NOx Control

Summary of Options and Issues as of December 3, 2015

Why prepare a summary?

- This summary is a guide to the NO_x information which appears in Power Plant Air Quality Decisions (PPAQS).
- PPAQS is a system for NO_x decision makers. It is available to operators (coal, cement, WTE, refining, etc.) at no charge and by subscription to others.
- The summary is used as a basis for discussions in periodic webinars.
- Subscribers are encouraged to submit additional case histories and analyses for inclusion in the system.
- The current information in the system is quickly accessed by decisive keywords e.g., application, contaminant, product, process, and company.
- McIlvaine is pursuing improved classifications in multiple languages e.g., consensus on catalyst cleaning, rejuvenation and regeneration as the three maintenance options.
- Every corporation has a corporate number to identify all facilities in multiple languages. This is very important for Chinese companies where confusion reigns.

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Control Options	SNCR/SCR – Fuel Tech	Catalyst HT	MHPS HG Cat	NH ³ CEMS options
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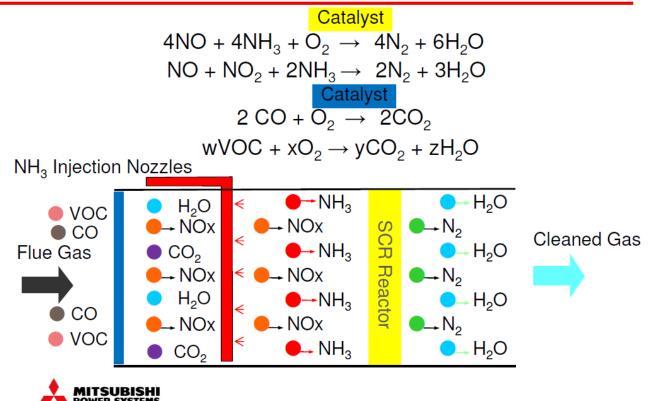
Control Options

1

DeNOx decisively classified options for coal, cement, incineration			
Option	*	Details	
SCR	Е	Ammonia injection followed by a catalytic reactor	
	А	High efficiency and accepted by regulatory authorities	
	D	Cost, catalyst plugging, space	
SNCR	E	Urea injection in the furnace	
	А	Low cost, low maintenance, space	
	D	Low efficiency, ammonia slip	
Ozone	E	Ozone injection followed by scrubber	
Oxidation	xidation		
	A	Little space if scrubber already in place	
	D	Ozone cost, efficiency	
Hydrogen	E	Chemical injection converts to NO ₂ followed by scrubbing	
Peroxide	Peroxide		
	А	Low capital cost if scrubber already in place	
	D	Chemical cost	
Catalytic	E	Fabric filter has embedded catalyst	
Filter			
	A	Lower footprint with combination, lower capital and operating	
		cost	
	D	Lack of experience	
* E= explar	nation	, A=advantages D=disadvantages	

SCR reaction principles

PRINCIPLE OF SCR REACTION (DENITRIFICATION PROCESS)



DeNOx vs. SO₃ formation

Balance

Meeting the World Energy Challenge.

- DeNOx versus:
 - SO2 conversion
 - Pressure drop
 - Hg oxidation

> Typical Evaluation Factors

- DeNOx K \$50,000 to \$80,000 per 1 m/hr
- SO2 conversion \$150,000 to \$450,000 per 0.1%
- Pressure drop \$120,000 per 0.1 inch water
- Hg oxidation Normally none

SCR Converting to "Multi-Pollutant Reduction Reactor "MPRR"





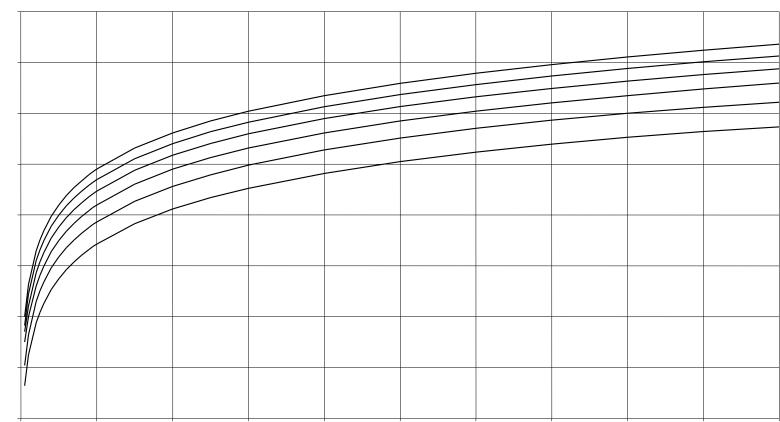
Catalyst Poisoning

Catalyst Poisoning & Degradation Mechanism

Degradation Source	<u>Mechanism</u>
High Temperature > 930F	Decreases available surface area by thermal sintering of ceramic material
Fine particulate	Reduces available surface area by masking surface and preventing diffusion into pre structure
Ammonia-sulfur compounds	Plugs pores and prevents diffusion
Alkaline metals, Na, K	Ion exchange with active sites
Alkaline earth metals, Ca, Mg	Typically in form of sulfates, bond with acid sites reducing the ability of catalyst to absorb NH_3 l.e. formation of CaSO ₄
Halogen	May react with and volatilize active metal sites
Arsenic	Gaseous arsenic diffuses into catalyst and covers active sites, preventing further reaction
V, Pt, Cr and Family	Deposit onto catalyst, increasing NH_3 to NO and/or SO_2 to SO_3



Minimum Continuous Operating Temperature (MCOT)

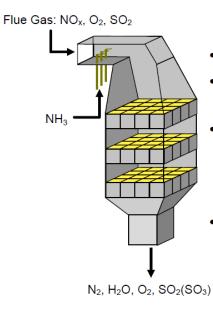


Minimum Operating Temperature f (NH₃, SO₃, H₂O, catalyst type)

NH₃*SO₃ (ppm)

SCR Basics

SCR Basics – Quick Review

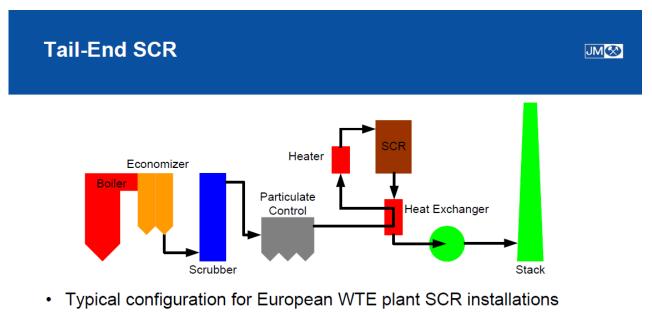


- SCR = <u>Selective</u> <u>Catalytic</u> <u>R</u>eduction
- Purpose is to reduce NO_x (NO & NO₂) from combustion exhaust
- Ammonia (NH₃) is injected into flue gas as reducing agent. Flue gas passes through catalyst layers installed in a reactor
- NH₃ reacts with NO_x on the catalyst surface to form nitrogen and water vapor

$$4NO + 4NH_3 + O_2 \xrightarrow{Catalyst} 4N_2 + 6H_2O$$
$$2NO_2 + 4NH_3 + O_2 \xrightarrow{Catalyst} 3N_2 + 6H_2O$$

JM🛠

Tail-end SCR

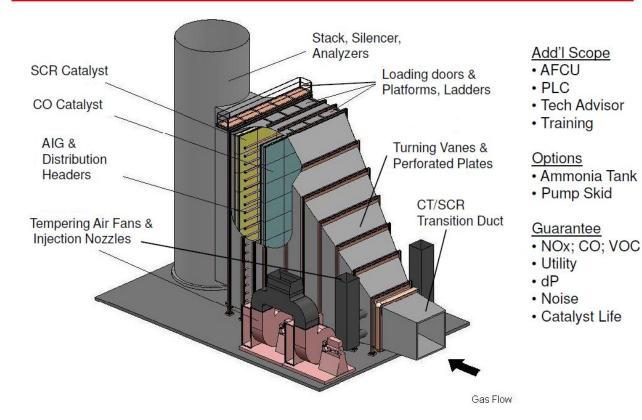


- SCR after scrubber/particulate collection equipment
- Long catalyst life expected
- Special catalyst formulations for low temperature, 400 540 °F
- Low concentrations of SO₂, SO₃ required



Simple Cycle SCR Scope

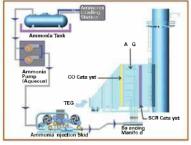
SCR FOR SIMPLE CYCLE GT (TYPICAL SCOPE)



Simple Cycle SCR Factors

Simple Cycle SCR Design Conditions

- □ Several Factors Dictate Design of SCR
 - Gas Flow...depends on size of engine
 - Engine exhaust NOx
 - Stack NOx (DeNOx) and NH₃ Slip...Local permit requirements
 - o Flue gas Temperature
 - o Footprint Available
 - Back Pressure





NOx Regulations – Ambient NO₂

NO₂ NAAQS

- Compliance with the old annual average NAAQS (100 µg/m3 or 0.053 ppb) was hard enough for isolated sources. This standard is retained. Modeling often required extended fence lines and arguments about atmospheric chemistry.
- New NAAQS is 188 µg/m3(or 100ppb) but for a 1 hour average. Depending upon the meteorology of the site this results in a 6.6 times lower threshold to meet. It therefore will be substantially harder to meet.



2 Option

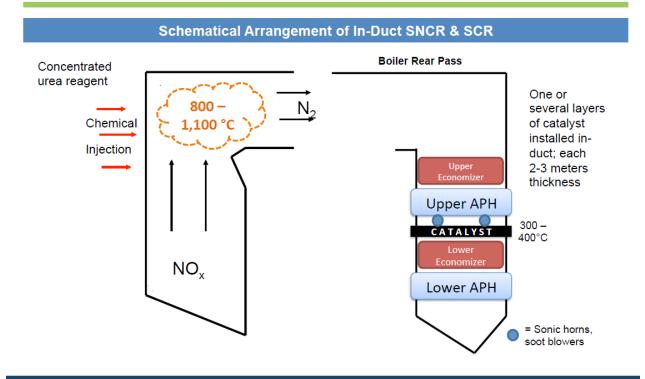
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Hybrid SCR/SNCR

Hybrid LNB / SNCR / SCR DeNOx Solution for Small & Medium Coal Boilers

LP AMINA Energy and Environmental

IN HYBRID ARRANGEMENT, AMMONIA INJECTORS ARE INSTALLED IN UPPER FURNACE, AND ONE (OR MORE) IN-DUCT CATALYST INSTALLED IN BOILER REAR PASS



Hybrid SCR/SNCR in China

Hybrid LNB / SNCR / SCR DeNOx Solution for Small & Medium Coal Boilers

LP AMINA Energy and Environmental

LP AMINA'S FIRST HYBRID TECHNOLOGY WAS INSTALLED ON YIXING UNION'S UNITS 5/6 IN CHINA'S JIANGSU PROVINCE, TOTAL 80% OF THE NOX REDUCTION WAS ACHIEVED



Yixing Union Units 5 and 6 Project Overview

Units Overview:

- Power generation capacity: 2 x 50 MW
- Combustion type: T-Fired
- Fuel: Bituminous coal

Scope:

- SOFA and Low NOx Firing Systems
- Proprietary SNCR/SCR Hybrid
- Patented coal classifiers

Results:

- NOx reduced from 0.44 to 0.08 lb/MMBTu
- LOI below 1.5%
- · Expanded fuel flexibility
- Increased unit efficiency
- Significant cost reduction due to the large savings in ammonia and catalysts
- Currently working on few more units for Yixing

SCR/SNCR combo - Fuel Tech

I-NOX TECHNOLOGY

- Combining technologies is not easy
- Design must be truly integrated:
 - SNCR design must account for combustion output and varying operational conditions of your typical boiler, easier if SNCR/SCR retrofit onto existing boiler where data can be measured
 - SCR design must account for SNCR output and varying operational conditions of the combustion and SNCR systems as boiler conditions fluctuate
- Challenges:
 - Highly maldistributed NOx and NH3 from boiler
 - Increased SCR velocity due to restrictions in catalyst installation space
 - » Both require expert knowledge in the design of all of the technologies being combined
 - » Both require computational and experimental fluid dynamics modeling coupled with flow distribution device optimization
- Benefits:
 - Capital cost, reagent consumption, dP, catalyst replacement, SO2-SO3 oxidation (lower minimum operating temperature)



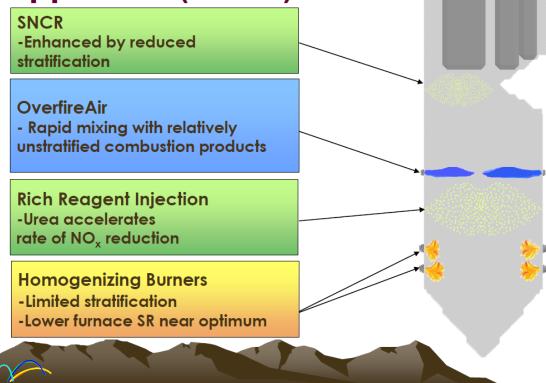
ROFA + LoTOx - AECOM

Summary and Conclusions

- Non-SCR boilers are being pushed to further reduce NO_x emissions
- ROFA and Rotamix are cost-effective, but cannot achieve SCR-like emissions reductions
- LoTOx is best-suited to applications with low baseline NO_x emissions
- The combination of ROFA and LoTOx provides a cost-effective alternative to SCR, with fewer operational constraints

Burners, SNCR and SCR combination-Reaction Engineering

Advanced Layered Technology Approach (ALTA)



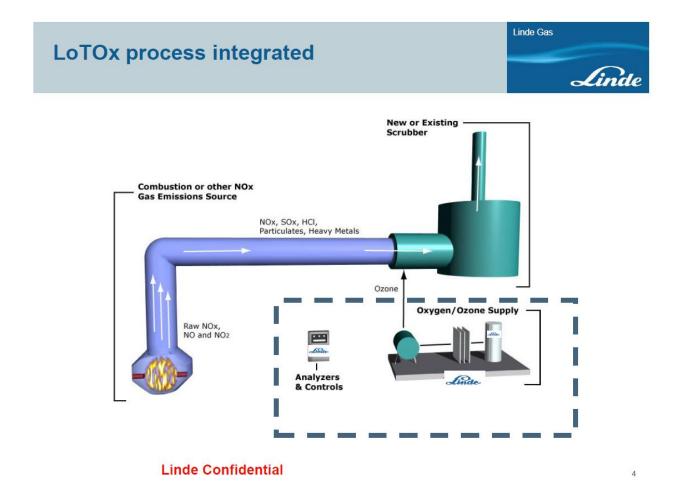
LoTox Ozone (AECOM)

LoTOx[®] NO_x Control Technology

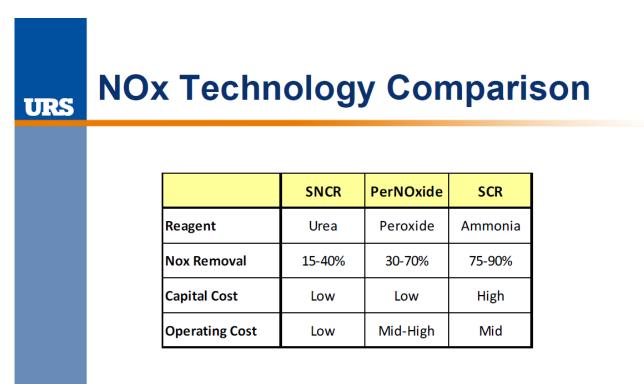
- Low-temperature oxidation
- Offered by Linde Group
- NO_x scrubbing
- Widely used in refining industry with ~30 FCCU installations
- 25 MW coal-fired institutional boiler installation
- EPRI pilot demonstration at Coal Creek
- 90% NO_x removal



Linde LoTOx system



Peroxide provides modest NOx Reduction



PerNOxide offers moderate NOx reductions with low upfront capital investment



NOx Control as part of Optimization

Optimization Opportunities and Benefits

Pre-Combustion

- Coal/Fuel Blending Optimization 1-2% production increase
- Mill Optimization lower LOI, heat rate improvement, pluggage detection

Combustion

- NOx Reduction 10-30%
- Heat Rate Improvement 0.25-1.5%
- Dynamic Steam Temperature Control +/- 1%, reduce steam turbine cyclic life expenditure
- Ramp Rate Improvement up to 100%
- Intelligent Soot-blowing up to 0.25% heat rate improvement, lower EFOR
- LOI Reduction 10-30%

Post-Combustion

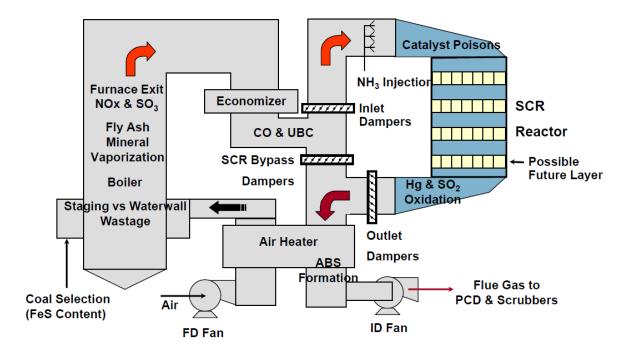
- SCR's Reduce NH₃ slip; Lower capital equipment costs;
 - 2% additional reduction in NOx
- FGD's Increase SO₂ removal efficiency with less limestone

consumption

i n v e. n s .9 s Operations Management

Boiler/SCR optimization - EPRI

Boiler / SCR Optimization





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CO, NOx and LOI reduction (Invensys)

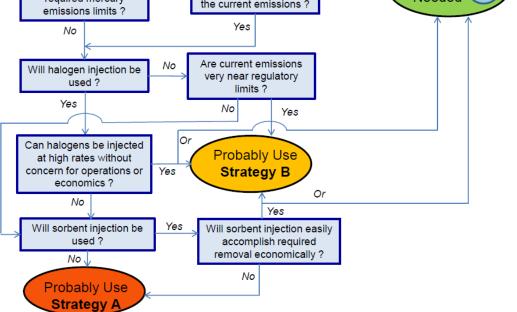
Combustion Optimization



i n v e. n s . y s Operations Management

Catalyst management strategies to achieve Hg oxidation

Management Strategy Selection: Decision Tree



3. Options

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Aggressive catalyst management strategy to maximize Hg oxidation

Strategy A

- Most Aggressive Strategy
- Manages Upper Catalyst Layers for DeNOx
- Manages Final Catalyst Layer for Mercury Oxidation
- Insures that Entire Final Catalyst Layer Operates with Very Low Slip (< 2 ppmv normally)
- Results in One Extra Layer Always Being Present in Reactor
- Fine Tuning Parameters: Frequency of Final Layer Replacement, Use of Advanced Catalyst, Allowable Slip Entering Final Layer, Halogen Injection Level (if used)
- Costs: Full Layer of Additional Catalyst, Pressure Drop, Maintenance, Sootblowing/Horn Provisions, More Frequent Management Events

Moderate catalyst management strategy to achieve Hg oxidation

Strategy B

- Moderate Strategy to Improve Mercury Oxidation
- Manages Reactor as a Whole, Following Typical Management Strategy in General Approach
- Relies on "Excess Potential" to Insure that Some Portion of Catalyst Operates at Very Low Slip Over the Life of the Installation.
- Results in More Frequent Catalyst Replacements, or Requires More Potential Per Layer (via deeper beds, tighter pitch, or possibly more active catalyst)
- Caution: Do Not Allow Excess Potential to be an Excuse for Sloppy Operation and Maintenance of the SCR System
- Fine Tuning Parameters: Required Excess Potential, Use of Advanced Catalyst, Halogen Injection Level (if used)
- · Costs: additional catalyst, more frequent management events

Catalyst Design - HT

Haldor Topsoe's SCR Catalyst Products

- Homogeneously Corrugated Composite SCR Catalyst
- TiO₂ with V₂O₅ as the principal active component including WO₃
- Design temperature range: 300 1,050°F
 - > low temperature SCR \rightarrow higher V:W ratio
 - > high temperature SCR \rightarrow low V:W ratio (low V to no V catalyst is optimal choice for simple cycle SCR if no dilution air is used





HTI SCR Experience

HTI Experience

•	Utility Boilers	80 units
•	Combustion Turbines	352 units
	 including (> 800 F up to 1,050 F) 	135 units
•	Refinery & Industrial Boilers, Heaters	328 units
•	Stationary Diesel and Gas Engines	56 units
	Total Experience	816 units

* Additional HTAS experience of ~ 400 units includes refinery units.

* Leading supplier of Combustion Turbine, Refinery, and Industrial DeNOx catalyst in the US.

HALDOR TOPSOE 🖪

Catalyst Management - CERAM

Affect on Catalyst Management Planning

Current Practice: NOx and NH ₃ Slip Based Plans	Future: NOx, NH ₃ Slip and HgOx Based Plans		
• Consider Required NOx/NH ₃ Slip	• + Consider HgOx Targeted		
Performance	Performance		
Track K/Ko Trends	• + Track HgOx K/Ko Trends		
Assess Fuel Quality	• + Assess More Fuel Quality Data		
Assess Operations	• + Assess More Operations Data		
 Assess Catalyst Pluggage 	• + Consider Halogens /ACI		

Optimization and Effective Planning Will Minimize Outage Schedule Impacts, Halogen Additions, and/or Activated Carbon Additions

CERAM Has Adapted Proprietary Manage CATLife® Model for Combined NOx and Hg Ox Catalyst Management Planning

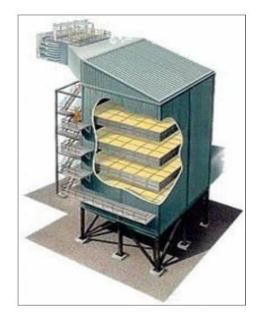


Select catalyst by thinking outside the box

Summary

Meeting the World Energy Challenge.





- Think of the SCR as an "MPRR"
- Think outside the "SCR Box"
- SCR catalyst is an asset not a consumable
- Select the "right" catalyst for each layer
- Mix layers if it adds value

Honeycomb vs. Plate Catalyst

SCR Catalyst Types

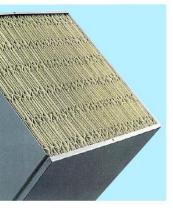
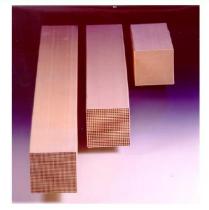


Plate-Type

- Ceramic material on SS substrate
- · Individual flexible plates
- Rectangular flow channels
- Ideal for particulate-laden flue gas



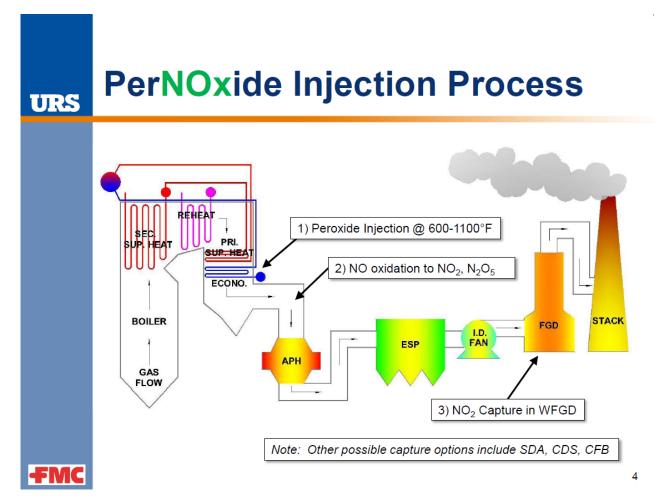
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Honeycomb

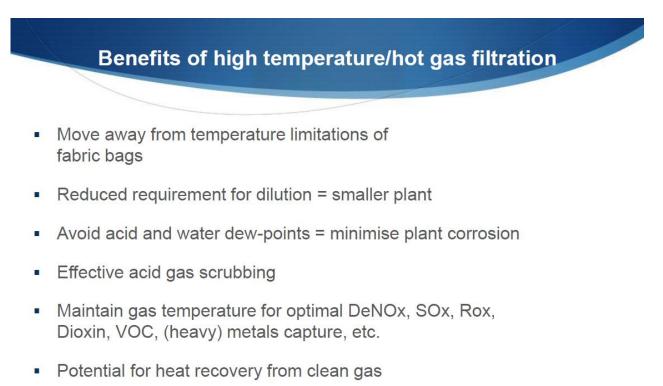
- · Homogenously extruded ceramic
- · Rigid structure, square channels
- · High cell density, high surface area
- · Ideal for particulate-free flue gas



Peroxide combines with scrubber for NO_2 capture



Catalytic Filtration with embedded catalyst-advantages



Increased stack buoyancy

CERAFIL Top Kat

Catalytic filter technology Cerafil TopKat™



CERAFIL TopKat

Combination of two well established and effective technologies







SCR





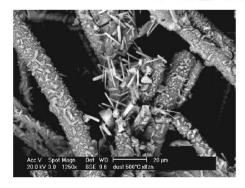
Cerafil XS



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Catalyst distribution in filter

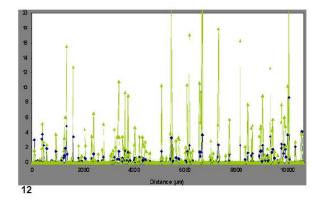
Catalyst distribution



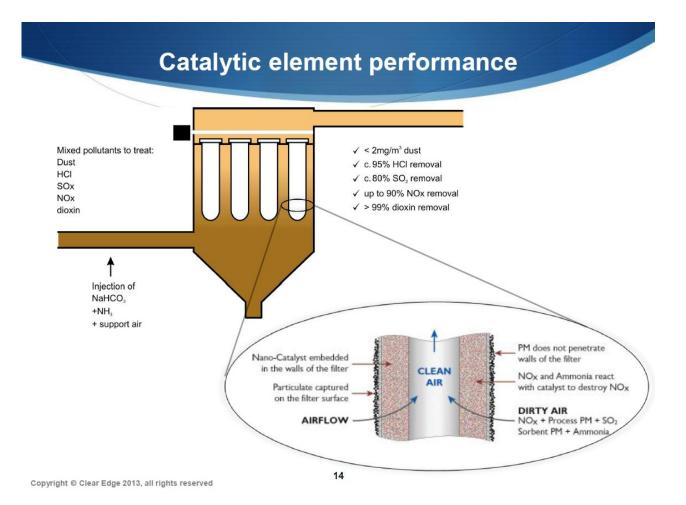
Nano sized catalyst particles promote access to active surfaces

Catalyst distributed throughout element wall

Residence time and efficiency maximised



Catalytic filter system design



Catalytic Filter applications

Applications, such as

- Cement production
- Chemicals manufacture
- Diesel Engines
- Gasification processes
- Glass furnaces
- Metal smelting
- Mineral processing
- Sewage sludge incineration
- Waste incineration
- Power plants & Boilers

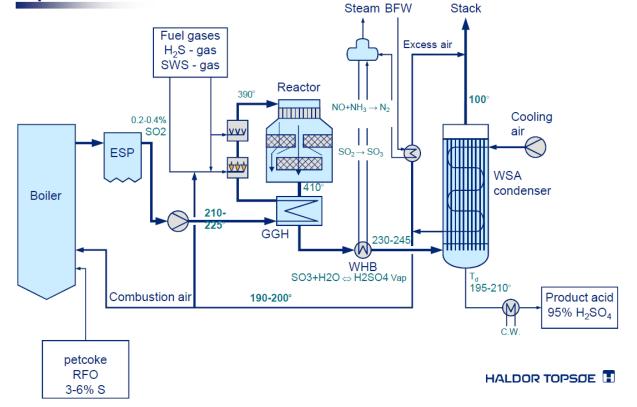
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SNOx[™] for acid production and NOx reduction

Boiler with SNOX[™] for high sulfur coal or petcoke



4. Factors

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Mercury Oxidation Factors

Summary



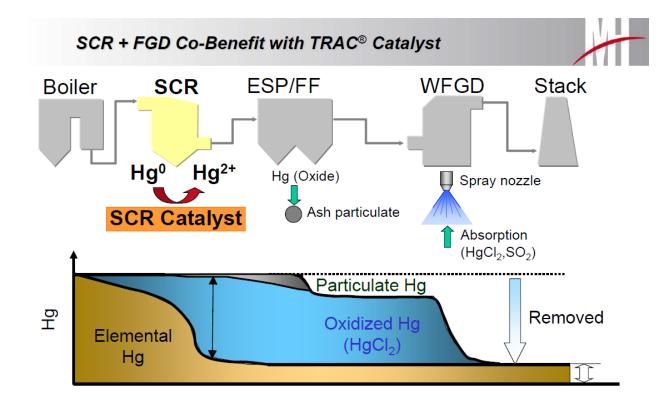
- Hg oxidation is influenced by multiple factors.
 - Layer dependency
 - More factors in setting design conditions
 - Impacts of catalyst type & formulation
- Cormetech has developed testing capabilities needed to characterize performance under all operating conditions.
- COMET™
 - <u>testing and modeling technology</u> allows us to predict system performance and evaluate options for catalyst actions.
 - <u>advanced Hg oxidation catalyst</u> can significantly improve SCR co-benefit for Hg oxidation.
 - Used in combination to provide optimal solutions.

Impacts on mercury capture (Hinton)

Factors Affecting SCR Mercury Oxidation

- Fuel Composition (mercury and halogen Levels)
- Supplemental Halogens (chlorine or bromine addition)
- Catalyst Design (pitch, formulation, etc.)
- Volume/Potential
- Catalyst Age
- Temperature
- Flow Rate
- Ammonia

Mercury oxidation with SCR

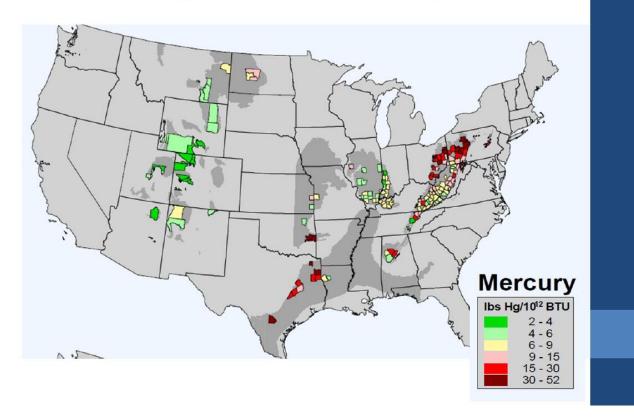


SCR catalyst is a key component for mercury oxidation

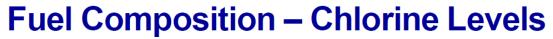
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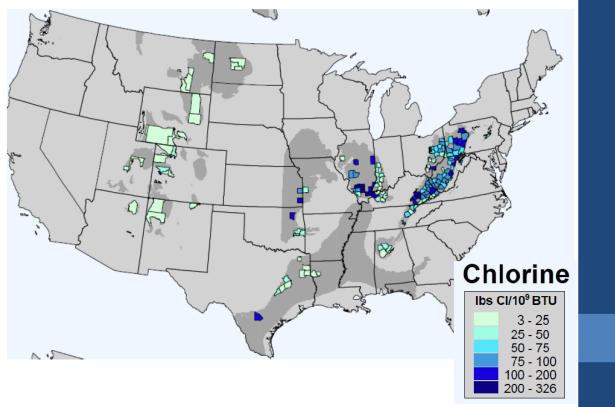
Mercury in Fuel

Fuel Composition – Mercury Levels

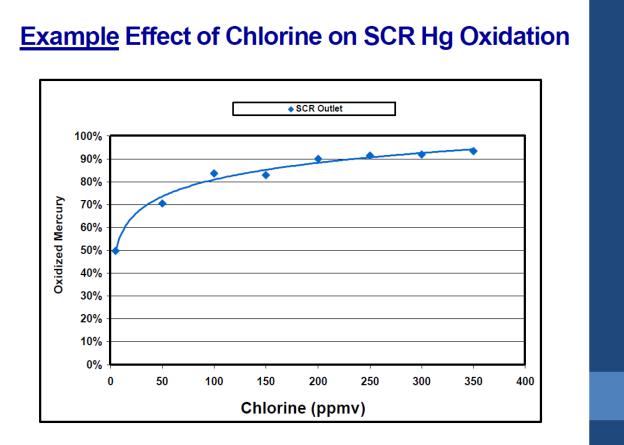


Chlorine in Fuel





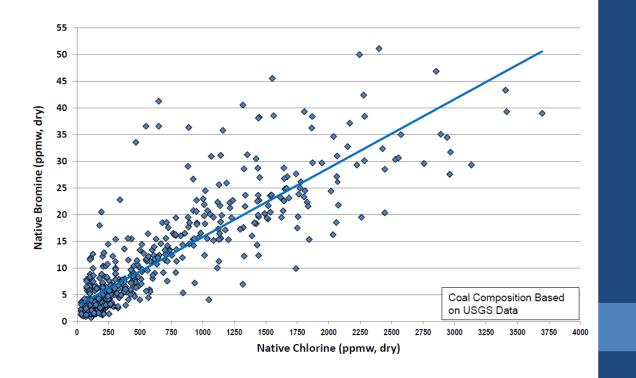
Effect of Chlorine on SCR HG Oxidation



Bromine and Chlorine inter-relationship

Bromine and Chlorine Inter-Relationship

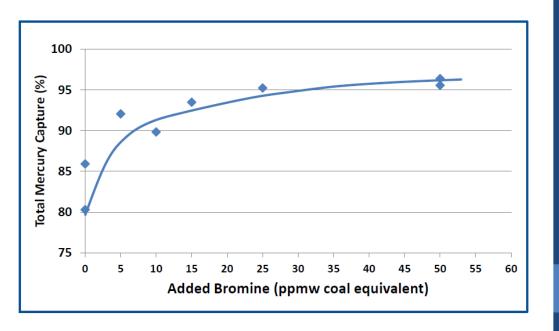
Coals low in Chlorine will also generally be low in Bromine



Bromine, SCR impact on Hg oxidation

Bromine Addition with SCR-Wet Scrubber

MRC Data - low chlorine eastern bituminous coal

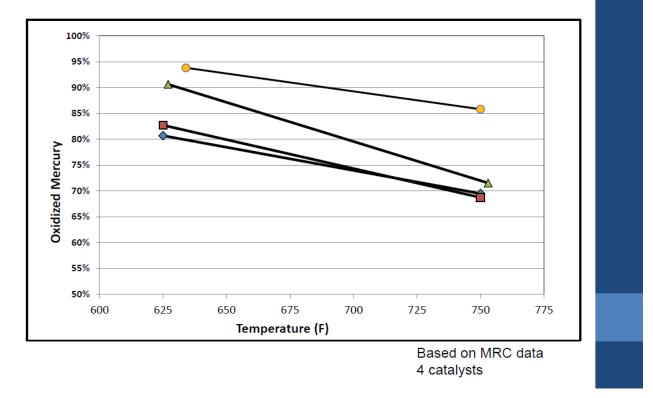


Caution ! Example only -effects may be significantly shifted in the field.

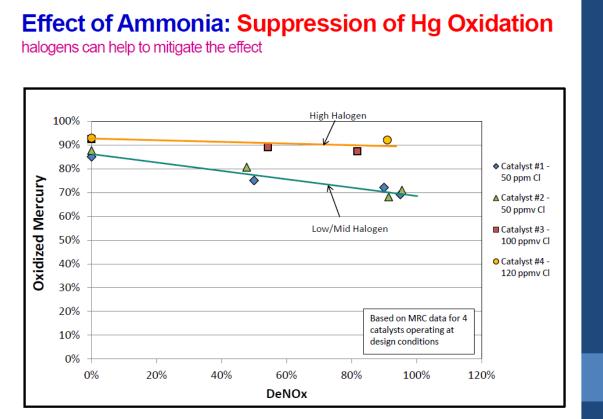
Oxidized mercury vs. temperature

SCR Outlet Oxidized Mercury vs. Temperature





Ammonia impact on Hg oxidation



Caution ! Example only - halogen effects may be significantly shifted in the field.

Catalyst Management-evaluation of condition

Flexibility - Brokering



Meeting the World Energy Challenge

Why catalyst may not meet current operating conditions?

Pitch

- Too small (pluggage, pressure drop)
- Too large (Low DeNOx potential)
- Catalyst Length
 - Too long (pressure drop, SO2 conversion)
 - Too Short (Low DeNOx potential)
- Catalyst Type Normally a customer specific preference
 - Honeycomb
 - Corrugated
 - Plate

SCR Catalyst is an Asset Not a Consumable



Select different catalyst for each layer

Mixed Layers

Meeting the World Energy Challenge.



Consider different catalyst for different layers when pluggage is a issue!

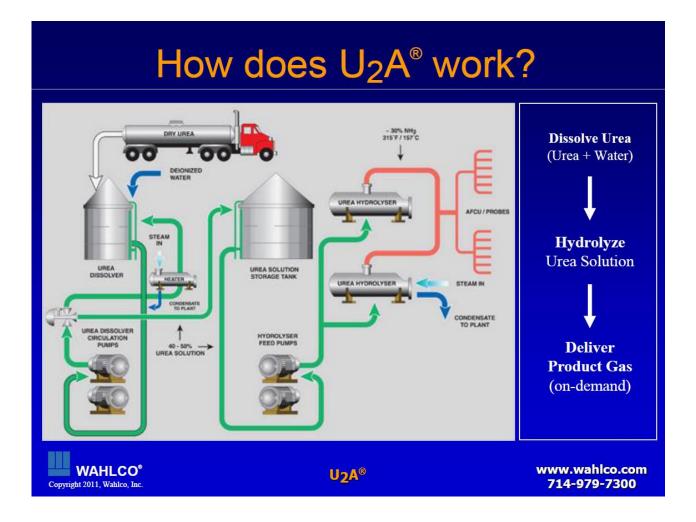
- Top Layer
 - Pluggage due to high ash volumes (especially boiler wall rows)
 - Pluggage due to LPA
 - Erosion resistance
- Other Layers Balance
 - DeNOx potential
 - SO2 conversion
 - Pressure drop

Select the "Right" Catalyst for Each Layer

5. Systems

1. Overview	2. Options	3. Options	4. Factors	5. System
Overview	Hybrid SCR/SNCR	HG aggressive	HG oxidation	Urea-Ammonia
Integration in System	SNCR/SCR China	HG moderate	System factors	Pumps
Control Options	SNCR/SCR – Fuel Tech	Catalyst HT	MHPS HG Cat	NH ₃ CEMS options
Reaction principles	ROFA + LoTOx	HT Experience	Fuel mercury	Extractive pluses
DeNOx vs SO ₃	Burners/SCR/SNCR	Ceram Cat Mgmt.	Fuel chlorine	Extractive-UV
Catalyst poisoning	LoTOx -AECOM	CoaLogix Mgmt.	Chlorine impact	In situ pluses
SCR Basics	Linde LoTOx	HC vs. Plate	Bromine/chlorine	In situ - UV
Tail End SCR	Peroxide	Cat. Filter	Bromine impact	Mixers-Sulzer
GT Simple Cycle	Optimization Benefits	Top Kat	Temperature impact	Need input on ammonia quality and
GT Simple factors	Optimization-EPRI	Catalyst distribution	NH_3 impact	options from Yara, Koch etc.
NOx Regulations	CO/NOX/LOI Invensys	Catalytic filter Systems	Catalyst condition	
More on regulations in	Hg Cat Management	Catalytic F. Applications	Layer selection	
each country but lots in system already.		SNOx		

Urea to Ammonia



Grundfos pumps for urea

- The situation and the Grundfos solution
 The CIM/CIU 150 is a standard interface for data transmission between Profibus DP network and a Grundfos pump
 or controller. It makes data exchange
 possible between Grundfos pumping systems and a PLC or SCADA system.
- BOT Elektrownia Opole S.A. power plant has an existing installation of several Grundfos CRNE multistage pumps (delivering solution water and urea which is sprayed through nozzles into the power plant's chimney). The current system contains:
- • 10 CRNE 1-23 (product no. 96570982)
- • 2 CRNE 5-29 (product no. 96518538)
- In the power plant these pumps should be controlled by the main process control system Teleperm (Siemens). The complete pump system was delivered and installed by an external Swedish company using a local Polish contractor. The existing data transmission used Profibus protocol, but the existing system was delivered without CIM/CIU modules.
- Grundfos Poland offered the prefect solution: Grundfos CIM/CIU. For Grundfos CIM/CIU 150 modules no custom programming is needed to integrate them in a Profibus network. The system integration is very straight-forward. Now the new add-on-equipment includes Grundfos CIU modules and a Siemens PLC system, which provides full control of pumps and S7 300.

The outcome

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BOT Elektrownia Opole S.A. power plant is very satisfied because all Grundfos pumps and the new control solution have performed very well. Now local technicians can control and monitor all connected pumps via CIM 150. And these pumps are very critical ones: If they stop running and the NOx concentration reaches a too high level the control system will immediately stop the complete power block.

NH₃ measurement options

Comparison of NH₃ measurement methods

Table 1. Technologies for Continuous Measurement From Ammonia						
Technique	Advantages	Disadvantages	Well Suited For			
NOx differential	 Experience & familiarity with method Cost 	 Measures a surrogate Sensitivity for high NOx situations can be poor 	 Low NOx (gas turbines or gas boilers) 			
UV photometry	Experience & familiarity with method	Strong Interference from SO ₂	Natural Gas applications, or other low SO ₂			
TDL (IR)	 Relatively interference free (except for water) Solid-state In-Situ - no sample handling required Sensitivity 	 Moderate moisture interference must be properly addressed Alignment needs to be maintained High particulate loading may require shortening of path length 	 All applications, especially coal 			
IR (multicomponent)	Multiple species	Tends to be Expensive	All applications			

The above are general statements that reflect the author's overall impression based upon his close familiarity with NOx reduction technology and ammonia monitoring technology. This is not intended to be a complete list. However, it is a list of the most important approaches in the author's opinion. In some cases companies may claim to have addressed certain disadvantages. The author neither disputes nor confirms their claims.

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NOx and NH₃ extractive CEMs

P

Extractive Basics

SICK Sensor Intelligence.

Extractive...there are some advantages

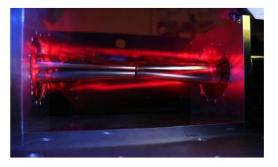
: Multi-path (white cells) allow for long path lengths, leading to lower minimum ranges, in existing enclosure.

: Sample switching and redundant analyzer systems are easily achievable.

: Capable of measuring gases in process conditions outside the limits of in-situ.

: Main hardware located in climate controlled shelter.



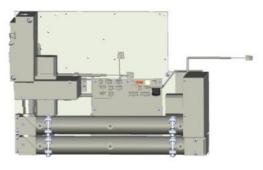


Sick extractive UV analyzers

E

Extractive: UV NOx and NH3 Analyzer

- : Measuring component: NO, NO₂, SO₂, Cl₂, H₂S, NH₃, COS, CS₂
- : Minimum Range: 0-10ppm NOx, 0-50ppm NH3
- : Measuring principle:
 - UVRAS (UV resonance absorption spectrometry)
 - NDUV IFC
- Measurement of up to 3 UV-absorbing components
- : 19" rack mounting for easy integration into an existing sample system
- : Option: heated cuvette with heated gas lines (up to 212 F)



5ІСК

Sensor Intelligence.

DEFOR

10

In situ NOx and NH₃ Cems

In-situ Basics

In-Situ...there are some advantages

No gas transport

- : Fast response time
- : No loss of components in a sample system
- : No filters, sample lines, pumps to clean

Lower planning expenses

- : Support for heated sample gas lines
- : Analysis container
- : Disposal of sample gas and condensate

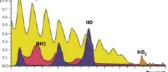
Lower installation and operation cost

- : Heated sample gas lines approx. \$80/ft
- + support construction approx. \$50/ft
- : Cost for shelter or space in existing analyzer rooms.



SICK

Sensor Intelligence.



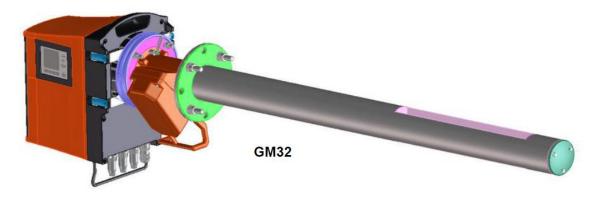
Sick in situ UV NOx, NH₃ CEMs

In-situ: UV NOx and NH3 Monitor



GM32 – UV Gas Analyzer

- One-hole installation
- Simple start-up & measurement
- Internal calibration filters for daily zero/span (EPA Part 60)
- On-line testing with test gases for daily and quarterly (CGA) checks
- Simultaneous measurement of NO and NO2. No convertor.



Sick Maihak GmbH

: Confidential

DeNOx ammonia mixing

Sulzer Chemtech - Moving Ahead

SULZER

Sulzer Static mixers for SCR DeNOx applications



S. Hirschberg

