REINHOLD ENVIRONMENTAL Ltd.

2012 NOx-Combustion Round Table & Expo Presentation

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NO Oxidation and Capture with Wet and Dry Scrubbers

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2012 RE NOx and Combustion Round Table and Expo

PerNOxide is a mark of FMC Corporation

Agenda

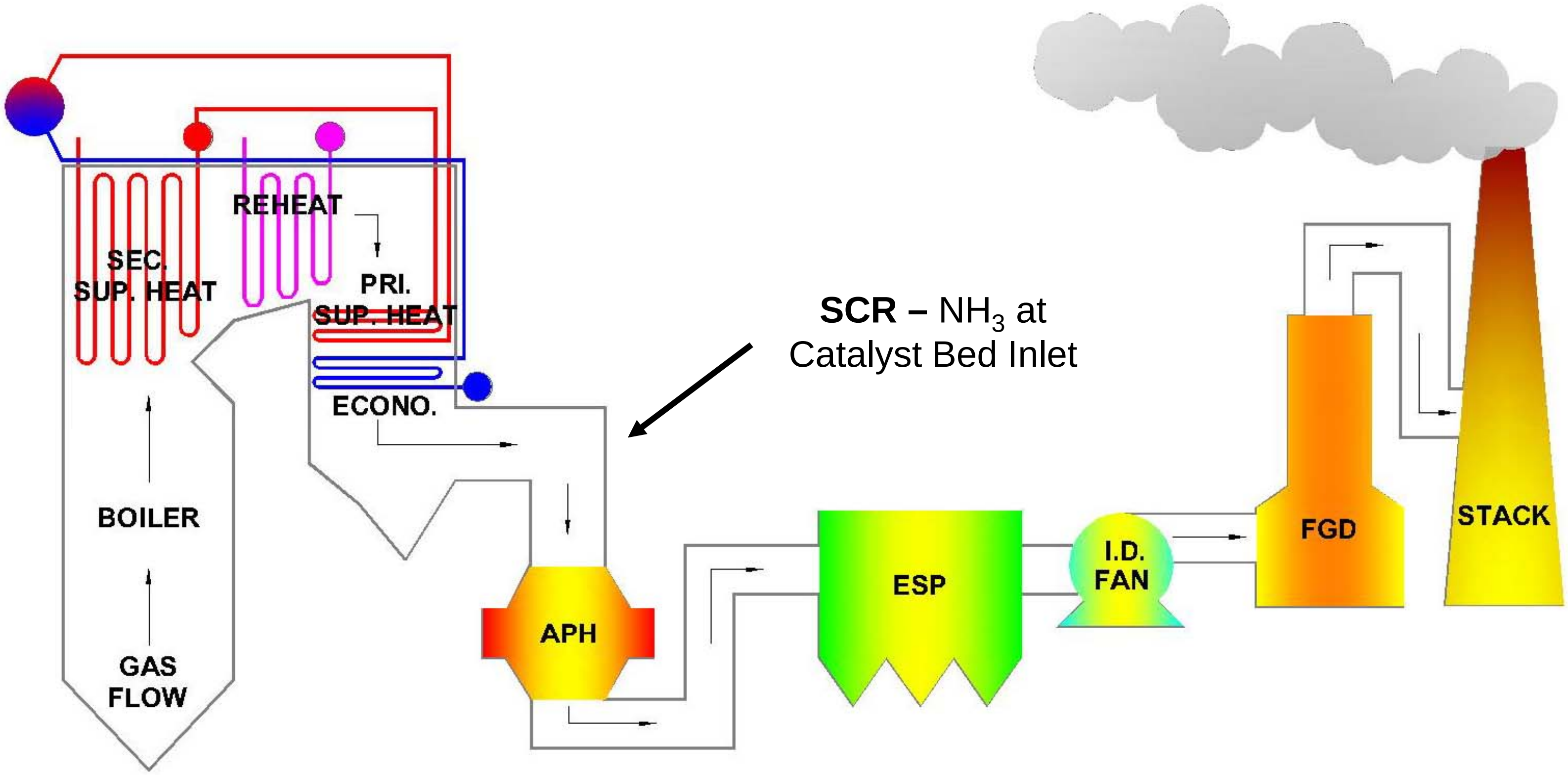
- Overview of Post Combustion NOx controls
- Overview of Oxidation Technologies
- FMC PerNOxide Technology
- Wet Chemistry Research
- Dry Chemistry Research
- Economic Analysis
- PerNOxide Advantages & Challenges
- Applications
- Summary

Post Combustion Technologies

- Selective Catalytic Reduction - SCR
- Selective Non-Catalytic Reduction – SNCR
- Others, including FMC's PerNOxide

SCR

NO_x Control Options - SCR

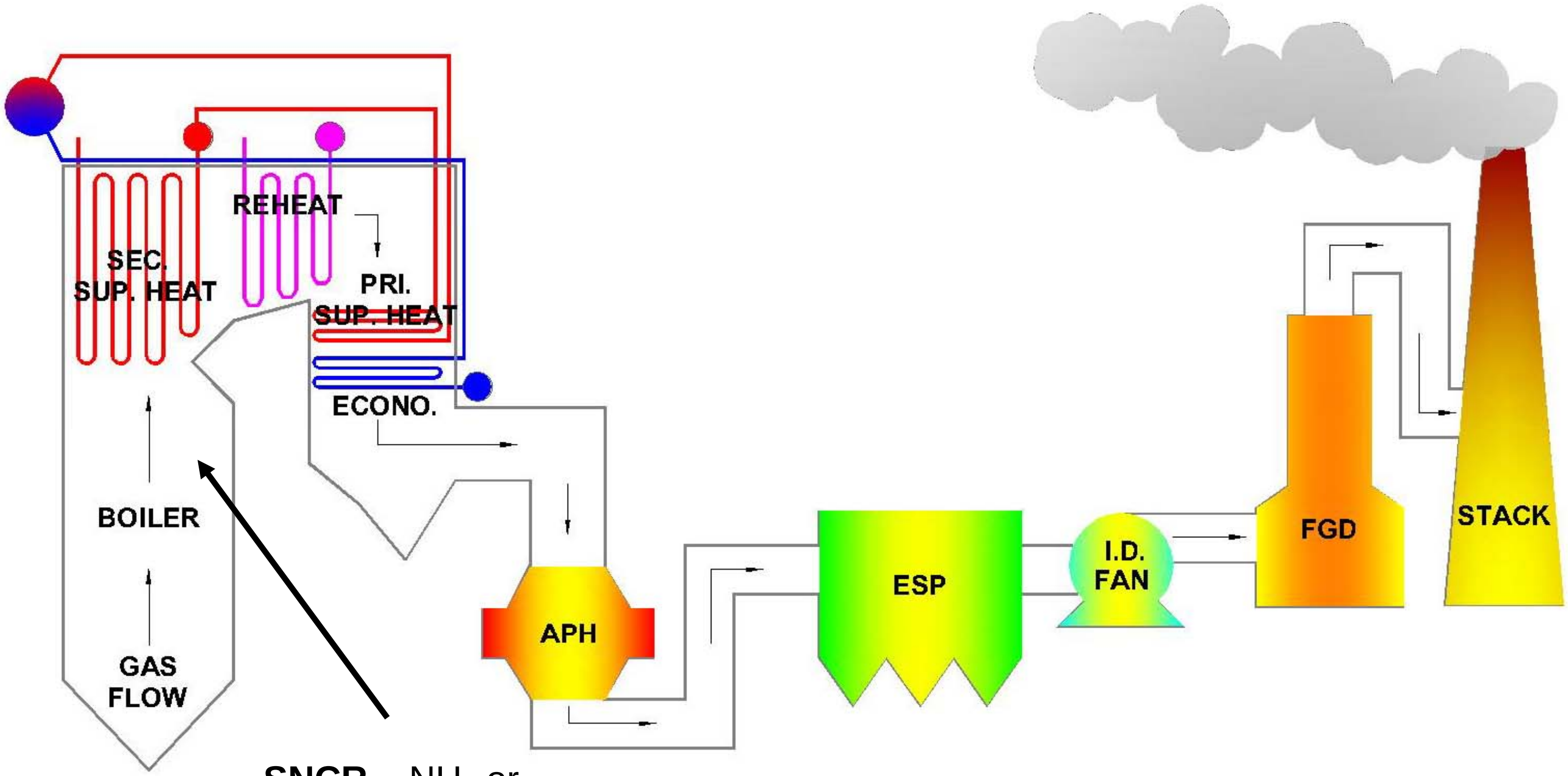


SCR

- Inject NH_3 ahead of catalyst
  - Anhydrous or aqueous
- NO chemically reduced to N_2
- $4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$
- $NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$
- NOx reductions of 75-90%
- Excess NH_3 can react with SO_3 to form ammonium bisulfate (NH_4HSO_4)
  - Causes air preheater and catalyst fouling
- Catalyst pluggage (ash) and poisoning (As)

SNCR

NO_x Control Options - SNCR



SNCR – NH_3 or Urea into Boiler

SNCR

- Injection at high temperatures in boiler
- Injection temperature is critical - ~1400 - 2000 °F
- Usually multiple injection levels to get close to temperature “sweet spot” under varying operating conditions
- Urea or NH_3 injected. No catalyst needed
- $4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$
- $2NO + (NH_2)_2CO + 1/2O_2 \rightarrow 2N_2 + 2H_2O + CO_2$
- NOx reductions of 15-40%

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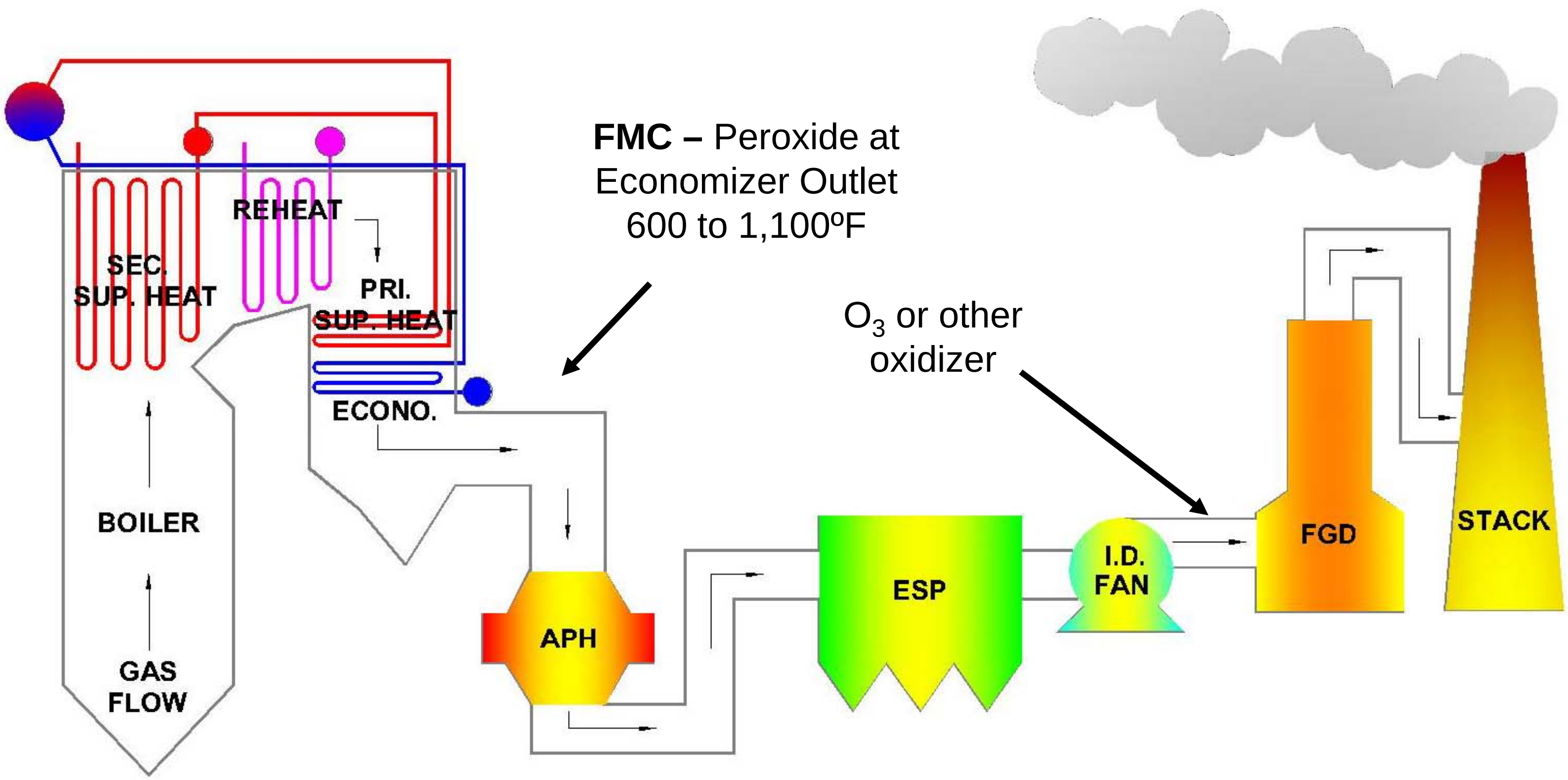
Oxidation Technologies

NO_x Control Options - Oxidation



NOx Capture by Wet Scrubber

- Not new. Considered since 1970s when scrubbers became popular and technologists were looking for "multi-pollutant" use of scrubbers
- NO is not water soluble
- Oxidation of NO can lead to many N species
  - NO_2, N_2O_5, HNO_3, HNO_2
- NO_2 is water soluble, but less than SO_2
- N_2O_5 reacts with H_20 to form HNO_3, which is highly water soluble

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Ozone (O_3) Oxidation

- Ozone generation required
- $NO + O_3 \rightarrow NO_2 + O_2$
- $2NO_2 + O_3 \rightarrow N_2O_5 + O_2$
- $N_2O_5 + H_2O \rightarrow 2HNO_3$
- HNO_3 is highly water soluble
- Technologies:
  - LoTOx, Lextran, Comply 2000, Power Span ECO
- All inject at low temperatures
- Claim up to 90% NOx reduction

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PerNOxide Process

- Inject hydrogen peroxide (H_2O_2)
- Normal decomposition: $H_2O_2 \rightarrow H_2O + 1/2\ O_2$
- At elevated temperatures dissociates into
  - **$H_2O_2 \rightarrow 2\ OH^{\bullet}$**
  - **$H_2O_2 \rightarrow OH^{\bullet} + H$**
- Oxidizes NO to NO_2 and N_2O_5
- Can achieve > 80% oxidation
- Up to 70% NOx reduction with wet scrubbers
- Up to 50% NOx reduction with dry scrubbers

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Hydrogen Peroxide (H_2O_2)

- Strong, environmentally friendly oxidizing agent
- Major end uses: pulp & paper, chemicals, food, hair treatment, antiseptic, and electronics
- Product provided in various grades and concentrations
- North American Capacity – 850,000 tons/yr
  - FMC is a leading North American supplier

Peroxide Characteristics

- Specific gravity: 1.2
- Weight: 10 #/gal @ 50% concentration
- Apparent pH: ≤ 3.0
- Freezing point: -62 °F @ 50% concentration

Peroxide Injection

- Injected into duct between economizer and APH inlet
- Concentration controlled to achieve required NOx reduction
- Two fluid nozzles (air assisted atomization) used to produce fine droplets
- Water evaporates and peroxide dissociates
- NO oxidized

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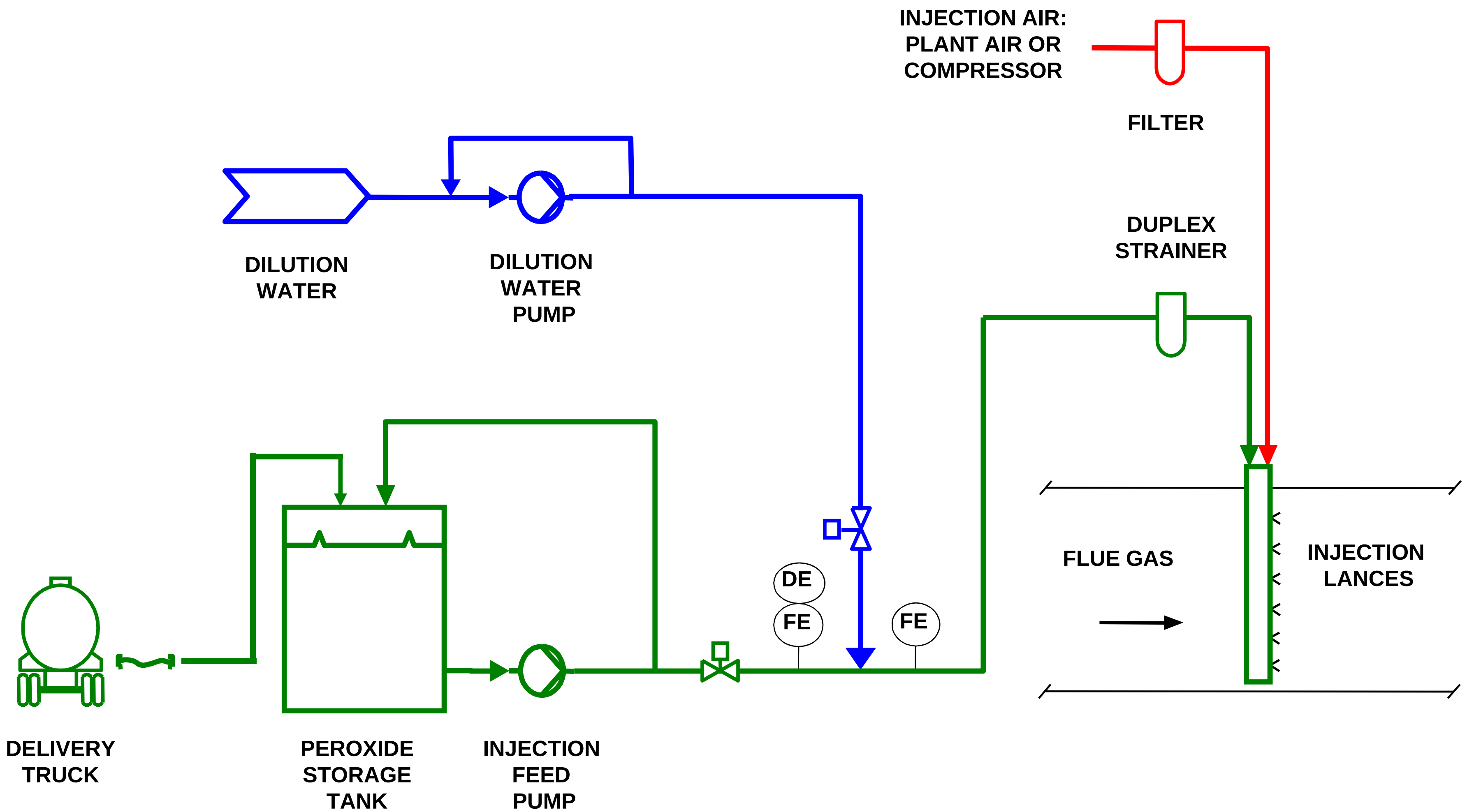
Simplified Process Flow Diagram



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Injection Lances

Injection Ports

NO_x Capture Options

- NO_x Capture Enhancement
  - Wet lime / limestone / sodium scrubbers
  - Circulating Dry Scrubbers (CDS)
  - Spray Dryer Absorbers (SDA)

PerNOxide Process Development

- NASA Patent 6,676,912
  - Use of peroxide to oxidize NO to soluble species
  - FMC has exclusive license from NASA
- 3 full scale demonstrations
- FMC & URS Collaboration
  - Process development
  - Technology demonstrations
  - Commercial applications
- FMC testing at EERC on pilot SDA/FF

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Full Scale Demo Conclusions

- High NO oxidation up to 80%
- Disappointing NOx reduction ~20%
- Need to understand wet scrubber chemistry

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URS Wet Chemistry Study

URS Test Program Objectives

- Conduct Bench-Scale FGD Testing
  - Quantify effect of solution comp. on NO_x removal
  - Key Variables: Liquid sulfite, pH, buffer additives, thiosulfate
- Perform Computer Modeling of FGD Chemistry
  - Process material balances
  - Aqueous Chemical and Physical Properties Model
  - Investigate how to achieve solution composition necessary for significant NO_x removal
  - Consider accumulation of dissolved nitrogen species

Bench-Scale Test Conditions

- Flue Gas "Bubbler" Contactor
- Contactor Adjusted to Representative Levels
  - Max removal of ~98% SO_2; ~ 70% NO_2
- Flue Gas Composition:
  - Simulated flue gas (O_2, SO_2)
  - 40 ppm NO, 70 ppm NO_2
- Solution Composition:
  - Dissolved sulfite: 0 – 9,000 mg/l
  - Solution pH: 5 – 7 (11)
  - Adipic acid: 0 – 5,000 mg/l
  - Thiosulfate: 0 – 2,000 mg/l

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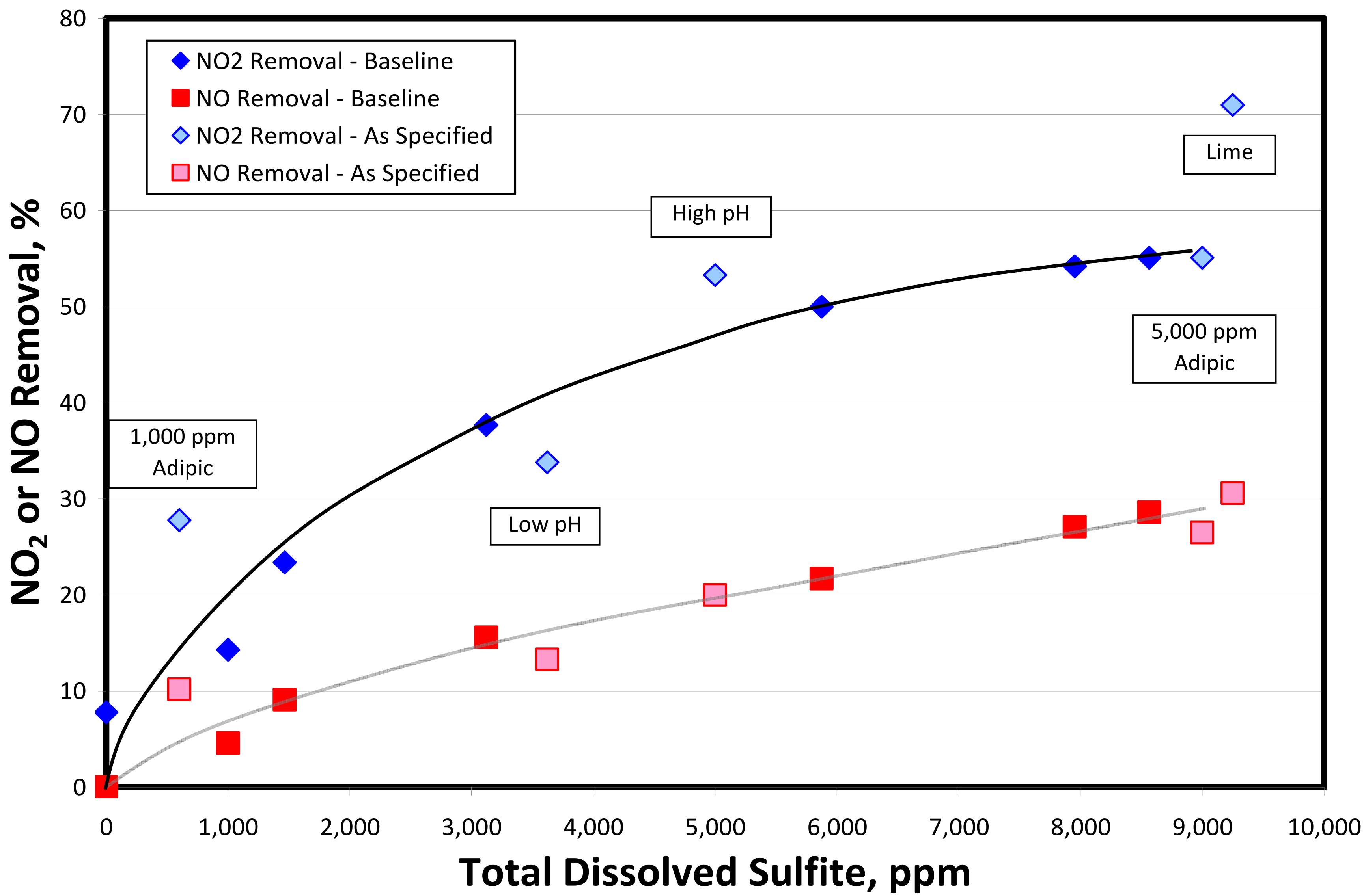
NO_x Removal Efficiencies



NO_x Removal in Wet Scrubbers

- Higher-order nitrogen oxides are very soluble with removal efficiencies > 95%
- NO_2 is less soluble, but removal is enhanced by dissolved sulfite
- Reaction products include:
  - Nitrate, S-N species, N_2 gas
- Dissolved sulfite levels must be elevated using scrubber additives:
  - Sodium, magnesium
- Confirmation of bench-scale data needed

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Pilot Wet Scrubber Test Program

- Being conducted in 1stQ - 2012
- Use URS pilot wet scrubber (slip-stream)
- NO_2 Addition to simulate Oxidation
- Test NO_2 capture relative to FGD chemistry
  - Sodium
  - Lime, inhibited oxidation
  - Limestone, Inhibited oxidation
  - Limestone, forced oxidation
- Assess longer term impact of N species capture on scrubber chemistry

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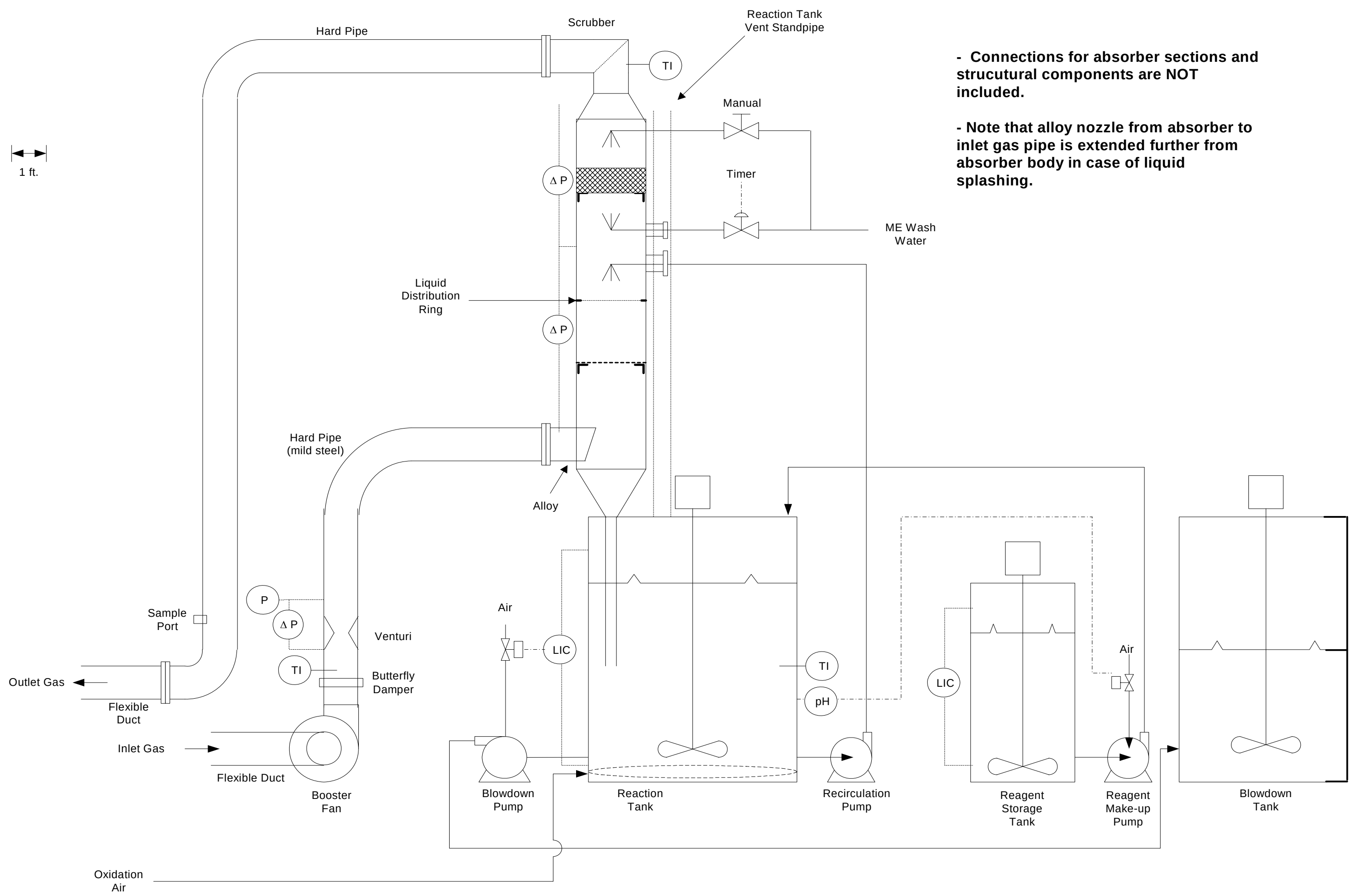
Pilot Wet Scrubber Diagram



- Connections for absorber sections and strucutural components are NOT included.

- Note that alloy nozzle from absorber to inlet gas pipe is extended further from absorber body in case of liquid splashing.

Pilot Wet Scrubber System

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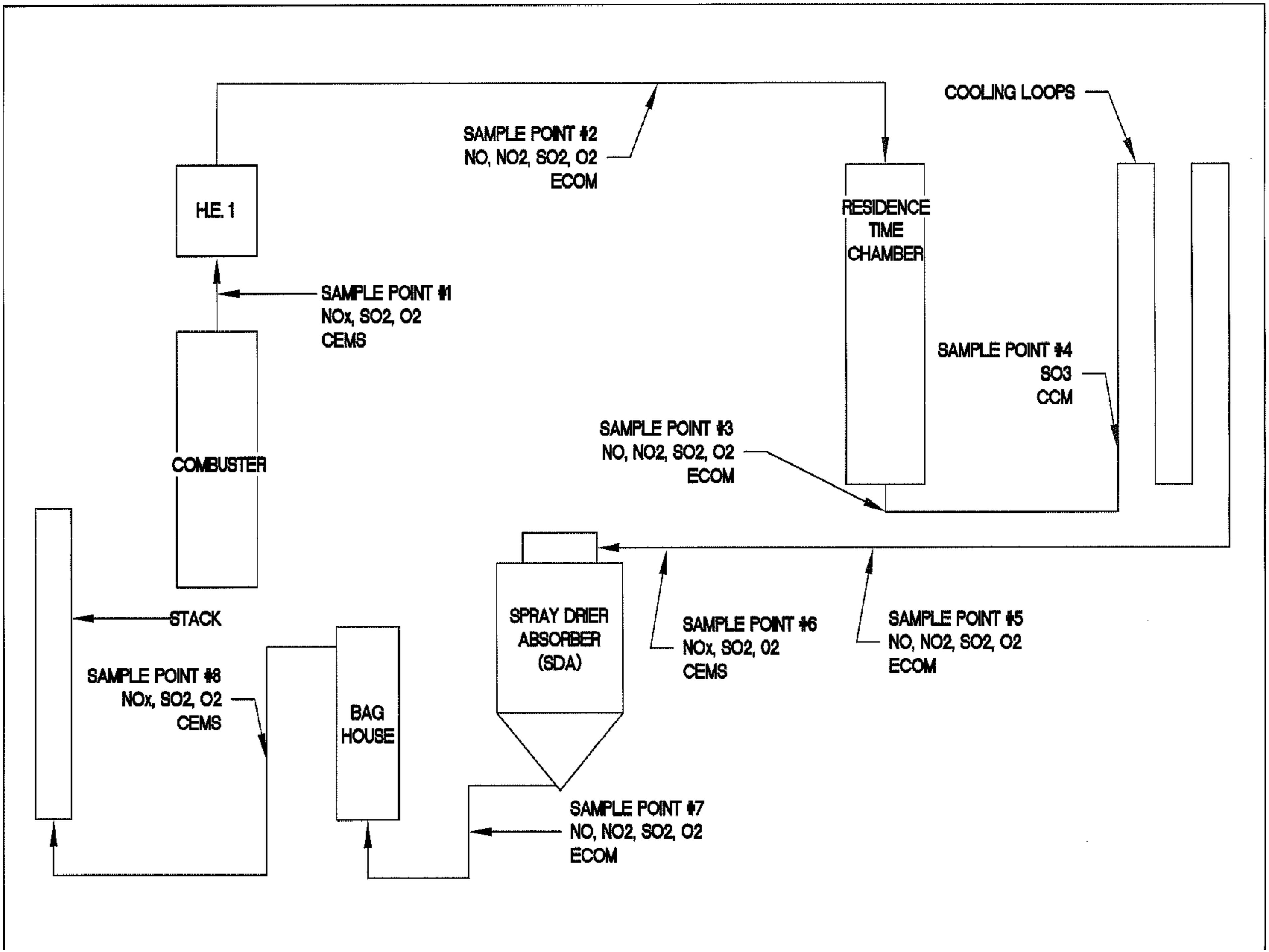
Dry Chemistry Study

Pilot Combustor Specifications

- Combustor
  - Coal or natural gas
  - 555,000 #/hr, 130 scfm
- Reaction tower
  - Simulate duct residence time
- SDA – rotary atomizer
  - 8 second treatment time
- FF – Pulse jet
  - A/C ratio of 4
  - Teflon bags with Teflon membrane



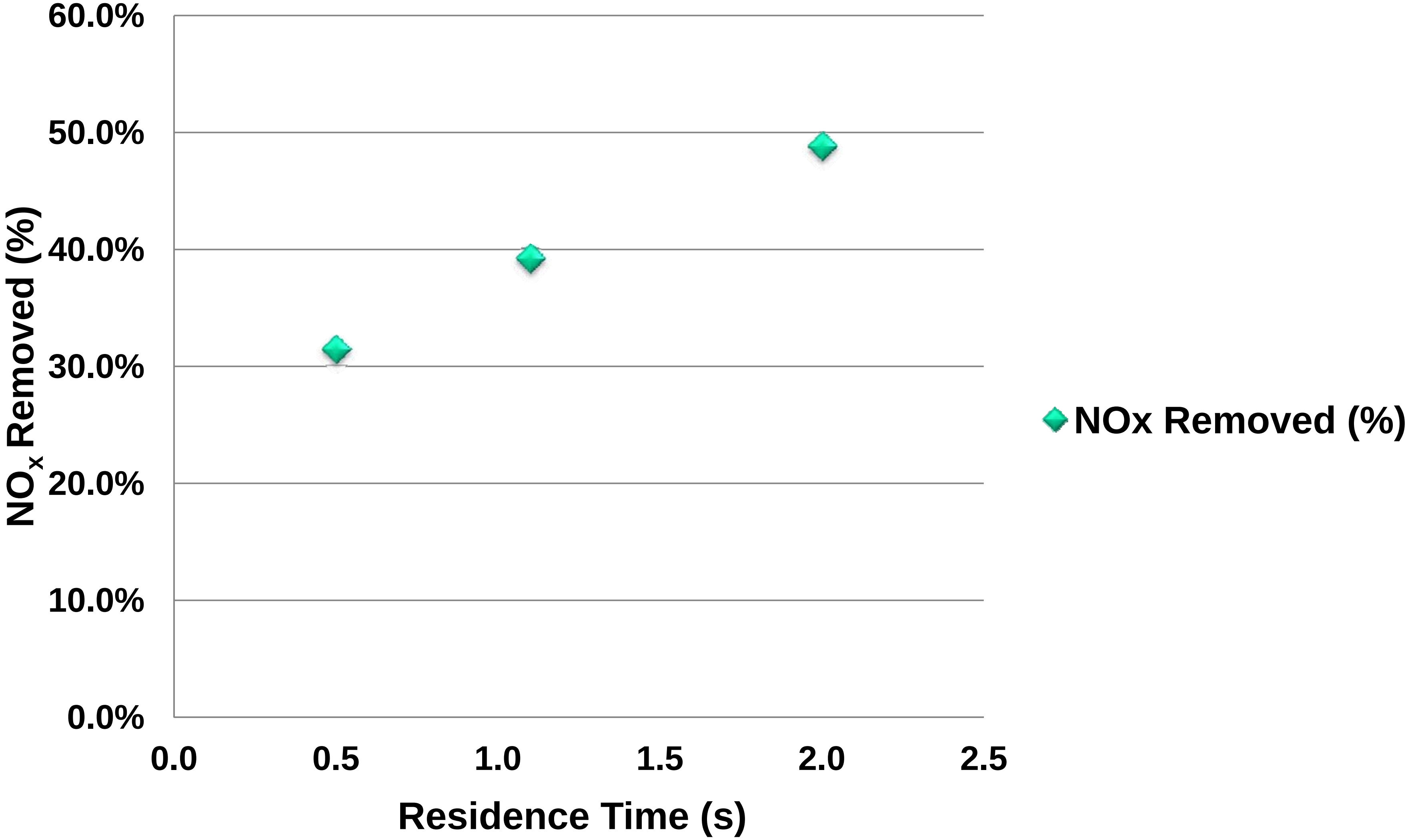
COOLING LOOPS
SAMPLE POINT #2
NO, NO2, SO2, O2
ECOM
H.E. 1
RESIDENCE
TIME
CHAMBER
SAMPLE POINT #1
NOx, SO2, O2
CEMS
SAMPLE POINT #4
SO3
CCM
SAMPLE POINT #3
NO, NO2, SO2, O2
ECOM
COMBUSTER
SPRAY DRIER
ABSORBER
(SDA)
STACK
SAMPLE POINT #6
NOx, SO2, O2
CEMS
SAMPLE POINT #5
NO, NO2, SO2, O2
ECOM
SAMPLE POINT #8
NOx, SO2, O2
CEMS
BAG
HOUSE
SAMPLE POINT #7
NO, NO2, SO2, O2
ECOM

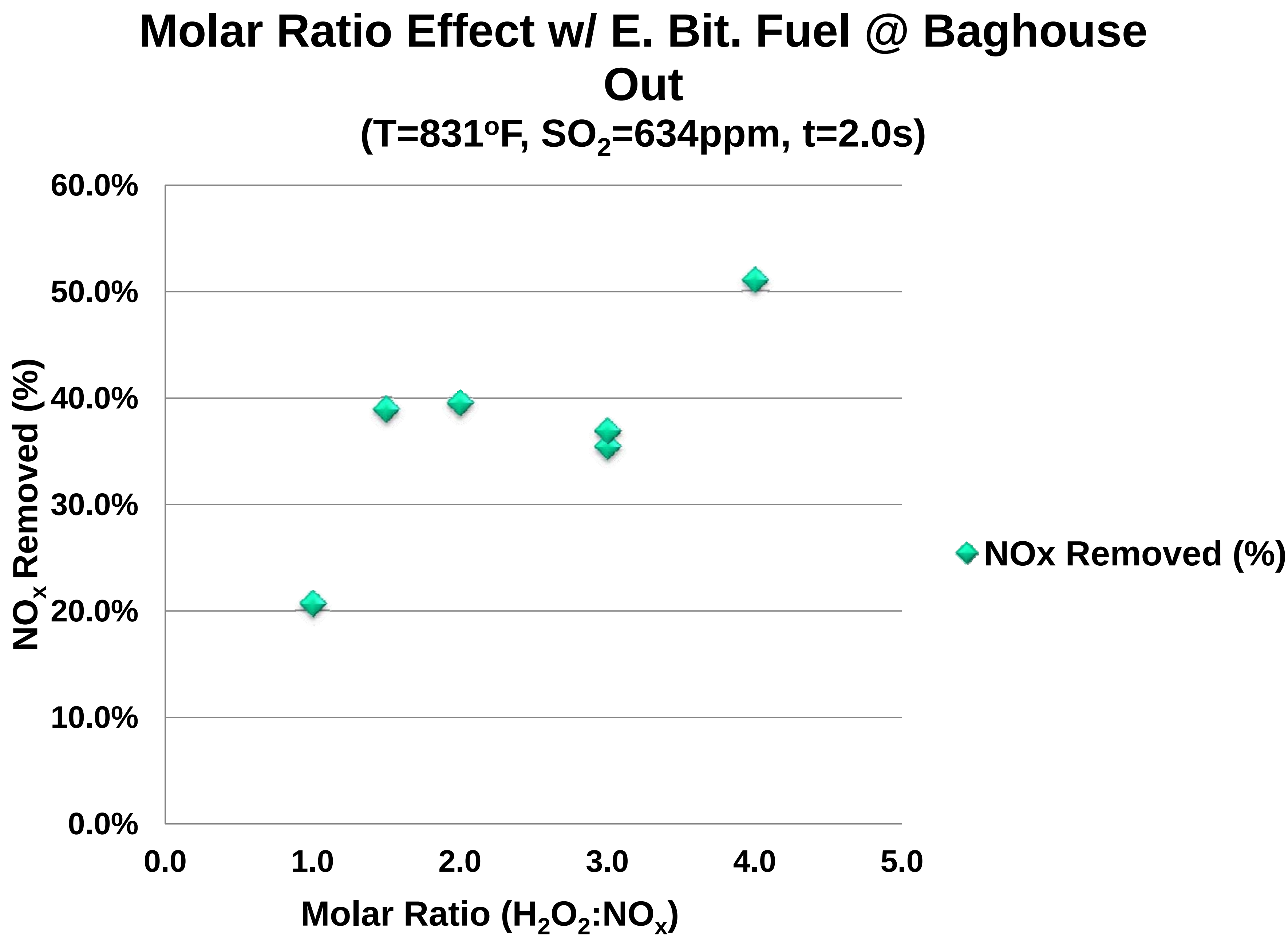
Purpose of Test Program

- NOx oxidation
  - Comparison to full scale test programs
- NOx capture
- Parametric study
  - Fuel – Natural gas, Bit, Sub-bit, Lignite coal
  - Treatment time: 0.5 – 2.0 sec
  - Temperature: 600 – 900 °F
  - Peroxide molar ratio:1.0 - 4.0
  - SO2 concentration: 0 – 2000 ppm

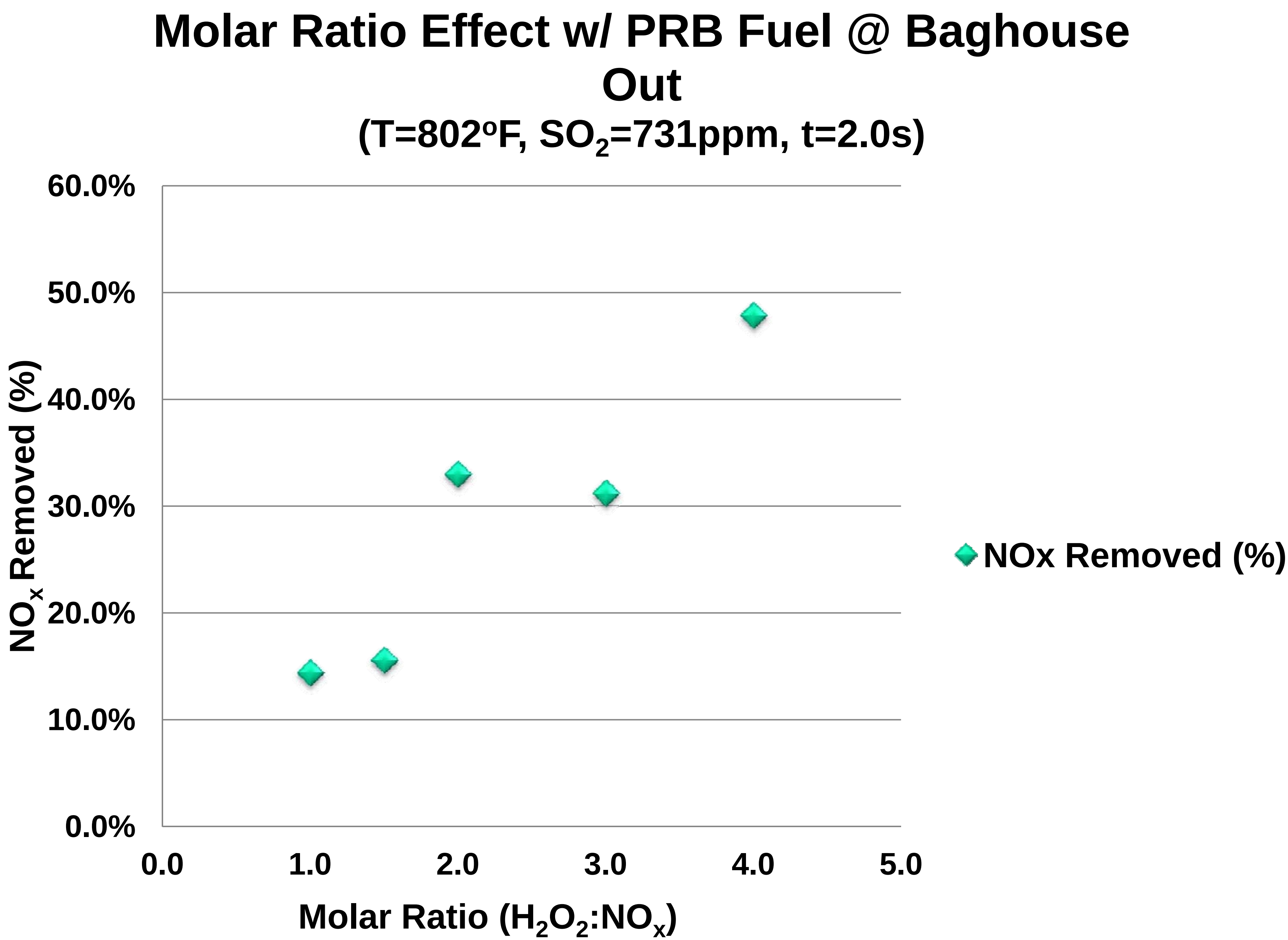
Residence Time Affect w/ Lignite Fuel@ Baghouse Out

(T=800ºF, SO_2=?ppm, MR=1.5)





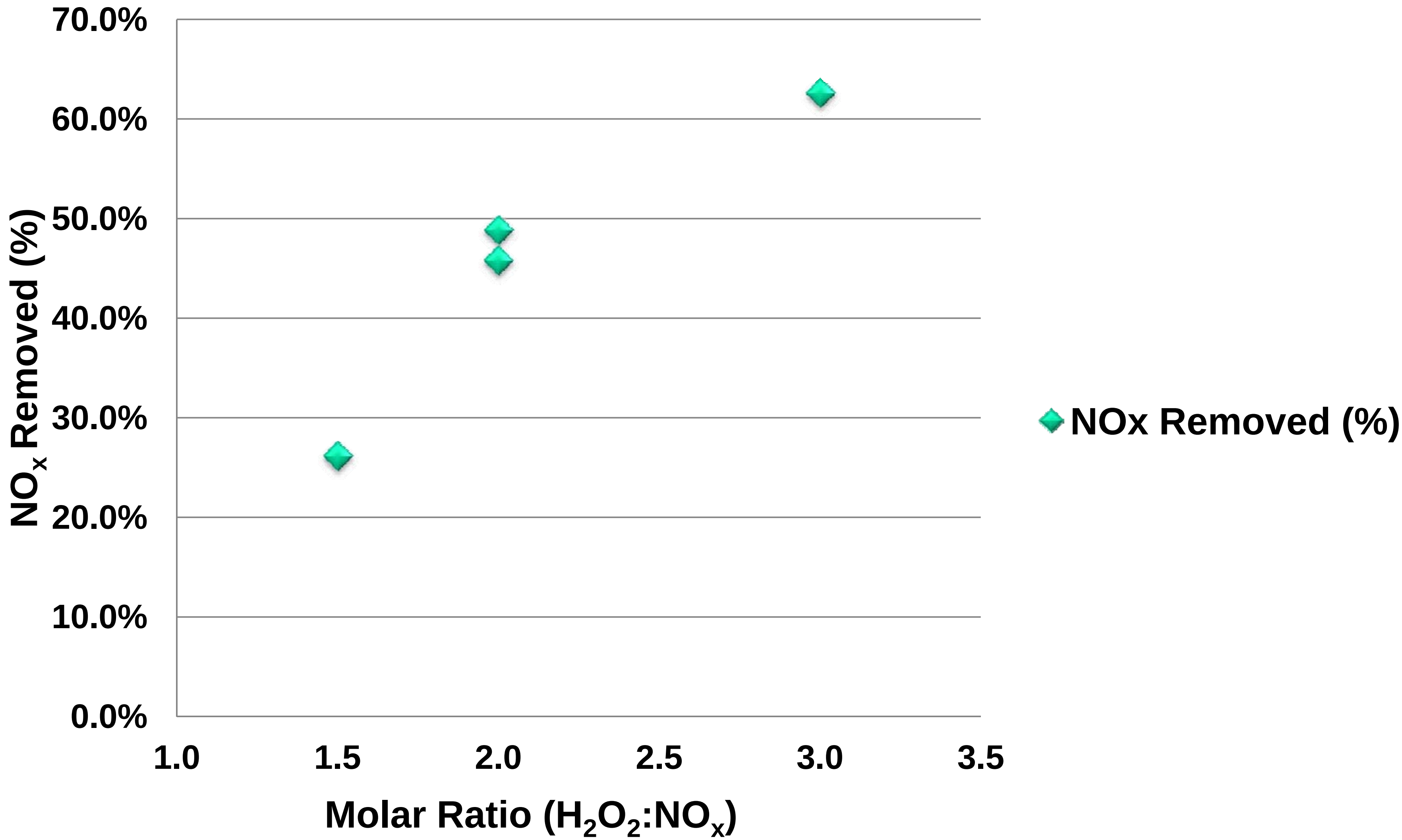
Molar Ratio Effect w/ E. Bit. Fuel @ Baghouse Out
(T=831ºF, SO2=634ppm, t=2.0s)
60.0%
50.0%
40.0%
30.0%
20.0%
10.0%
0.0%
NOx Removed (%)
0.0
1.0
2.0
3.0
4.0
5.0
Molar Ratio (H2O2:NOx)
NOx Removed (%)



Molar Ratio Effect w/ PRB Fuel @ Baghouse Out
(T=802ºF, SO_2=731ppm, t=2.0s)
60.0%
50.0%
40.0%
30.0%
20.0%
10.0%
0.0%
NO_x Removed (%)
0.0
1.0
2.0
3.0
4.0
5.0
Molar Ratio (H_2O_2:NO_x)
NOx Removed (%)

Molar Ratio Effect w/ Lignite Fuel @ Baghouse Out

(T=800ºF, SO_2=?ppm, t=2.0s)

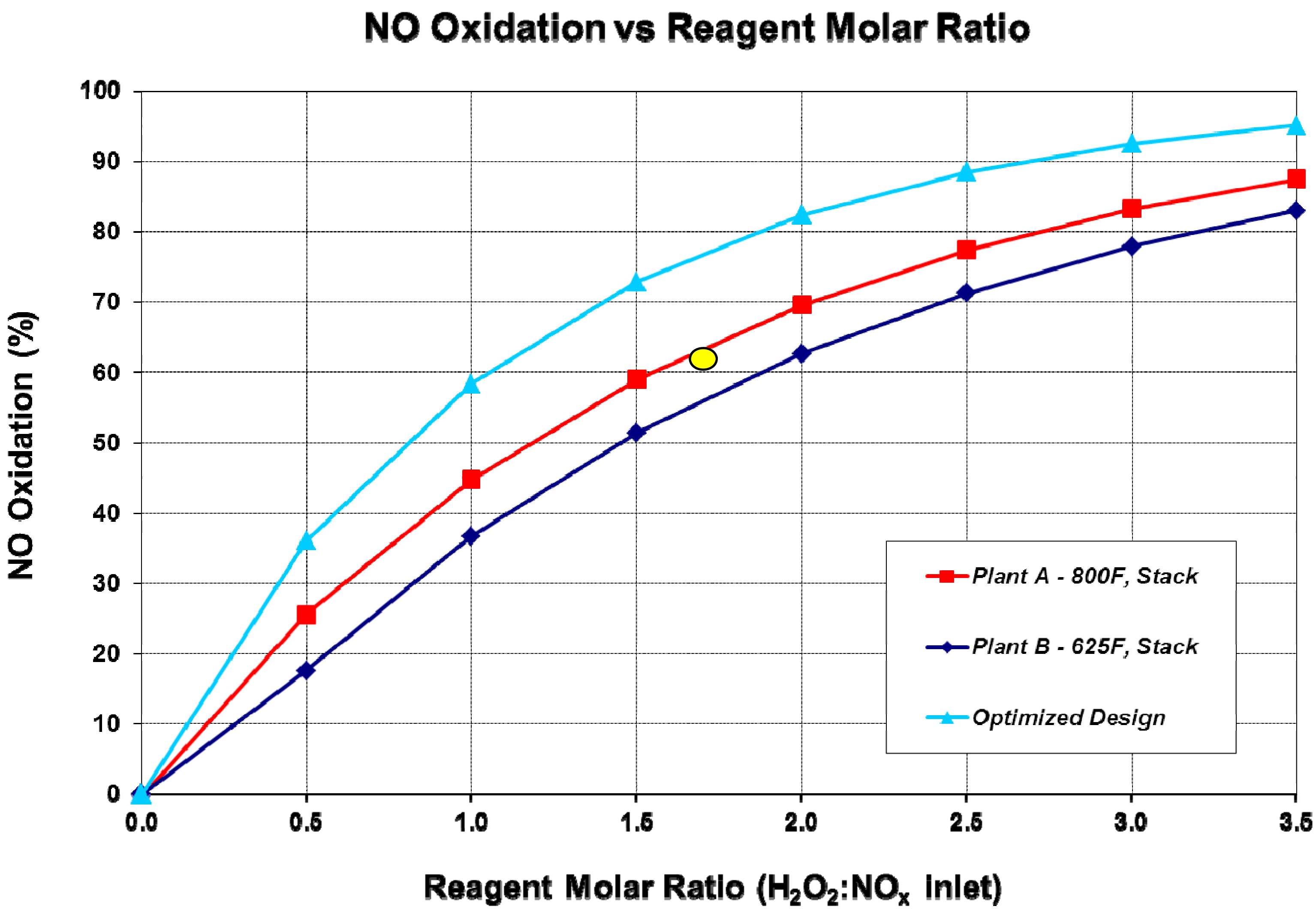


Conclusions from EERC Program

- EERC pilot is a good system to evaluate NOx oxidation and capture across SDA/FF system – limitations of pilot scale
- Better oxidation and capture with
  - Higher temperature
  - Higher SR
  - Longer treatment time
- Variations with fuels – Lignite better
- No effect of SO_2
- Still need further analysis of this data

Economic Comparisons

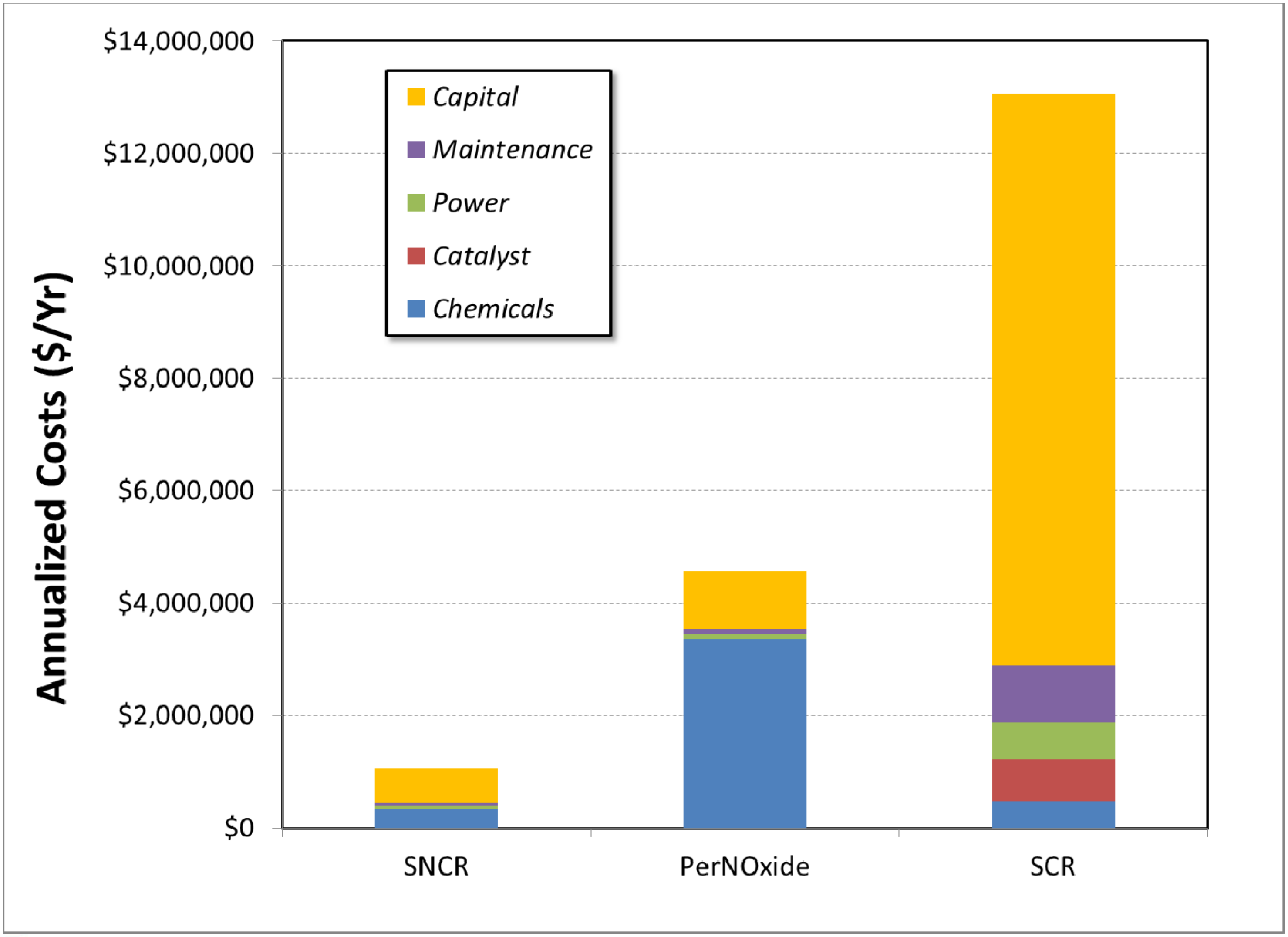
NO Oxidation Projections



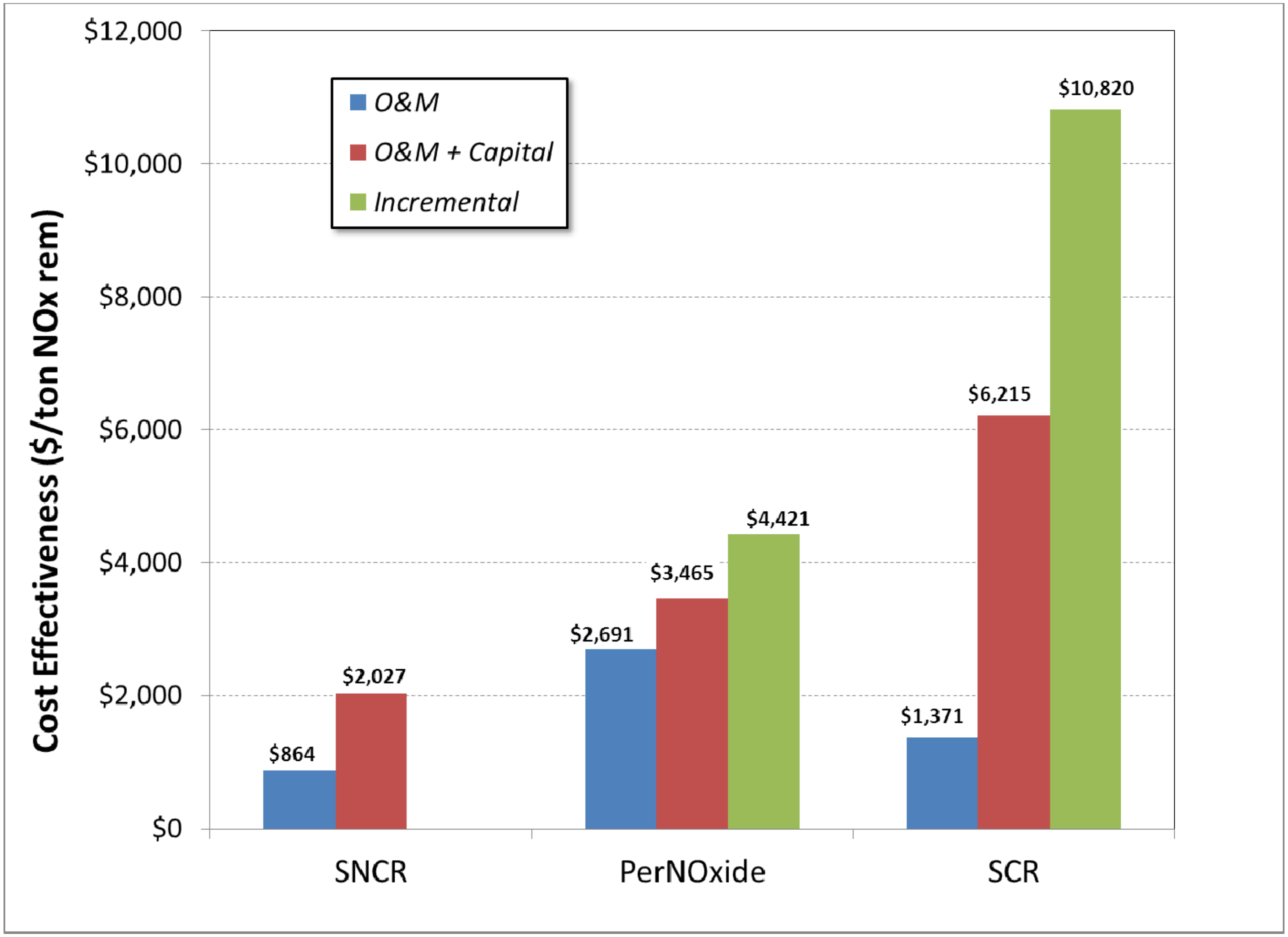
Technology Cost Comparison

Basis	Units	SNCR	PerNOxide	SCR
Capacity Treated	MW	400	400	400
Inlet NOx	lb/MMBtu	0.20	0.20	0.20
NOx Removal	%	20	50	80
NOx Emissions	lb/MMBtu	0.16	0.10	0.04
NOx Removed	TPY	526	1,316	2,102
Capacity Factor	%	75	75	75
Reagent		Urea	Peroxide	Ammonia
Reagent Molar Ratio	mol:mol NOx	0.20	1.50	0.80
Reagent Cost	$/ton	$500	$1,000	$600
Soda Ash Cost	$/ton	$0	$300	
Catalyst Cost	$/c.f.			$150
SCR Catalyst Life	Yrs			3
Power Cost	$/MW-hr	$30	$30	$30
Annual Maint. Cost	% of Capital	1.0	1.0	1.0
Capital Cost	$/kW	$15	$25	$250
Capital Recovery Period	Yrs	20	20	20
Capital Discount Rate	%	8	8	8
Capital Recovery Factor	%	10	10	10

Annualized Costs



Cost Effectiveness Analysis



Take Aways…

- PerNOxide is cost-effective alternative to SCR for modest NOx reductions
- PerNOxide economics more favorable for …
  - Lower inlet NOx levels
  - Smaller unit size
  - Lower capacity factor
  - Sodium and lime scrubbers
  - Space constrained site (difficult retrofit)
- PerNOxide can be final "layer" of controls before SCR required…
  - LNB, OFA, SNCR, ….

PerNOxide Advantages and Challenges

PerNOxide Technology Advantages

- Lower capital & maintenance costs than SCR
- Higher removal efficiencies than SNCR
- Operational flexibility
- Mercury oxidation and capture
- Immune to SCR catalyst poisons
- Environmentally friendly reagent
- Limited downtime for installation
- Project execution < 1 year

PerNOxide Technology Challenges

- Developing Technology
- May Require Modification to FGD Chemistry
- Possible Increase in NO_2 Emissions
- Possible Increase in SO_3 Formation
- Waste Stream Management

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PerNOxide Bridges NO_x Control Gap

	SNCR	SCR
NO_x Removal	20-30%	75-90%
Capital Costs	Moderate	High
Boiler Impacts	Yes	No
Operational Issues	Ammonia Slip	Ammonia Slip & SO_3 Generation

PerNOxide Bridges NO_x Control Gap

	SNCR	PerNOxide	SCR
NO_x Removal	20-30%	30-70%	75-90%
Capital Costs	Moderate	Low	High
Boiler Impacts	Yes	No	No
Operational Issues	Ammonia Slip	Potential Visible Emissions	Ammonia Slip & SO_3 Generation

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Summary

- PerNOxide technology is a 2-Step Process
  - Oxidation of NO to NO_2 and other N-O forms
  - Capture of NO_2 and other N-O forms
- High NO oxidation achieved using peroxide
- Capture of NO_2 is critical
  - Bench scale testing to explore NO_2 Removal
  - Key variables: Scrubber mass transfer, dissolved sulfite, pH, & additives
  - Modification of scrubbing liquor composition may be required

Summary

- Economics are favorable compared to SCR
- Example 400 MW plant:
  - Capital costs 1/10th that of SCR
  - Annualized costs 1/3rd that of SCR
  - Cost effectiveness ($/ton) half that of SCR
  - Incremental SCR costs > $10,000/ton NOx
- Favorable economics driven by:
  - Low capital costs
  - Moderate (30 to 70%) NO_x removal effectiveness
  - Operational flexibility (NO_x removal "on demand")

Path Forward

- FMC and URS seeking opportunities for full scale demonstrations on both wet and dry scrubber applications

Thank You!

Questions???

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