REINHOLD ENVIRONMENTAL Ltd.

2011 NOx-Combustion Round Table
& Expo Presentation

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

ELECTRIC POWER
RESEARCH INSTITUTE

Methods for Mitigating SO_3 in Coal-fired Power Plants Equipped with SCR

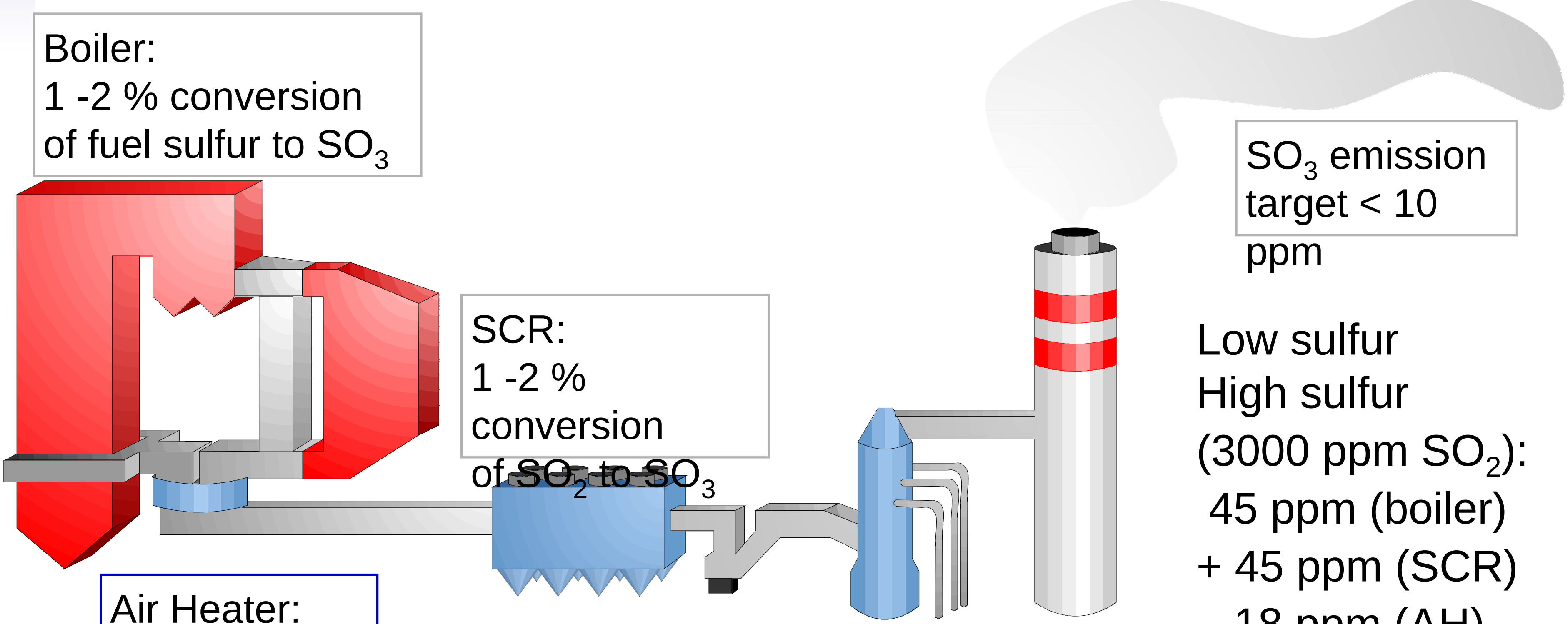
Dave Broske, *EPRI*
Senior Project Manager
Post-Combustion NO_X Control Program

Reinhold's NO_X-Combustion Round Table
February 8, 2011
Birmingham, AL

SO_3 in Boilers and SCR Systems

- Boiler produced SO_3 --- on the order of 0.5 to 1.5% of the SO_2 in flue gas
- SO_3 combines with moisture in flue gas to form H_2SO_4 (sulfuric acid) above 500 F
- Condensation of vapor phase $H_2SO_4 < 300$ F
- Chronic problem for duct corrosion and air heater corrosion and pluggage
- SCR catalyst has, historically, produced 0.75 to 1.5% SO_2 oxidation to SO_3
- Early retrofit applications of SCR to coal-fired units resulted in visible blue plumes
- Under some conditions, 5 ppm of SO_3 can cause a plume

Fate of SO_3 in Power Plants



Boiler:
1 -2 % conversion of fuel sulfur to SO_3

SCR:
1 -2 % conversion of SO_2 to SO_3

SO_3 emission target < 10 ppm

Air Heater:
20 – 30 % H_2SO_4 condensation

ESP:
10 – 30 % SO_3 removed with fly ash

Wet-FGD:
30 – 70 % SO_3 removal

Low sulfur
High sulfur
(3000 ppm SO_2):
45 ppm (boiler)
+ 45 ppm (SCR)
– 18 ppm (AH)
– 18 ppm (ESP)
– 42 ppm (WFGD)
≡ 12 ppm at stack

12 ppm at stack

Source: E.ON Engineering Corp

Model for Estimating Total Sulfuric Acid Emissions from Stationary Power Plants

- Section 313 of the Emergency Planning and Community Right-to-Know Act (EPCRA), also known as Toxic Release Inventory (TRI) requires facilities that “manufacture,” “process,” or “otherwise use” a listed chemical above certain threshold amounts to report their annual releases of the chemical to EPA and state agencies.
- Sulfuric acid is a listed TRI chemical.
- The deployment of 115 GW of SCR from 1997 through 2009 has prompted power plant owners to conduct extensive measurements documenting the fate of SO_3 and sulfuric acid in power plants.
- Between 2000 and 2005, Southern Company Services developed several versions of the estimation methodology for SO_3 emissions.

Model for Estimating Total Sulfuric Acid Emissions from Stationary Power Plants (continued)

- In 2007, EPRI received permission to modify the SCS estimation method to include additional data and improvements, and to publish it under EPRI sponsorship.
- The 2008 version of the model added the ability to estimate emissions based on a specified sulfuric acid flue gas concentration at the stack.
- Three process steps lead to the manufacture of sulfuric acid in a fossil fuel-fired electricity generation unit: the combustion process, selective catalytic reduction (SCR) for NOx control, and flue gas conditioning.

Model for Estimating Total Sulfuric Acid Emissions from Stationary Power Plants (continued)

- **TSAR = ERComb + ERSCR/SNCR + ERFGC** where,
  - TSAR = Total release of sulfuric acid
  - ERComb = Combustion
  - ERSCR/SNCR = SCR (or SNCR)
  - ERFGC = Flue gas conditioning
- EMERComb = EMComb ● F2 (all that apply)
- ERSCR = [EMSCR – (Ks • B • fsreagent • SNH3)] • F2x
- ERFGC = [EMFGC – (Ke • B • fe • INH3)] • F3FGC • F2
- Model applies to coal- and oil-fired steam generating units as well as simple-cycle and combined-cycle natural gas- and oil-fired combustion turbines.
- Reference --- *Estimating Total Sulfuric Acid Emissions from Stationary Power Plants: Version 2010a.* EPRI, Palo Alto, CA: 2010. 1020636.

SO_3 Control Technologies

- **Physical Methods**
  - Fuel blending or switching
  - Wet ESP
  - Condensing air heater
- **SCR Catalyst**
  - While SCR catalyst is a producer of SO_3, recent innovations can minimize its formation
- **Chemical Methods**
  - Additive injection with the fuel or in the flue gas
  - Reaction with SO_3 to form solid compounds that can be removed in a particulate collection device

SO_3 Control Technologies – Physical Methods

- **Fuel blending or switching**
  - Lower sulfur fuel reduces the SO_3 concentration in the flue gas
  - Potential Issues
    - SO_3 content in flue gas may reduce the effectiveness of the electrostatic precipitator
    - Slagging of furnace walls or fouling of convection pass tubes
    - Boiler derating
    - Increased fuel cost

SO_3 Control Technologies – Physical Methods

- **Wet ESP**
  - New technology for the power industry
  - Condense sulfuric acid from vapor phase onto the collection plate
  - Allow acid to drain from the plate and subsequently clean the aqueous waste
  - Wet ESP improves the submicron particle collection compared to a dry ESP largely because the continuously wetted collection plates prevent re-entrainment.
  - Condensing the acid mist does require that the ESP collection plates or pipes be made of alloys (or newly developed non-metallic membranes) to reduce corrosion.

SO_3 Control Technologies – Physical Methods

- **Condensing Air Heater**
  - Similar in concept to the wet ESP
  - Sulfuric acid mist is condensed on fly ash particles collected on tubes cooled internally by water.
  - Alkaline material, such as lime or limestone, would then be added to neutralize the pH of the ash
  - Requires special corrosion-resistant alloys or ceramics for the air heater tubes

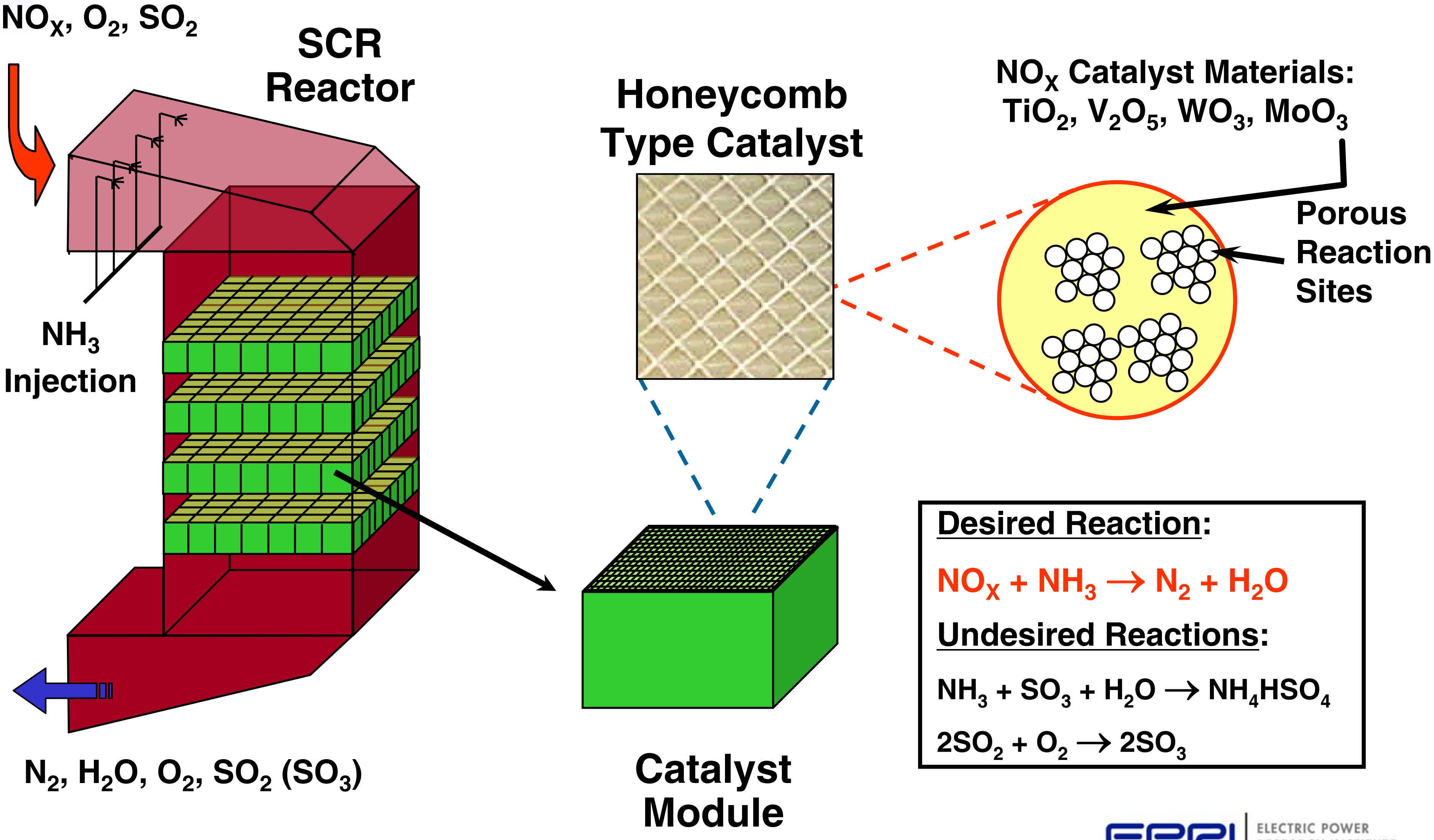
SO_3 Control Technologies – SCR Catalyst

1990's SCR Applications

- 0.75 to 1.5% SO_2 oxidation
- < 1% would probably avoid SO_3-based plumes
- Operating experience on higher sulfur units in the US demonstrated otherwise
- German SCR experience did not prepare US SCR operators

Source: URS

SO_3 Control Technologies – SCR Catalyst



NO_X, O_2, SO_2

SCR Reactor

NH_3 Injection

N_2, H_2O, O_2, SO_2 (SO_3)

Honeycomb Type Catalyst

Catalyst Module

NO_X Catalyst Materials:
TiO_2, V_2O_5, WO_3, MoO_3

Porous Reaction Sites

Desired Reaction:

$NO_X + NH_3 \rightarrow N_2 + H_2O$

Undesired Reactions:

$NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4$

$2SO_2 + O_2 \rightarrow 2SO_3$

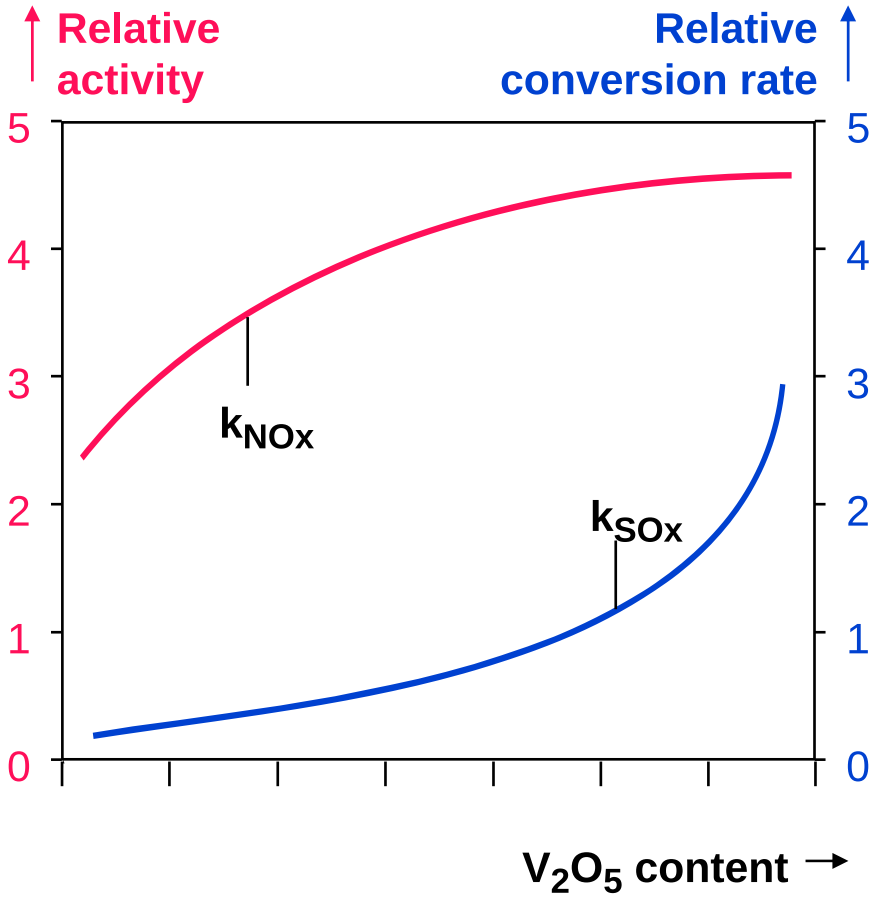
Methods for Limiting SO_2 Oxidation by Catalyst

- **Methods for reducing SO_2 oxidation levels**
  - Selection of active ingredients
  - Redistribution of active ingredients within the catalyst
- **Active ingredients**
  - Substitute molybdenum- and tungsten-based compounds in place of vanadium
- **Redistribution**
  - NO_X removal within 50 microns of the catalyst surface
  - SO_2 oxidation takes place throughout the catalyst volume

Vendor's Strategies for Limiting SO_2 Oxidation by Catalyst

- **Ceram**
  - Historically low
- **Cormetech**
  - Altered active ingredient distribution
- **Haldor Topsoe**
  - Historically low, 0.3%
- **Hitachi**
  - Developing low SO_2 oxidation, combined with higher Hg oxidation
- **Johnson Matthey** (formerly Argillon)
  - Changes in formulation

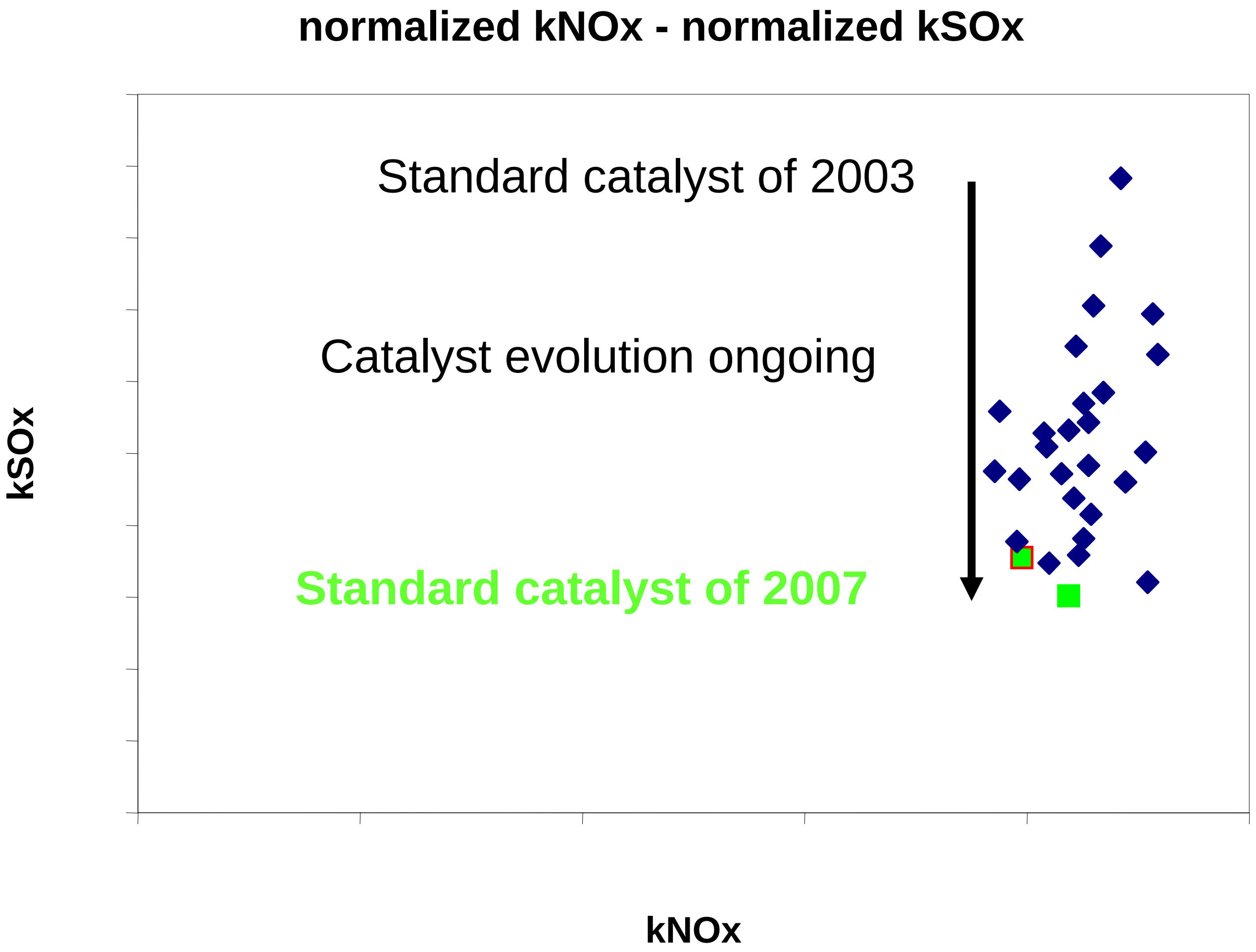
Improving LowSOx Catalyst
Catalyst SO_2 conversion rate linked to NO_x activity



If an attempt is made to decrease the conversion rate of an SCR catalyst the NO_x activity typically decreases simultaneously.

R&D efforts are made to develop catalysts which have lower SO_2 oxidation, while at the same time the NO_x activity remains high.

Achievements in Development of low SOx-Catalyst

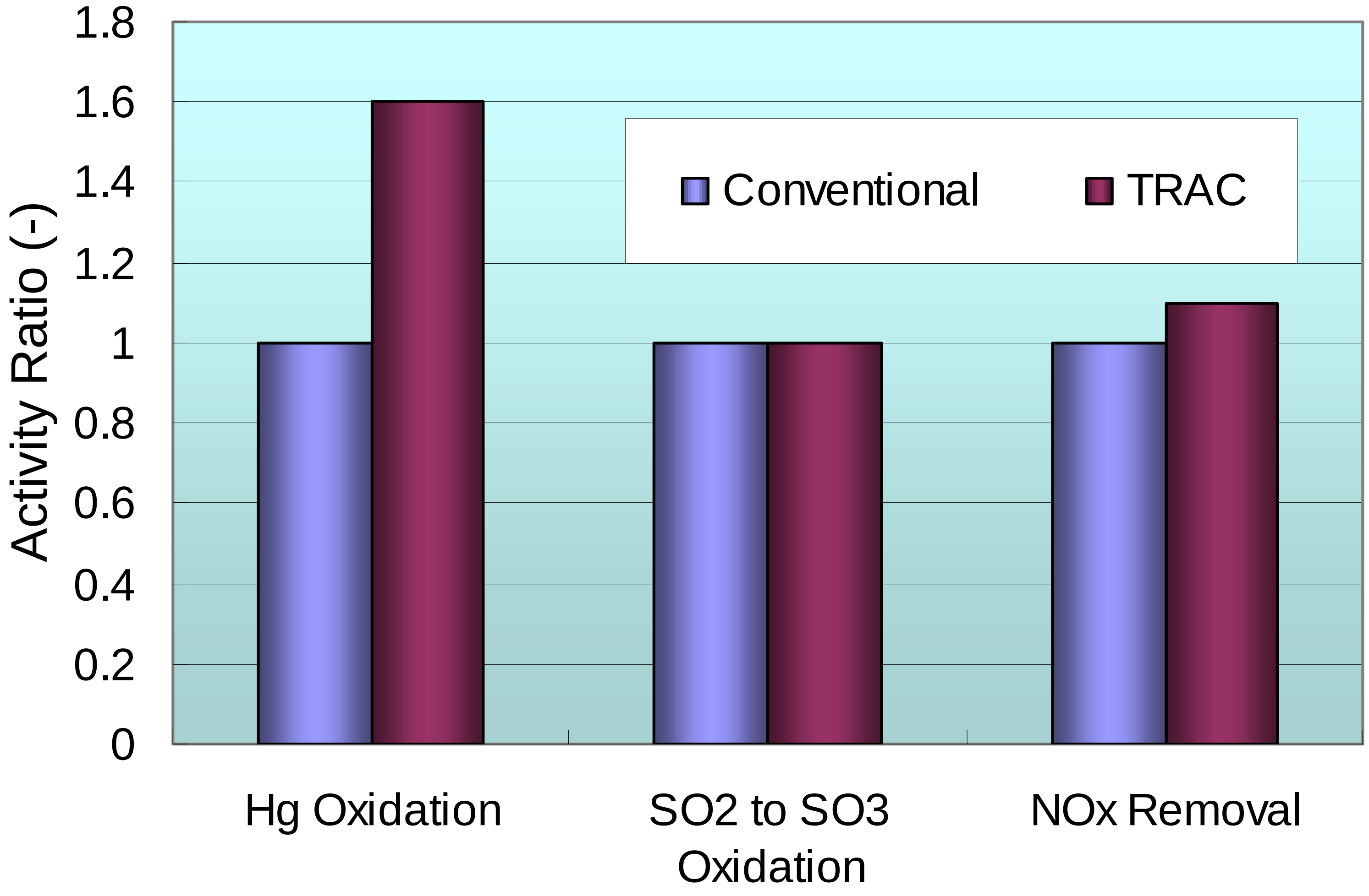


Benefits

- Reduced costs
- Reduced catalyst volume
- Reduced pressure drop

Typical Performance of TRAC®

*TRAC® – TRiple Action Catalyst**



Summary for Newly Developed Catalysts

1. CM and TRAC® catalysts can be applied for both PRB and E.B. coals
2. Both are able to achieve less than 0.25% of SO_2 / SO_3 oxidation rate per layer for E.B.
3. Both reduce the need for sorbent injection for SO_3 mitigation
4. TRAC ® enhances Hg oxidation capability with 95% Hg oxidation possible at A/H outlet to avoid ACI for E.B. coal, and PRB with minimal or no Halogen Injection required

Development continues thru Hitachi's R&D efforts to further enhance our SCR catalyst performance.

SO_2 Oxidation by Catalyst Over Time

- Testing by E.ON Engineering appears to show that catalyst formulated for low SO_2 oxidation can evolve to a higher rate over time.
- At present, the observation is limited to plate-type catalyst
- Increase may be associated with an accumulation of iron oxide (Fe_2O_3)
- Specific crystalline form, perhaps prompted by exposure to moisture

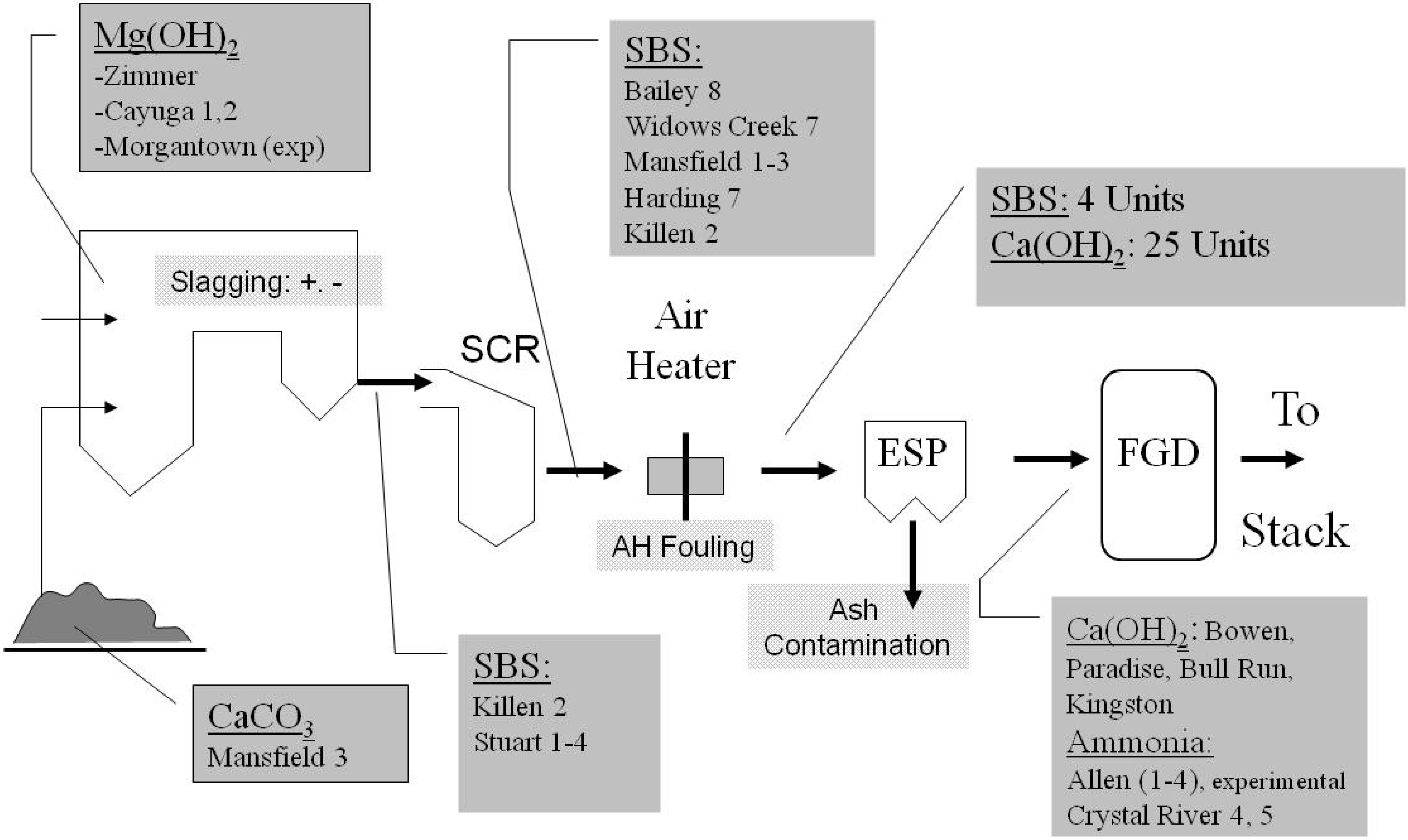
SO_2 Oxidation by Catalyst Over Time (continued)

- Claims of extremely low SO_2 oxidation (0.2%) should be viewed with caution.
- Conducting an accurate measurement of SO_2 oxidation is a challenge.
- Controlled condensation technique can under report SO_3, depending on how the measurement is conducted
- Variability of inlet SO_2 in terms of average content and distribution across the duct will affect results.
- Not clear that field measurements currently conducted are adequate
- Should SO_2 oxidation measurements be conducted in the lab, under well-controlled conditions?

Chemical Methods for SO_2 Control (Reagent Injection)

- Limestone (widely available, usually low cost)
- Dry dolomite powder ($CaCO_3MgCO_3$) or dolomite
  - Contains magnesium as a supplemental alkali material
- Lime (CaO)
- Hydrated lime and pressure hydrated lime
- Magnesium hydroxide ($Mg(OH)_2$)
- Solutions of sodium sulfite and/or bisulfite
  - Used for initial deployment of the SBS process
- Soda ash, known as sodium carbonate (Na_2CO_3)
  - Presently used in SBS process
- Trona, predominantly Na_2CO_3NaHCO

Locations for Reagent Injection or Addition



<u>$Mg(OH)_2$</u>
-Zimmer
-Cayuga 1,2
-Morgantown (exp)

<u>SBS:</u>
Bailey 8
Widows Creek 7
Mansfield 1-3
Harding 7
Killen 2

<u>SBS:</u> 4 Units
<u>$Ca(OH)_2$</u>: 25 Units

Slagging: +. -

AH Fouling

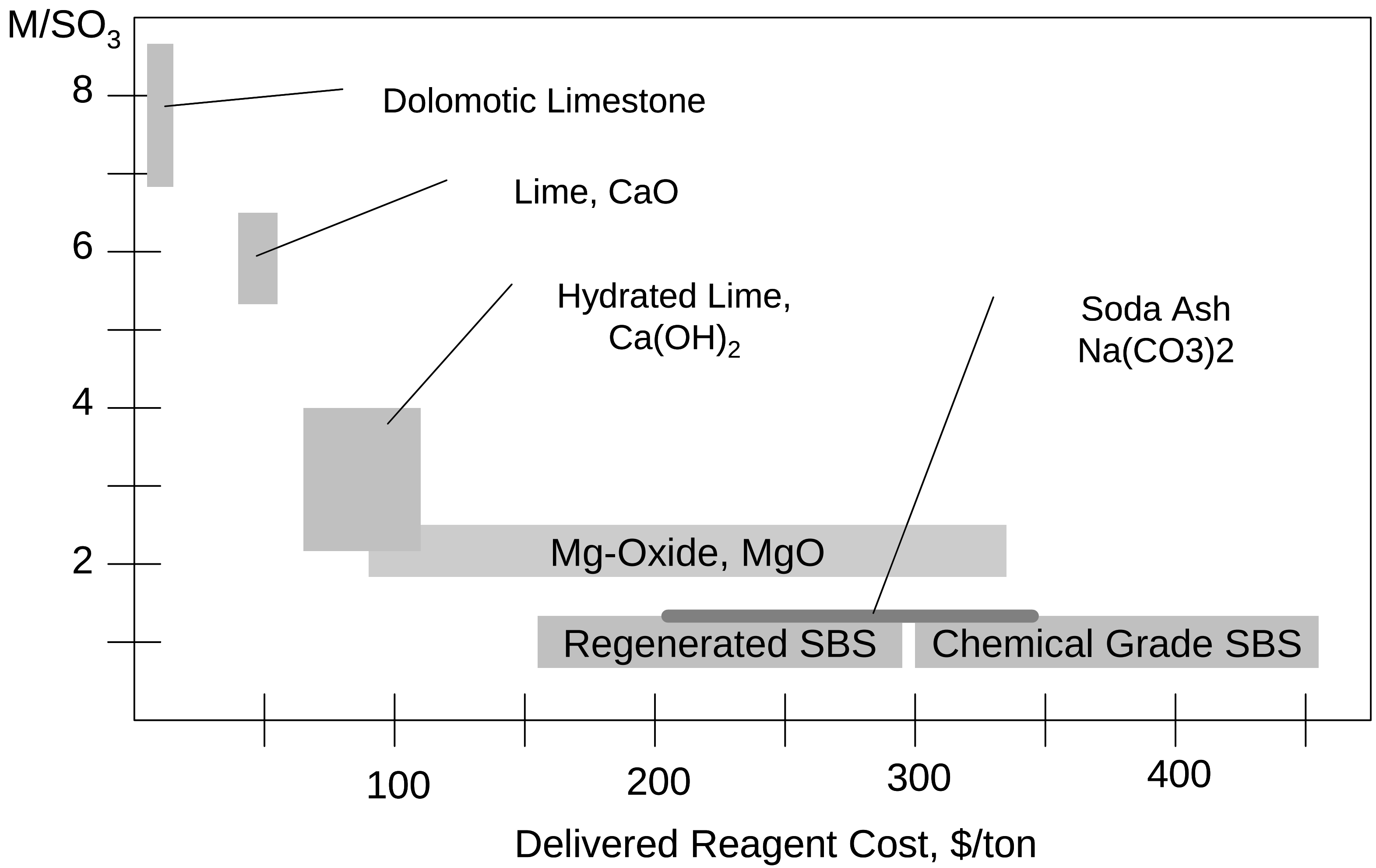
Ash Contamination

<u>$CaCO_3$</u>
Mansfield 3

<u>SBS:</u>
Killen 2
Stuart 1-4

<u>$Ca(OH)_2$</u>: Bowen, Paradise, Bull Run, Kingston
<u>Ammonia:</u>
Allen (1-4), experimental
Crystal River 4, 5

Reagent Addition Rate (Molar Basis) for 80-95% SO_3 Removal vs. Delivered Cost



Alkali-Containing Reagents for SO_3 Control

Reagent	Active Alkali	Approximate Cost ($/ton)	Injection Locations Tested to Date	Comment
Conventional Limestone ($CaCO_3$)	Calcium	15-20	Added to coal	Widely available, relatively low cost
Dry dolomite limestone ($CaCO_3 \bullet MgCO_3$)	Calcium and magnesium	15-20	Furnace and convective sections	Mg resists sulfation at high temp
Lime (CaO)	Calcium	50-80	Furnace and convective sections	Widely available and used in dry scrubbers
Pressure hydrated lime, $Ca(OH)_2$, and pressure hydrated dolomitic lime $Ca(OH)_2 \bullet Mg(OH)_2$	Calcium, Magnesium	70-100	Furnace and convective sections; duct locations	Provides higher activity when decomposed
Magnesium hydroxide [$Mg(OH)_2$] or magnesium oxide [MgO]	Magnesium	150-325 depending on byproduct or raw source	Furnace and convective sections; duct locations	Used on oil-fired boilers for SO_3 control
Sodium sulfite and/or bisulfite solutions	Sodium	Highly variable, to 300; depends on proximity to source	Preceding air heater; following AH	Adequate residence time necessary to evaporate transport water. Sodium may favorably affect ESP performance.
Soda Ash (Na_2CO_3) or sodium sesquicarbonate	Sodium	Similar to sodium sulfite or bisulfite solutions	Preceding air heater; following AH	More widely available than sodium sulfite or bisulfite. Sodium may favorably affect ESP performance.
Trona	Sodium	Highly variable; transported from WY	Following air heater, and preceding ESP	Dry injection of sodium may improve ESP performance

Commercial Applications of SBS Injection for SO_3 Control

Reagent	Utility	Station/Unit	Capacity (MW)	Injection location (Design SO_3 Value, ppm))	Date Commercial
Sodium Carbonate	Duke	Gibson 1-5	5x650	Air heater outlet (110)	2 units since Nov. 2003; others in 2004 and 2005
SBS: Sodium Sulfite	First Energy	Bruce Mansfield Units 1-2	3x860	Air heater inlet (54)	March-April 03 for Units 1/2; January 04 for Unit 3
"	TVA	Widows Creek Unit 7	550	Air heater inlet (80)	April 2003
Sodium Carbonate	PPL	Montour Units 1,2	776	Air heater outlet (42)	August 2004
Sodium Carbonate	NiSource	Bailly Unit 8 and Unit 7	365 and 180	Air heater outlet (59)	Unit 8 in April 04; Unit 7 in 07
Byproduct Sodium Bisulfate	Vectren	Culley Unit 3	287	Air heater outlet (48)	July 2004
Sodium Carbonate	DP&L	Killen Unit 2	635	Economizer outlet (34) and air heater inlet (36)	October 2007
Sodium Carbonate	IP&L	Harding Street Unit 7	465	Air heater inlet (58)	November 2007

Calcium, Magnesium, and Trona Applications for SO_3 Control

Reagent	Utility	Station/Unit	Capacity (MW)	Injection Location	Date Commercial
Trona (Na_2CO_3* $NaHCO_3$)	AEP	Gavin Unit 2	1300	Air Heater Outlet	4Q 2003
	Duke	Zimmer Unit 1	1x1300	Air Heater Outlet	2005
	AES	Somerset	635	Air Heater Outlet	Demo 2007
	AEP	Mitchell Unit 1	850	Air Heater Outlet	Commercial 2007
Hydrated Lime $Ca(OH)_2$	TVA	Widows Creek Unit 8	550	Air Heater outlet	2nd generation system November 2005
	TVA	Cumberland Unit 1	1300	Air Heater outlet	November 2005
	Duke	Zimmer Unit 1	1 x 1300	Air Heater Outlet	2003-2005
	AEP	Gavin Unit 2	1400	Dry hydrated lime at air heater outlet	Demo: Summer 2003

Annual Reagent Based SO_3 Mitigation Methods

Reagent Type, Stoichiometric Ratio	Annual Operating Cost ($M/y) (40 ppm SO_3)	Annual Operating Cost ($M/y) (60 ppm SO_3)	Annual Operating Cost ($M/y) (80 ppm SO_3)
$Ca(OH)_2$ @ 2.5/1	0.54	0.81	1.1
Trona @ 0.9/1	0.73	1.1	1.5
SBS @ 1.2/1	0.81	1.2	1.6
Annualized Catalyst Cost (@$200/c.f.)	0.85	Same	Same
NH_3 Reagent for NO_x Reduction (@$400/ton)	1.05	Same	Same

Together…Shaping the Future of Electricity

References

- Dinah Dux, E.ON Engineering Presentation, EPRI SCR Workshop, Nov. 11-13, 2008.
- *Estimating Total Sulfuric Acid Emissions from Stationary Power Plants: Version 2010a.* EPRI, Palo Alto, CA: 2010. 1020636.
- *SO_3 Mitigation: Current Utility Operating Experience.* EPRI, Palo Alto, CA: 2006. 1010754.
- Ken Jeffers, Johnson Matthey Catalysts LLC, Presentation at the Web Conference on SCR Operation & Maintenance Thursday, June 10, 2010
- Stephen Guglielmo, Hitachi Power Systems America, Inc., Presentation at the Web Conference on SCR Operation & Maintenance Thursday, June 10, 2010
- *Operation and Maintenance Guidelines for Selective Catalytic Reduction: 2010 Update.* EPRI, Palo Alto, CA: 2010. 1019707.