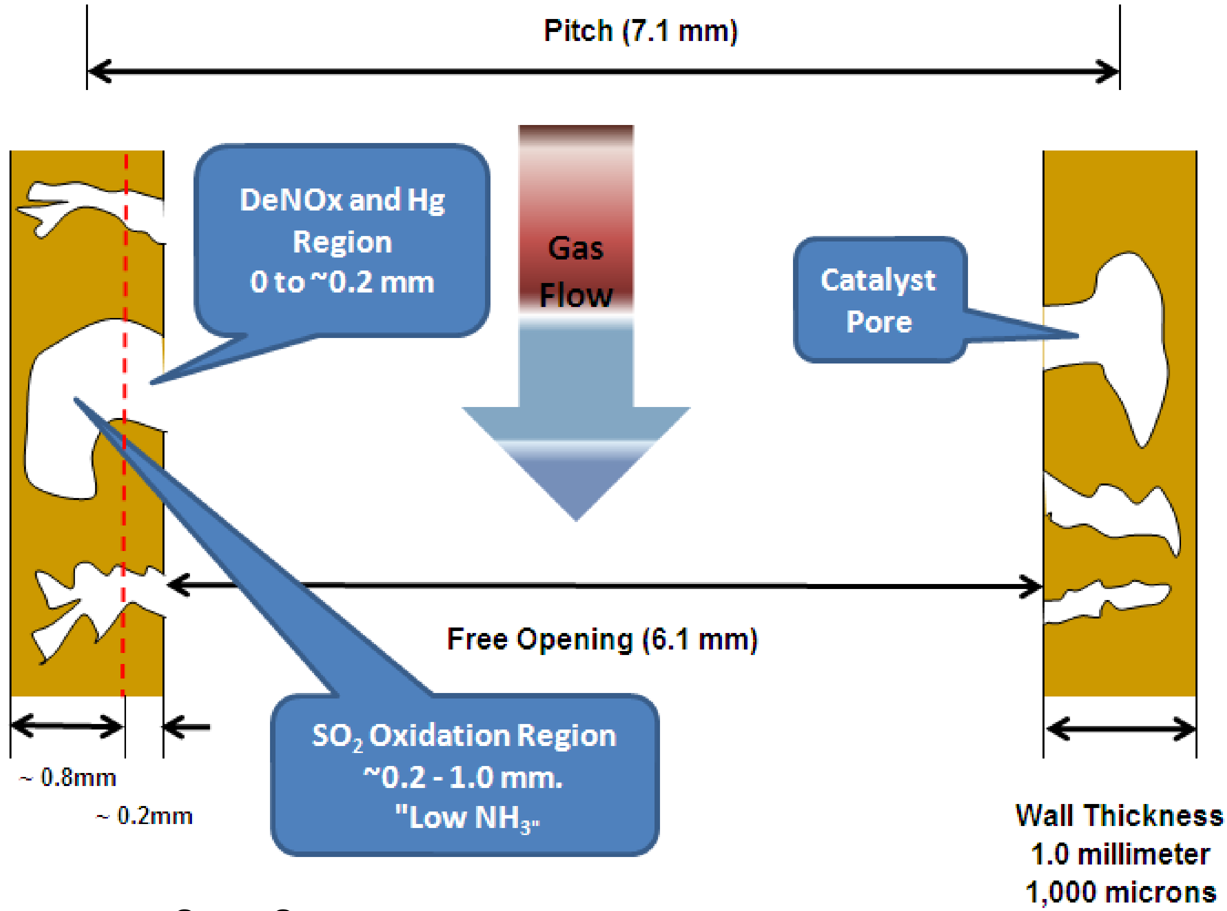
	Corrugated	Honeycomb	Plate
Before			
After			

SCR Catalyst Overview



Honeycomb Element



- Visible surface ~ 400 m^2/m^3
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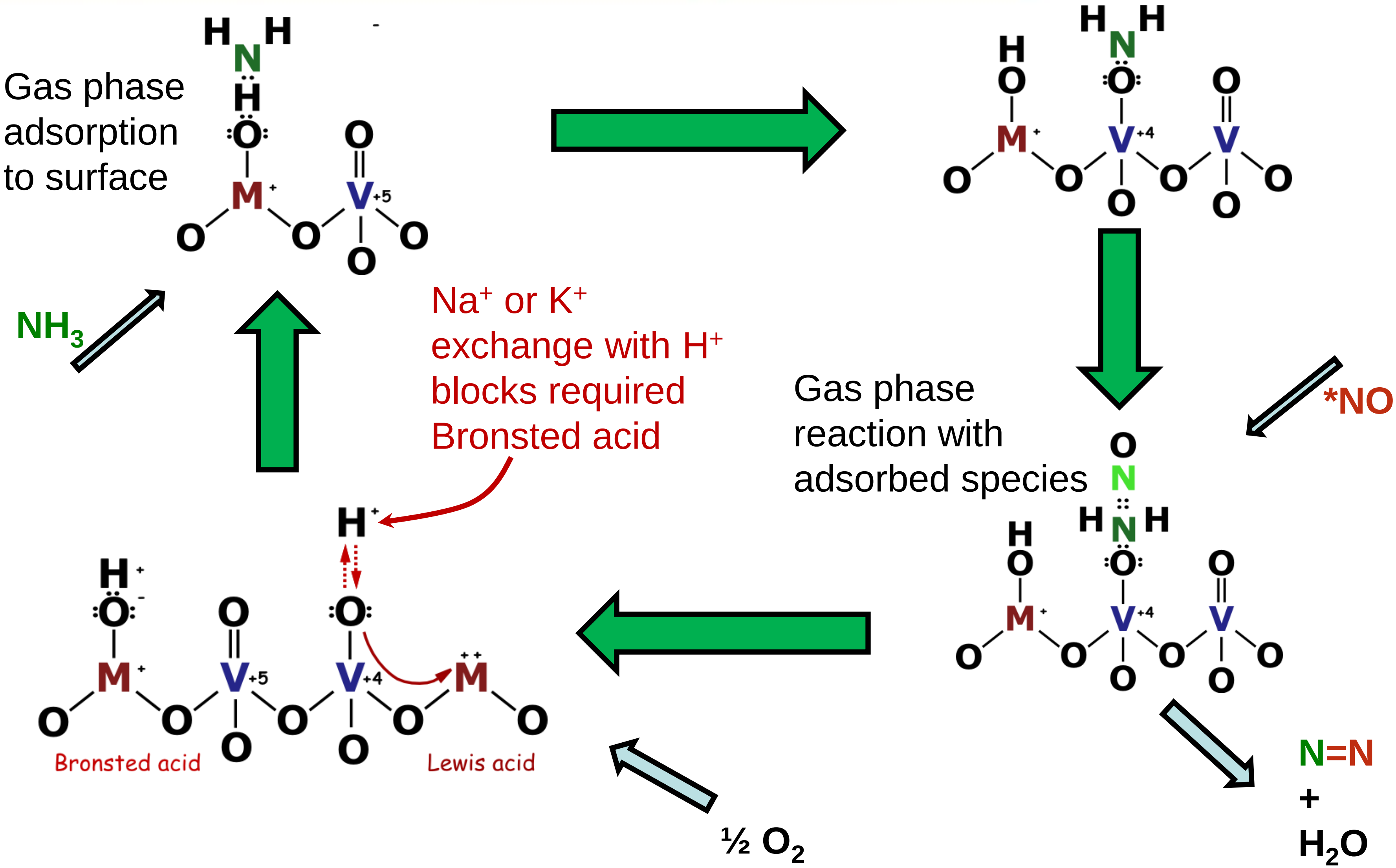
Fuel Related Catalyst Deactivation Mechanisms: Physical

Pore mouth blinding

- Silica & aluminosilicate particles block access at pore mouths
- Silica deposition as "glass" $(-[SiO_2]-)_n$ blocks catalyst access at pore mouths
- CaO in fly ash reacts with SO_3 to form $CaSO_4$ *(gypsum)* or CO_2 to form $CaCO_3$ (*calcium carbonate*)
- A common form of activity loss (reversible *via* regeneration)

NOx Reduction Reaction Mechanism



SCR Catalyst Deactivation Mechanism: Chemical Poisons

- **Alkaline metal poisoning (Na, K)**
  - Formation of metal salt complexes reduces V_2O_5 activity
  - Alkaline metal adsorption changes surface Bronsted/Lewis acid balance (reversible *via* regeneration)
- **Phosphorous poisoning**
  - High phosphorous coals fired in "reducing environment" (low NOx burners) generated PX_3 species that actively poison V_2O_5 (reversible *via* regeneration)
- **Arsenic poisoning**
  - Gaseous arsenic (As_2O_3) condenses in catalyst pores
  - Further oxidation to solid As_2O_5 to permanently plugs pore mouths
  - Combines with vanadium to form inactive V-As species
  - Mitigation by high-Ca coal or addition of limestone ($CaCO_3$)
  - $CaO + As_2O_3 + H_2O$ forms solid calcium arsenate trihydrate
  - Distinct chemical signature (reversible *via* regeneration)
- **Some heavy metals, i.e. chromium, cannot be easily removed**

Deactivation & Regeneration: Honeycomb Catalyst

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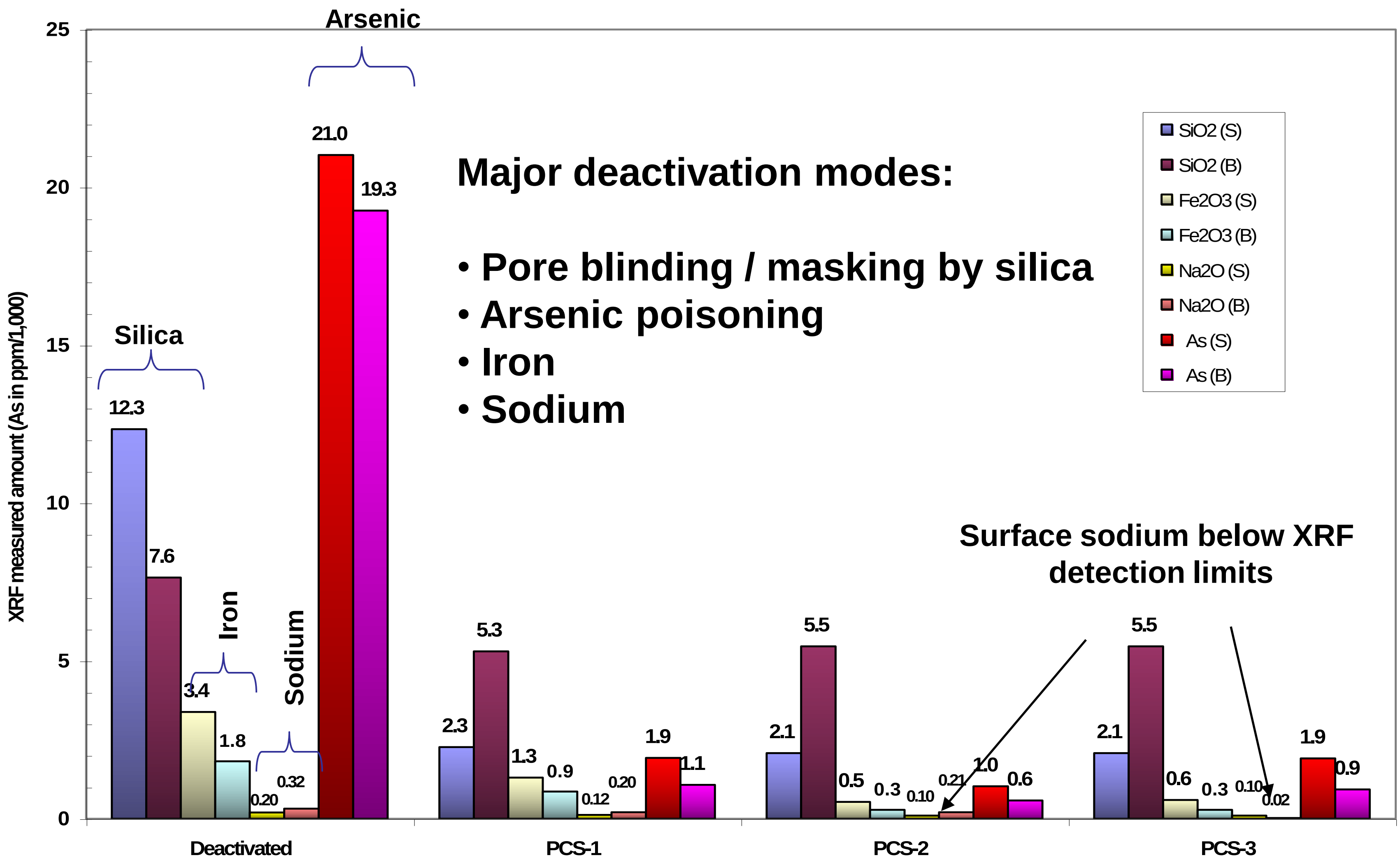

Deactivation & Regeneration: Corrugated Catalyst

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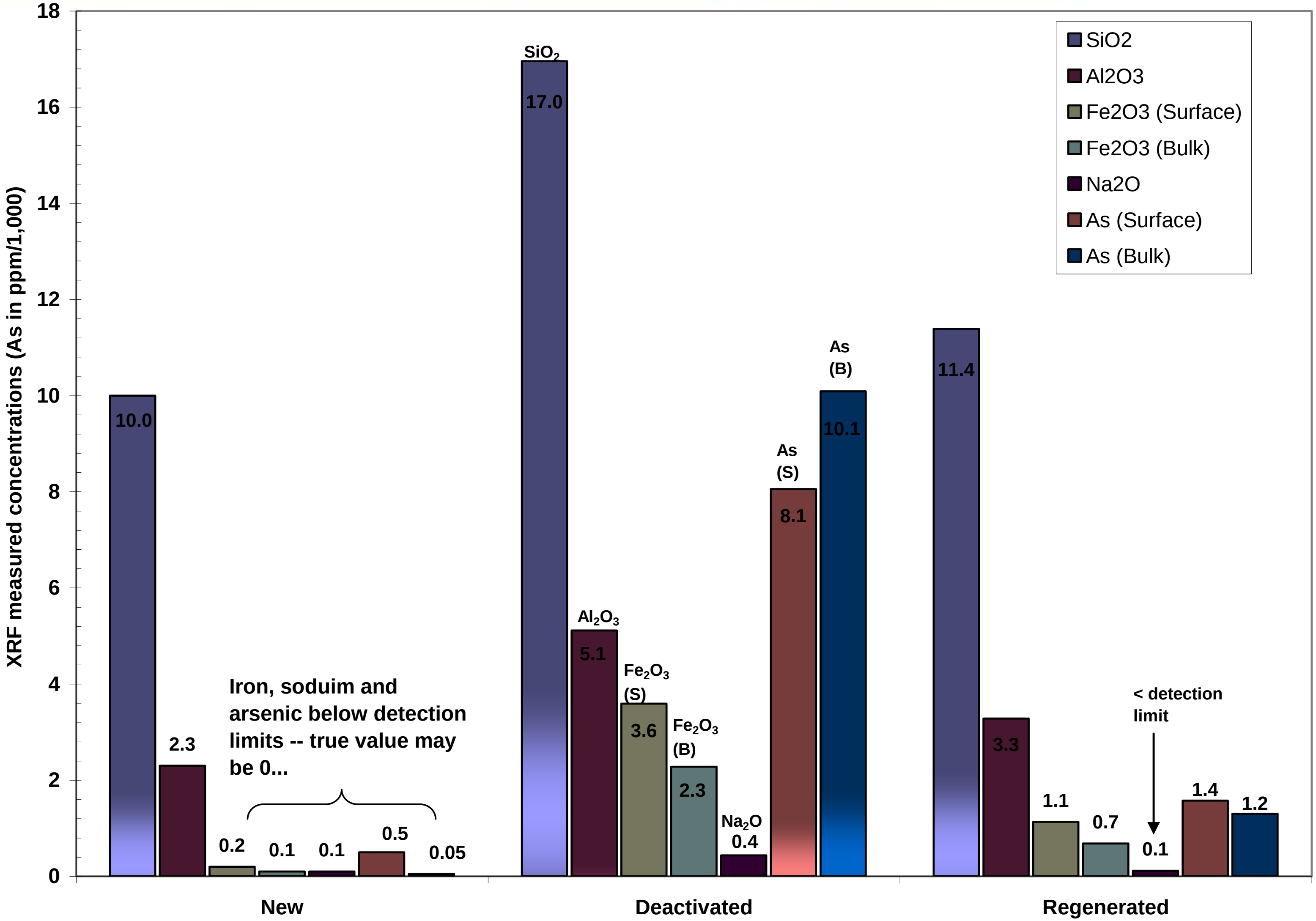

Coal General Characteristics

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- **Lignite and sub-bituminous coals**
  - High in alkali and alkaline earth metals: Na, K, Ca, Mg
  - High in silicates, alumina, aluminosilicates, phosphates and Hg°
  - Low in sulfur and halogen
- **Bituminous coals**
  - High in sulfur, iron, arsenic, "heavy metal" pyrites (metal sulfides)
  - Low in calcium and alumina
- **Biomass**
  - High in alkali (Na, K) and phosphates
- **Pet coke**
  - Enriched in vanadium and heavy metals – chromium, cadmium

Coal Resource Classification System (U.S. Geological Survey)

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- **High-ash coal:** > 15 percent total ash (as-received basis**)**
- **Medium-ash coal:** 8 percent to 15 percent ash
- **Low-ash coal:** < 8 percent total ash

- **High-sulfur coal:** > 3 percent or more total sulfur
- **Medium-sulfur coal:** 1-3 percent total sulfur
- **Low-sulfur coal:** < 1 percent total sulfur

Coal Sulfur Content

Region	No. Samples	Organic % S	Pyritic % S	Total % S
N. Appalachian	227	1.00	2.07	3.01
S. Appalachian	35	0.67	0.37	1.04
E. Midwest	**95**	**1.63**	**2.29**	**3.92**
W. Midwest	**44**	**1.67**	**3.58**	**5.25**
Western	44	0.45	0.23	0.68

Rank	Sulfur Content Range (% w/w)			
	0 - 0.07	**0.08 – 1.0**	**1.1 – 3.0**	**≥ 3.1**
Anthracite	95.6	0.6	2.9	
Bituminous	**14.3**	**15.2**	**26.2**	**44.3**
Sub Bituminous	66.0	33.6	0.4	
Lignite	77.0	13.7	9.3	
U.S. Average	46	19	15	20

The “Glue” That Blinds: SO_3

- **Reacts with alkaline earth metal oxides to form masking and blinding agents – $CaSO_4$**

- **Reacts with NH_3 to form sulfates (e.g. NH_4HSO_4)**
  - Temperature range 350°F to 450°F when molar concentration of SO_3 exceeds molar concentration of NH_3 plugs air heater
  - Temperature range of 530°F to 620°F may condense in SCR and plug / blind (defines minimum operating temperature)

- **Reacts with vanadium from pet-coke combustion to form vanadyl sulfate**
  - Deposit at high levels on SCR catalyst – 20% or more
  - Increase in SO_2 to SO_3 oxidation rate
  - Slows increase in rate of DeNOx activity loss until pores are blocked then activity drops rapidly

Deactivation Generalizations

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Fuel Type	Primary Deactivation Elements	Expected Activity @ 16,000 h
Petcoke	Heavy metals	$K/K_0 > 0.80$
Sub-bituminous Coal - Powder River Basin	Calcium (Ca) and Phosphorus (P)	$K/K_0 = 0.65 – 0.85$
Bituminous Coal	Arsenic (As)	$K/K_0 = 0.60 – 0.75$
Lignite	Sodium (Na) & Potassium (K)	$K/K_0 = 0.60 – 0.70$
Biomass	Phosphorus (P) , Potassium (K), Sodium (Na)	$K/K_0 = 0.45 – 0.55$
Municipal Solid Waste (MSW)	Heavy metals, halogens, Potassium (K), Sodium (Na)	$K/K_0 < 0.50$

Summary

- **Consult your SCR Catalyst Manager to model fuel change impacts on catalyst life and system performance**

- **Less expensive coal generally "trumps" more frequent catalyst replacement; but total economics and system performance must be evaluated**

- **Most important factors to determine catalyst type, formulation and geometry:**
  - Ash content
  - Sulfur content
  - Arsenic & calcium content
  - Operating temperatures
  - Flue gas velocity