# NO<sub>x</sub> Control

### **Decision Guide Webinar**



# **Meeting Structure**

- The discussion format will be based on quick displays of a number of slides with the assumption that participants will ask questions or make comments when a relevant slide appears.
- End users are free to ask specific questions and their requests will be prioritized.
- This 90 minute webinar will be recorded and access provided to thousands of power plant personnel and other DeNOx system operators at no charge.
- Others will have access to the ppts and recording through a variety of Mcilvaine subscriptions.

# Table of Contents

- Overview
- Coal
- Chemicals
- Catalytic filtration
- Mercury
- System Components
- Cement
- Incineration
- Refinery
- Mobile
- Gas Turbine (separate decision guide)



## Overview



### **Major Issues and Options**

- DeNOx has to be considered as one of multiple pollutants for which a coordinated removal strategy is essential.
- Cross pollination among industries provides the ozone insights of refineries, the catalytic filter insights from glass furnaces, VOC and NO<sub>x</sub> reduction from gas turbines and the catalyst management insights from coal-firing.
- Heat recovery with improvements in efficiency and reduction in greenhouses gases is a big potential with catalytic filtration.
- The replacement of precipitators with catalytic filters creates a huge market opportunity.
- Can the automotive suppliers learn from the stationary equipment suppliers?



## **Control Options**

DeNox decisively classified options for coal, cement, incineration					
Option	*	Details			
SCR	E	Ammonia injection followed by a catalytic reactor			
	А	High efficiency and accepted by regulatory authorities			
	D	Cost, catalyst plugging, space			
SNCR	CR E Urea injection in the furnace				
	A	Low cost, low maintenance, space			
	D	Low efficiency, ammonia slip			
Ozone	E	Ozone injection followed by scrubber			
Oxidation					
	A	Little space if scrubber already in place			
	D	Ozone cost, efficiency			
Hydrogen E Chemical injection converts to NO2 followed by scrubbing		Chemical injection converts to NO2 followed by scrubbing			
Peroxide					
A Low capital cost if scrubber already in place		Low capital cost if scrubber already in place			
	D	Chemical cost,			
Catalytic E Fabric filter has embedded catalyst		Fabric filter has embedded catalyst			
Filter					
A Lower foot print with combination, lower capital and operative					
		cost			
	D	Lack of experience			
* E= explanation, A=advantages D=disadvantages					



:

### **SCR Reaction Principles**





### **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"







### NOx Regulations – Ambient NO<sub>2</sub>

### NO<sub>2</sub> 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.





# NO<sub>x</sub> 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 NH<sub>3</sub> slip; Lower capital equipment costs;
  - 2% additional reduction in NOx
- FGD's Increase SO<sub>2</sub> removal efficiency with less limestone

consumption

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

# Coal



### **Boiler/SCR Optimization - EPRI**

### **Boiler / SCR Optimization**



© 2012 Electric Power Research Institute, Inc. All rights reserved.





## Burners, SNCR and SCR Combination -Reaction Engineering

### Advanced Layered Technology Approach (ALTA)

SNCR -Enhanced by reduced stratification

OverfireAir - Rapid mixing with relatively unstratified combustion products

Rich Reagent Injection -Urea accelerates rate of NO<sub>x</sub> reduction

Homogenizing Burners -Limited stratification -Lower furnace SR near optimum



### **SCR Basics**

#### **SCR Basics – Quick Review**

Flue Gas: NO<sub>x</sub>, O<sub>2</sub>, SO<sub>2</sub>



• SCR = <u>Selective</u> <u>Catalytic</u> <u>R</u>eduction

JM🐼

- Purpose is to reduce NO<sub>x</sub> (NO & NO<sub>2</sub>) from combustion exhaust
- Ammonia (NH<sub>3</sub>) is injected into flue gas as reducing agent. Flue gas passes through catalyst layers installed in a reactor
- NH<sub>3</sub> reacts with NO<sub>x</sub> on the catalyst surface to form nitrogen and water vapor

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

e al le ser d'al de la companya de l



### 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

9

- Benefits:
  - Capital cost, reagent consumption, dP, catalyst replacement, SO2-SO3 oxidation (lower minimum operating temperature)





## CO, NO<sub>x</sub> and LOI Reduction (Invensys)

#### **Combustion Optimization**



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



## Catalyst Management Strategies to Achieve Hg Oxidation

#### **Management Strategy Selection: Decision Tree**





## **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 <sub>4</sub>
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 $\rm NH_3$ to NO and/or $\rm SO_2$ to $\rm SO_3$





# 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)</li>
- 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
- TiO<sub>2</sub> with V<sub>2</sub>O<sub>5</sub> as the principal active component including WO<sub>3</sub>
- 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







HALDOR TOPSOE



### **HTI SCR Experience**

### HTI Experience

•	Utility Boilers	80 units
•	Combustion Turbines	352 units
	<ul> <li>including (&gt; 800 F up to 1,050 F)</li> </ul>	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 <sub>3</sub> Slip Based Plans	Future: NOx, NH <sub>3</sub> Slip and HgOx Based Plans		
<ul> <li>Consider Required NOx/NH<sub>3</sub> Slip Performance</li> </ul>	• + Consider HgOx Targeted Performance		
• Track K/Ko Trends	• + Track HgOx K/Ko Trends		
Assess Fuel Quality	• + Assess More Fuel Quality Data		
Assess Operations	• + Assess More Operations Data		
<ul> <li>Assess Catalyst Pluggage</li> </ul>	• + 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"

CoaLogix

CORPORIN

- 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

#### JM



Plate-Type

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



#### Honeycomb

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

#### (b) South Control Control Control Control (State Control State Control Stat Control State Control St State Control State Cont



# Chemicals



## LoTOx<sup>®</sup> Ozone (AECOM)

### LoTOx<sup>®</sup> NO<sub>x</sub> Control Technology

- Low-temperature oxidation
- Offered by Linde Group
- NO<sub>x</sub> 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<sub>x</sub> removal



Presented at Reinhold Environmental 2015 NOx/Combustion Round Table & Expo



### ROFA + LoTOx<sup>®</sup> - AECOM

#### **Summary and Conclusions**

- Non-SCR boilers are being pushed to further reduce NO<sub>x</sub> emissions
- ROFA and Rotamix are cost-effective, but cannot achieve SCR-like emissions reductions
- LoTOx is best-suited to applications with low baseline NO<sub>x</sub> emissions
- The combination of ROFA and LoTOx provides a cost-effective alternative to SCR, with fewer operational constraints



### Linde LoTOx System



Linde Confidential



## Peroxide Combines with Scrubber for NO<sub>2</sub> Capture





### Peroxide Provides Modest NO<sub>x</sub> Reduction

### NOx Technology Comparison

	SNCR	PerNOxide	SCR
Reagent	Urea	Peroxide	Ammonia
Nox Removal	15-40%	30-70%	75-90%
Capital Cost	Low	Low	High
Operating Cost	Low	Mid-High	Mid

PerNOxide offers moderate NOx reductions with low upfront capital investment



URS



### SNOx<sup>™</sup> for Acid Production and NO<sub>x</sub> Reduction

# Boiler with SNOX<sup>™</sup> for high sulfur coal or petcoke





# **Catalytic Filtration**



## Catalytic Filtration with Embedded Catalyst Advantages



- Move away from temperature limitations of fabric bags
- Reduced requirement for dilution = smaller plant
- Avoid acid and water dew-points = minimise plant corrosion
- Effective acid gas scrubbing
- Maintain gas temperature for optimal DeNOx, SOx, Rox, Dioxin, VOC, (heavy) metals capture, etc.
- Potential for heat recovery from clean gas
- Increased stack buoyancy


### Cerafil TopKat

Catalytic filter technology Cerafil TopKat™



Cerafil XS

#### CERAFIL TopKat

Combination of two well established and effective technologies



11





SCR



Copyright © Clear Edge 2013, all rights reserved



### **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



Copyright © Clear Edge 2013, all rights reserved



### Catalytic Filter System Design





### **Catalytic Filter Applications**

#### Applications, such as

18

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

Copyright © Clear Edge 2013, all rights reserved





MCILVAINE

#### US Industry Examples Utilizing DSI with Ceramic Filters

#### Tri-Mer UltraTemp & UltraCat Ceramic Filter Systems

orbent
∎®
acal®

## ClearChemFSI™ APC Profit Creation

#### APC Adding Value to Plant Economics



# Mercury



## **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.



Page 13

### 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

© 2014 MITSUBISHI HITACHI POWER SYSTEMS AMERICA – ENERGY AND ENVIRONMENT, LTD. All Rights Reserved.



1

### Mercury in Fuel

#### **Fuel Composition – Mercury Levels**





### Chlorine in Fuel





## Effect of Chlorine on SCR HG Oxidation

#### **Example 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





### Oxidized Mercury vs. Temperature



4 catalysts



# Ammonia Impact on Hg Oxidation

#### Effect of Ammonia: Suppression of Hg Oxidation

halogens can help to mitigate the effect



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



# System Components



### Urea to Ammonia





#### **NH3 Measurement Options**

# Comparison of NH<sub>3</sub> measurement methods

Table 1. Technologies for Continuous Measurement From Ammonia							
Technique	Adv	/antages		Disadvantages		Well Suited For	
NOx differential	<ul> <li>Experience</li> <li>method</li> <li>Cost</li> </ul>	e & familiarity with	•	Measures a surrogate Sensitivity for high NOx situations can be poor	•	Low NOx (gas turbines or gas boilers)	
UV photometry	<ul> <li>Experience</li> <li>method</li> </ul>	e & familiarity with	•	Strong Interference from SO <sub>2</sub>	•	Natural Gas applications, or other low SO <sub>2</sub>	
TDL (IR)	<ul> <li>Relatively (except fo</li> <li>Solid-state</li> <li>In-Situ - n required</li> <li>Sensitivity</li> </ul>	interference free or water) e o sample handling /	•	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 s	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.

www.AndoverTechnology.com



## $NO_x$ and $NH_3$ Extractive CEMs

P

#### **Extractive Basics**



#### 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.





: Confidential



### Sick Extractive UV Analyzers

P

#### **Extractive: UV NOx and NH3 Analyzer**

- : Measuring component: NO, NO<sub>2</sub>, SO<sub>2</sub>, Cl<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub>, COS, CS<sub>2</sub>
- : Minimum Range: 0-10ppm NOx, 0-50ppm NH3
- : Measuring principle:
  - UVRAS (UV resonance absorption spectrometry)
  - NDUV IFC

Sick Maihak GmbH

- : 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)



DEFOR



Confidential



## In-situ $NO_x$ and $NH_3$ 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

Sick Maihak GmbH

: 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.





2

## Sick In-situ UV NO<sub>x</sub>, NH<sub>3</sub> 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

Sensor Intelligence.

3



### **DeNOx Ammonia Mixing**

Sulzer Chemtech - Moving Ahead



#### Sulzer Static mixers for SCR DeNOx applications

Sulzer Chemtech

S. Hirschberg





## **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

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.



.

# Cement



## Chinese Cement NO<sub>x</sub> to be Cut by Nearly 1 Million Tons

- The co-processing of solid wastes in cement kilns shall apply Standard for pollution control on co-processing of solid wastes in cement kiln (GB 30485-2013), in addition to Emission standard of air pollutants for cement industry (GB 4915-2013), according to this official. In the principle of whole-process pollution control, the GB 30485-2013 sets corresponding control requirements for each of the pollution links in the co-processing, which include control of the waste varieties allowed for co-processing, control of batch feeding of toxic elements to the wastes, selection of feeding points, and control of flue gas pollutants. To enable the standards to be more feasible, MEP formulated the supplementary standard Environmental protection technical specification for co-processing of solid wastes in cement kiln (HJ 662-2013), which specify the environmental technical specifications for co-processing of solid wastes in cement kilns.
- It is estimated that, after enforcing the new standards, the PM emission from cement industry will be cut around 770,000 t (30.8%-38.5%) from the baseline of 2 million t to 2.5 million t; the NOx emission will be cut about 980,000 t (44.5%-51.6%) from the baseline of 1.9 million t to 2.2 million t, which makes the annual emission of NOx from this industry under 1 million t to 1.2 million t, effectively controlling the pollution load of HCl, HF, heavy metals, and dioxins, and meanwhile contributing to the reduction of greenhouse gas emissions.



### **GEA Low Dust SCR for Cement**



For the reduction of the nitrogen oxide emissions from cement plants the selective non catalytic reduction process, SNCR, is usually applied by dosing of ammonia or urea at high gas temperatures. However this process is limited in terms of NOx removal efficiency and produces a fairly high ammonia emission (slip). Therefore GEA is using the advanced SCR technology with catalysts, which reduces the reaction temperature from approximately 1000°C to range of 230°C to 400°C. High reduction rates can be realized with a minimum of ammonia slip. GEA prefers the low dust arrangement.



### GEA Low Dust SCR at Sudbayer

- At the end of March 2011 a new denitrification (DeNO<sub>x</sub>) plant was put into operation at the location of German cement manufacturer Südbayer. Portland-Zementwerk (SPZ) Gebr. Wiesböck & Co. GmbH, in Rohrdorf. The new selective catalytic reduction (SCR) system converts nitrogen oxides (NO<sub>x</sub>) and ammonium hydroxide from the kiln exhaust gas into atmospheric nitrogen and water, thus reducing emissions considerably to meet not only current but also future emission regulations. The DeNO<sub>x</sub> plant is the first of its kind in operation at a cement plant worldwide (Fig.).
- SPZ commissioned the new plant to meet their environmental responsibility, comply with current emission regulations and ensure that they will be able to meet future extensions of regulations. These aims are definitely achieved by the new plant and, using a new waste heat recovery system, power consumption and operational costs are minimized throughout the process. In spring 2010 GEA Bischoff was approached to design a SCR system that would enable the plant to run with a minimum NO<sub>x</sub> concentration in its flue gas. The company has over 10 years of experience in designing such plants and quickly identified an SCR plant, situated downstream of the kiln bag filter and equipped with a heat recovery system to boost the operating temperature, as the most appropriate solution.
- A catalytic reduction of the NOx output requires the operation temperature to be more than 250 °C. To achieve this, the kiln exhaust gas is heated up in a recuperative cross flow heat exchanger supplied by Ecoflex, another member of the GEA Group. In a second heat exchanging step the gas temperature is boosted by a thermal oil loop using back waste heat from the clinker cooler. The NO<sub>x</sub> content in the exhaust gas can definitely be reduced to below present and even future emission regulation limits.



# Schuech Semi Dust System in Operation at Lafarge Mannersdorf

- The 1.1Mta Lafarge Mannersdorf works in Austria is the country's largest cement plant and a pioneer of environmental protection within the European cement industry.
- As part of these endeavors, the world's first semi-dust SCR (catalytic reduction) system was installed at the plant in spring 2012 by Scheuch of Austria. Over the past three years, the existing system has been gradually optimized and guarantees reliable compliance with NO<sub>x</sub> and NH<sub>3</sub> emissions. By Scheuch, Austria.
- The installation of a special heat exchange tower resulted in a low operating temperature but with the disadvantage of a high dust content of up to 180g/Nm<sup>3</sup>. These dust values therefore required the installation of a pre-separator before the catalyst to ensure safe operation of the *SCR* system.



### Scheuch Semi Dust

SEMI - DUST SCR



Typical integration of the SCR unit





# GEA has Installed SCR in Glass Plants and is Involved with Catalytic Filters

- High efficient cleaning of deposits on top of catalyst and inside the channels of the catalyst. Top surface is completely cleaned by the rake arm traveling slowly over the complete surface.
- Cleaning air is heated by routing the compressed air pipes trough the clean gas
- This cleaning system is able to clean the catalyst also in emergency cases, e.g. power loss, when a higher dust load reaches the SCR.
- GEA SCR cleaning system secures over long years high cleaning efficiency, seen in various references, resulting in a long time of the catalyst.
- The SCR is direct after filter therefore no heating needed
- Selection of catalyst module mainly depending on dust content of SCR inlet
- For selenium glass production specific procedures have to be considered
- Meanwhile first plants are equipped with high temperature ceramic filter candles with catalytic-heat-dip. GEA is already involved in such development.



### **EU Cement Regulatory Status**

- Although the IED and the BAT conclusions have established a framework for NO<sub>x</sub> reduction in the cement industry, there is an enduring discussion about the appropriateness of the potential reduction measures.
- According to the BAT reference document for the cement industry, secondary abatement measures like SNCR and SCR (Selective Catalytic Reduction) are efficient NO<sub>x</sub> abatement technologies for achieving low emission levels.
- The SNCR process is cost-effective but entails the risk of additional NH<sub>3</sub> emissions (NH<sub>3</sub> slip) due to an over stoichiometric injection of ammonia solution. This can be of importance because individual countries have set an emission limit value for ammonia. In particular, this is based on the National Emissions Ceiling Directive (NEC Directive), the ammonia limits of which have been exceeded in some countries.



## **EU Cement Regulatory Status**

- The performance of the SNCR process has been improved more and more during the past years to comply with all environmental requirements. The application of the so-called "high-efficiency SNCR" process (he-SNCR) seems to be a promising approach for minimizing the proportion of unreacted ammonia which would lead to lower NH<sub>3</sub> emissions and a lower consumption of reducing agents.
- The catalytic SCR process, which is state-of-the-art in the power sector, was not investigated in the cement sector until a few years ago. This technology was therefore classified as BAT subject to appropriate catalyst and process developments.
- In the meantime, experiences from several full-scale SCR projects in Italy, Austria and Germany have been gained. These projects included different SCR variants, such as high-dust, semi-dust and tail-end solutions.
- As a result, certain authorities are of the opinion that SCR is now an available technology to meet challenging NO<sub>x</sub> and NH<sub>3</sub> abatement targets. It should be pointed out however, that SCR technology is very costly and due to the additional pressure drop the electrical energy demand of the plant increases by about 5 kWh/t of clinker.
- Catalytic filters and high temperature filters have been noted by the European Cement Research Academy as promising alternative approaches


## Lafarge SCR Performing Well

- In 2013, LaFarge Cement entered into a consent decree with the EPA and the US Justice Department as part of a settlement Lafarge was to retrofit its Joppa, Illinois "dry process" cement kiln with an SCR unit, record its effectiveness during stack testing, and report on the results of those tests by 2015.
- The unit is now operating and is achieving 80% removal compared with 40% for SNCR
- According to LaFarge, "the SCR control technology performed well and no operational problem was encountered."
- Holcim's Midlothian cement plant has already applied and been granted one by the Texas Commission on Environmental Quality for construction and operation of its own SCR unit. It should be up and running by the fall of 2016



#### **FLS Catalytic Filter**



Dirty gas and dust from outside the ceramic elements are sucked through the filter – through the porous layer. The dust is removed by pulsed, pressurized air. But the harmful gases are trapped and removed in the matrix of the ceramics – via a specially designed catalyst that converts and removes THC and  $NO_x$  emissions, which originate from the raw materials and the combustion process.



#### FLS has CataMax Order from U.S. Cement Plant

FLSmidth has secured an order for engineering, supply and installation of the new CataMax<sup>™</sup> catalytic solution for a U.S. cement producer. The order includes a new filter installation with catalytic elements, ID fan, flue gas ducts and dust transport equipment.

The CataMax<sup>™</sup> catalytic solution uses ceramic elements with an embedded catalyst; the porous elements not only remove dust particles from the flue gases, but the catalyst embedded will also remove total hydrocarbons (THCs) and organic hazardous air pollutants (O-HAPs) in the flue gas.

"The CataMax<sup>™</sup> catalytic solution is a patent-pending technology from FLSmidth, which will help U.S. cement producers to achieve compliance with the ever stricter environmental regulations. We are already seeing and increased interest in this technology from other customers in the U.S. as well as from customers in Europe and Asia where similar legislative restrictions are also expected in the future," says Jacob Sondergaard, Vice President, FLSmidth Airtech U.S., part of FLSmidth's Product Companies Division. The national Emissions Standards for Hazardous Air Pollutants (NESHAP) are emissions standards set by the United States Environmental Protection Agency (EPA). The U.S. is leading the way by having the most stringent regulations in the world today within the cement industry.



#### Yara SNCR Installations - Cement

Category Title	Fuel/ Type	Capacity M.Watts	Country	Delivery Year	Plant Line	Project
Coment	Comont		Νοργαγ	2012	11	PM1115
cement	Cement		Nonway	2012	11	PM1116
	Cement		Romania	2012	L1	PM1117
	Cement		Sweden	2012	P1	PM1119
	Cement		Italy	2011	P1	PM1011
	Cement		Germany	2011	Line 2 & 3	PM1101
	Cement		Ireland	2011	P1	PM1103
	Cement		Spain	2011	P1	PM1112
	Cement		Italy	2011	L1	PM1113
	Cement		Spain	2010	L1	PM0802
	Cement		Spain	2010	L1	PM0912
	Cement		Switzerland	2010	P1	PM0914
	Cement		Croatia	2010	P1	PM1002



## Incineration



#### Tail-End SCR



- Typical configuration for European WTE plant SCR installations
- SCR after scrubber/particulate collection equipment
- · Long catalyst life expected
- Special catalyst formulations for low temperature, 400 540 °F
- Low concentrations of SO<sub>2</sub>, SO<sub>3</sub> required

#### (b) Comparison Com Comparison Compari Comparison Com



## Low Dust SCR in Incineration is not an Environmental Improvement

- In most modern waste incinerators selective non catalytic reduction (SNCR) is applied to remove NO<sub>x</sub> from the combustion gas to reach the European emission limit value (ELV) of 200 mg/Nm<sup>3</sup>.
- If however the NO<sub>x</sub>-ELV for waste incinerators would be lowered to e.g. 100 mg/Nm<sup>3</sup>, SNCR, with a typical NO<sub>x</sub> removal efficiency of around 50%, would not suffice to reach the new ELV.
- In that case, selective catalytic reduction (SCR), with a NO<sub>x</sub> removal efficiency of up to 90% in tailend configuration could be an interesting alternative. However, from a life cycle perspective, the production, construction and operation of SCR equipment including the catalyst, also involve indirect (i.e. not from the process itself but related to other parts of the life-cycle) pollutant emissions and resource consumption with resulting environmental impacts
- .Replacing SNCR by tail-end SCR reduces the direct environmental impact of the incinerator (i.e. environmental impact of the NO<sub>x</sub> emitted at the stack) in the impact categories acidification, eutrophication and photo-oxidant formation, as expected from the lower NO<sub>x</sub> emissions in case of SCR.
- However, mainly due to the need to reheat the combustion gas, SCR has higher indirect impacts than SNCR, most notably in the impact category global warming. Because of these indirect impacts, the mentioned direct environmental impact reductions of SCR in the impact categories acidification, eutrophication and photo-oxidant formation are no net environmental benefits; when e.g. fuel oil is used as an energy source to reheat the flue gas, the indirect impact in the impact categories acidification and photo-oxidant formation is higher than the direct impact reduction related to the lower NO<sub>x</sub> concentration in the exhaust



### SCR at Palm Beach WTE

Palm Beach Renewable Energy Facility 2 is special, as it

- Uses state-of-the-art air pollution control technologies, making it the most advanced and cleanest waste-to-energy power plant in North America
- Babcock & Wilcox Vølund DynaGrate<sup>™</sup> technology to provide for more complete combustion of waste
- Selective Catalytic Reduction (SCR) for nitrogen oxides (NOx) control
- Processes more than 1 million tons of post-recycled municipal solid waste annually (at capacity)
- Provides enough power for an estimated 44,000 homes and businesses (that is enough power for all the homes in Boca Raton, FL)
- Recycles an estimated 27,000 tons of steel, aluminum, copper and other metals annually after the trash is burned
- Reduces reliance on the Palm Beach County landfill by up to 90%



#### Gore - Remedia



Worldwide

MCILVAINE

#### Gore DeNOx Filter



MCILVAINE

#### Gore DeNOx with Catalytic Felt

#### Gore<sup>®</sup> DeNOx Filter Technology





#### Urea vs. Ammonia for SNCR





#### **Urea SNCR System**





#### **Biomass - Yara Installations**

Category Title	Fuel/ Type	Capacity M.Watts	Country	Delivery Year	Plant Line	Project
Bark/Sludge	Bark/Sludge	65	Sweden	2003	Pl	NA8142
PioMass	PioMacc		Franco	2012	D1	DM1119
BIOMISS	BioMass		Swodop	2012		DM1110
	DioMass	22.2	Sweden	2010	D1	PMINO DM1002
		23.5	Sweden	2010	FI	PMIOOS
	BIOMass		Icaly	2009	LI	PM0906
	BioMass	16.4	UK	2008	Line 1, 2, 3 & 4	NA8349
	BioMass	13	Sweden	2008	Line 1 & 2	NA8327
	Multi BioMass	38	Sweden	2008	P1	NA8222
	BioMass	25	Sweden	2007	P1	NA8252
	BioMass	54	USA	2006	Line 1, 2 & 3	NA8299
	BioMass	54	USA	2006	Line 1, 2 & 3	NA8338
	BioMass	115	Sweden	1996	P11 (linked to NA8011)	NA8017
	BioMass/CFB	25	Sweden	1996	P1	NA8013



# Refinery



## Refinery FCC NO<sub>x</sub> Reduction





### Dupont Scrubber with LoTOx™



#### Scrubber with LoTOx

- LoTOx<sup>™</sup> = Low Temperature Oxidation
- Developed by Linde (previously BOC) and licensed to Dupont BELCO Clean Air Technologies for refinery FCCUs
- 2001 CARB's Clean Air Innovative Technology Demonstration at RSR Quemetco<sup>(1)</sup>
- Convert insoluble NO through ozone injection to highly soluble N<sub>2</sub>O<sub>5</sub> and HNO<sub>3</sub>

Note: 1) <u>www.arb.ca.gov/research/apr/past/icat99-2.pdf</u>, 2) picture from <u>www.dupont.com</u> and <u>www.digitalrefining.co</u> 1/23/2014 NOx RECLAIM



### **30 FCC LoTOx Installations**

#### Scrubber with LoTOx (cont.)

- Concurrently reduce particulates and SOx (refer to SOx RECLAIM Staff Report for information on SOx scrubbers)
- 90+ scrubber installations with 30+ LoTOx in refineries worldwide. Applications in gas-fired and high sulfur coal-fired units met 95% control and/or 2-5 ppmv
- Current installations in refineries met 8-10 ppmv, and manufacturers positively confirmed that LoTOx can be designed to achieve 2 ppmv NOx

Note: "Preparing wet scrubbing system for a future with NOx emissions requirements" Dupont Belco; "Wet scrubbing-based NOx control using LoTOx technology – first commercial FCC start-up experience. Belco and Marathon Petroleum. <u>www.digitalrefining.com</u>, and numerous other papers by Dupont Belco.

1/23/2014

NOx RECLAIM



#### Catalyst - Granular

#### **NOx-Control Additives**

- Intercat (Johnson Matthey), NOxGetterA or B (1, 2)
  - 30% 76% NOx reduction with 0.5%-5% wt% catalyst addition
  - Trial run in 20 FCCUs
  - Short 8-day trial run to establish baseline and efficiency
- Grace XNOx W (3,4)
  - 65% NOx reduction
  - Trial run at Petroplus Coryton UK Refinery
- BASF CLEANOx (5)
  - 72% NOx reduction with 1.4 wt% of Catalyst Addition

Note: 1) "FCC Flue Gas Scrubber Alternatives: Part I", Intercat (Johnson Matthey), 2009. <u>www.digitalrefining.com</u>. 2) "Reducing FCC Unit NOx Emissions", Intercat (Johnson Matthey), 2008. <u>www.digitalrefining.com</u>. 3) "Controlling FCC NOx Emissions", September 2011, Grace FCC Technology Conference in Munich, Germany, <u>www.refiningoperations.com</u>. 4) "FCC catalysts and additives for cost and emissions control." Grace Catalysts Technologies. <u>www.digitalrefining.com</u>. 5) Product and Performance Data on <u>www.basf.com</u>

1/23/2014

NOx RECLAIM

16



# **Refinery Cost Options**

#### **Incremental Cost Analysis**

	PWV (\$ million)	Emission Reduction (tpd)
SCRs for 85% Control	139	0.48
SCR for 2 ppmv	152	0.91
LoTOx for 2 ppmv	125	0.91
Incremental Cost Effectiveness SCR - SCR	(13/0.43/25/365) = 3,444 \$/ton	
Incremental Cost Effectiveness SCR - LoTOx	(-14/0.43/25/36	55) = -3,521 \$/ton

1/23/2014

NOx RECLAIM



### GEA says SCR less Costly than LoTOx for FCC





## Mobile



## Comparison of NO<sub>x</sub> Control Technologies

	Lean NO <sub>x</sub> trap (LNT)	Selective catalytic reduction (SCR)	Exhaust gas recirculation (EGR)	Combined SCR and LNT (SCR+LNT)
Principle	NO <sub>x</sub> is adsorbed onto a catalyst during lean engine operation. When the catalyst is saturated, the system is regenerated in short periods of fuel-rich operation during which NO <sub>x</sub> is catalytically reduced	A catalyst reduces NO <sub>x</sub> to gaseous nitrogen and water in the presence of ammonia. Most light-duty applications use an aqueous urea solution (diesel exhaust fluid, AdBlue <sup>™</sup> ) as an ammonia precursor	A fraction of exhaust gas is rerouted to the combustion chamber to lower combustion temperature and the production of engine-out $NO_x$ . For <i>high-pressure EGR</i> , exhaust gas is drawn from upstream of the turbine; for <i>low-pressure EGR</i> , exhaust gas is drawn from after the DPF. Both approaches can be used in combination	An SCR unit downstream of the LNT allows higher $NO_x$ conversion efficiencies. The ammonia synthesized by LNT reacts with $NO_x$ in the SCR
Typical application	Light-duty vehicles with engine displacements below 2 liters (<2.0 L)	Light-duty vehicles with engine displacements above 2 liters (>2.0 L)	Widespread deployment from Euro 3 to Euro 6 The application of EGR and other NO <sub>x</sub> control technologies is not mutually exclusive; SCR tends to be used in combination with EGR	Light-duty vehicles (high- end, larger vehicles)
Estimated cost per vehicle*	\$320 (engines <2.0 L)	\$418 (engines <2.0 L)	\$142 (engines <2.0 L)	
	\$509 (engines >2.0 L)	\$494 (engines >2.0 L)	\$160 (engines >2.0 L)	



### Takeaways

- The majority of DEF will be consumed by the large Class 8 trucks.
- Smaller trucks will also be major consumers.
- The market is growing rapidly in the passenger segment.
- Alternatives to SCR are rapidly disappearing due to the discovery that emissions soar during actual driving as compared to stationary testing.
- The off road market is relatively small but will grow faster than the others.
- The EU, U.S. China, and Japan will be the big consumers over the forecast period.
- Engine technology developments will have some impact on future markets.
- Diesel fuel will remain popular due to the lower greenhouse gases and fuel efficiency but European cities are presently wondering whether lower greenhouse gases are worth the smog which is prevalent in large cities with large diesel populations.



Worldwide Total-Mcilvaine Forecast



#### Worldwide AdBlue Use



#### AdBlue Use by Region





#### LNT Vehicles are not Meeting the Future Limits

- The implementation of NO<sub>x</sub> control technologies by a few manufacturers is delivering acceptable results over both cycles, whereas other manufacturers are mostly focusing on meeting the limit over the NEDC while neglecting real-world operating conditions, even on the relatively low-load WLTC. All vehicles tested by ADAC except one met the legislative limit of 80 mg/km of NO<sub>x</sub> over the (less demanding) NEDC cycle. Most EGR- and SCR-equipped vehicles performed better than LNT-equipped vehicles over the WLTC, but their average emissions were still far higher than those over the NEDC (by a factor of 2.3 for EGR-equipped vehicles and 2.8 for SCR-equipped vehicles). The same factor was 8.0 for the average of all LNT-equipped vehicles.
- Three LNT-equipped vehicles exhibited very poor performance over the WLTC, with one car emitting up to 1,167 mg/km of NO<sub>x</sub> (i.e., 15 times the regulated limit).
- This casts a shadow of doubt over the real-world performance of all current (pre-RDE) NO<sub>x</sub> control approaches, especially those relying on LNTs, and underscores the importance of engine and after treatment calibration to realize the full potential of available technologies and achieve satisfactory real-world performance.



## Technology - Future Trends

- Urea-SCR technology is increasingly used in diesel engine applications, driven by the engine efficiency and fuel economy demands. The increasing NO<sub>x</sub> conversion efficiency of SCR systems may eventually enable the elimination of engine-based NO<sub>x</sub> control strategies—for example EGR—providing more flexibility in optimizing the engine for performance and fuel economy. The development trends in urea dosing systems include:
- Increasing NO<sub>x</sub> conversion efficiency:
  - Improved control strategies, closed-loop control using ammonia sensors.
  - Higher urea dosing rates and larger urea tanks.
- Close-coupled SCR installation (including SCR-on-DPF):
  - Size reduction and simplification of the dosing system.
  - Better urea atomization and mixing path reduction.
- Reduction of system complexity:
  - Airless dosing systems.
  - Freeze proof design, with no purging requirements.
- Increased robustness, durability and high temperature tolerance.
- Cost reduction.



# **Ongoing Services from Mcilvaine**

#### **Suppliers**

- <u>59EI Gas Turbine and</u> <u>Combined Cycle Supplier</u> <u>Program</u>
- <u>N035 NOx Control World</u>
  <u>Market</u>
- <u>N032 Industrial Air Plants</u>
  <u>and Projects</u>
- <u>42EI Utility Tracking System</u>
- Diesel SCR

#### End users and Suppliers

- <u>441 Power Plant Air Quality</u> <u>Decisions</u>
- <u>59D Gas Turbine and</u>
  <u>Combined Cycle Decisions</u>
- <u>SABC FGD and DeNOx</u>
  <u>Knowledge Systems</u>