Enhanced Coal Reburning Under Oxidizing Conditions

Eric G. Eddings, Chris Thurston, Alejandro Molina, Adel Sarofim

Dept. of Chemical and Fuels Engineering
University of Utah

DOE Grant: DE-FG26-02-NT41550

DOE UCR/HBCU/OMI Contractors Review Meeting

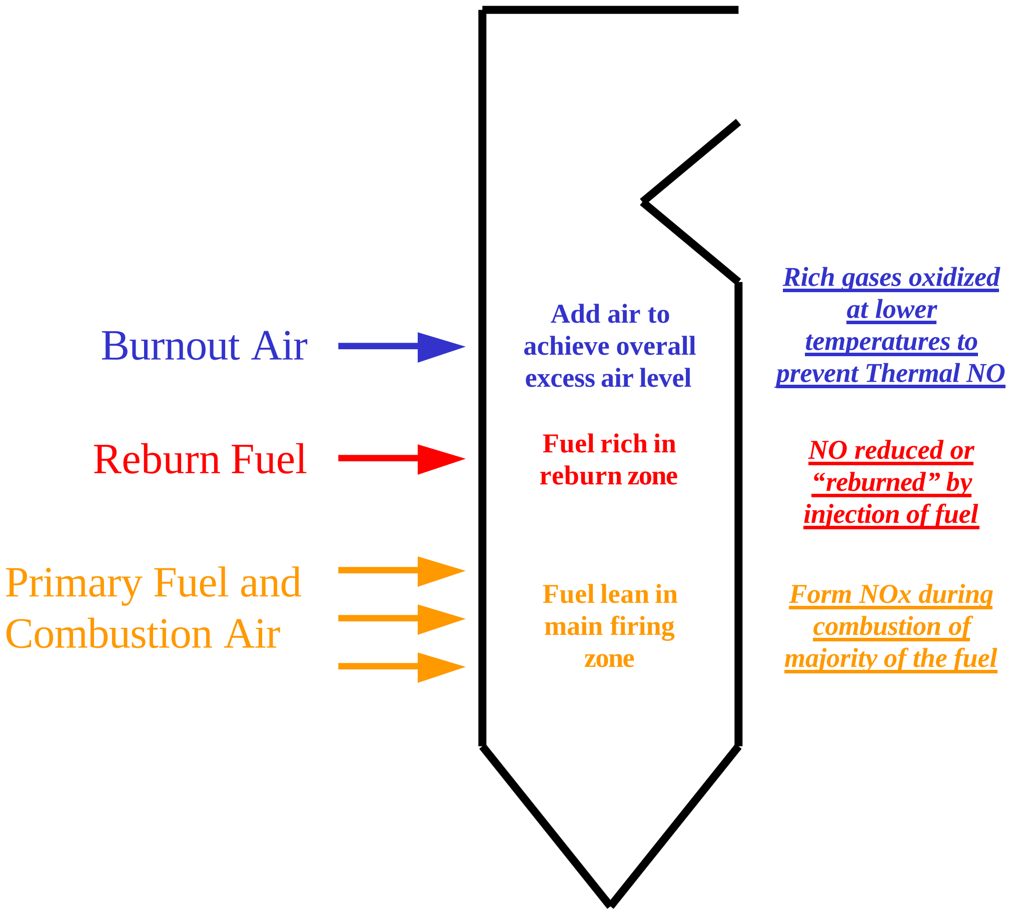
Pittsburgh, June 3-4, 2003

NOx Control in Pulverized-Coal-Fired Utility Boilers

- NOx control via combustion
  - Low NOx Burners
  - Air staging
  - Reburning
- Post-combustion control
  - SNCR
  - SCR
- Hybrids, other novel approaches
  - e.g, oxygen addition

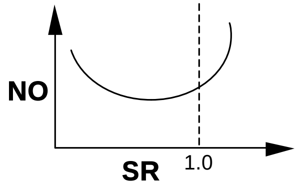
Basic Reburning Approach

- Various Types:
  - Natural Gas Reburning
  - Other gases (syngas: H_2, CO; etc.)
  - Advanced Reburning
  - Fuel-Lean Gas Reburning (FLGR)
  - Amine-Enhanced Fuel-Lean Gas Reburning (AEFLGR)
  - Coal Reburning



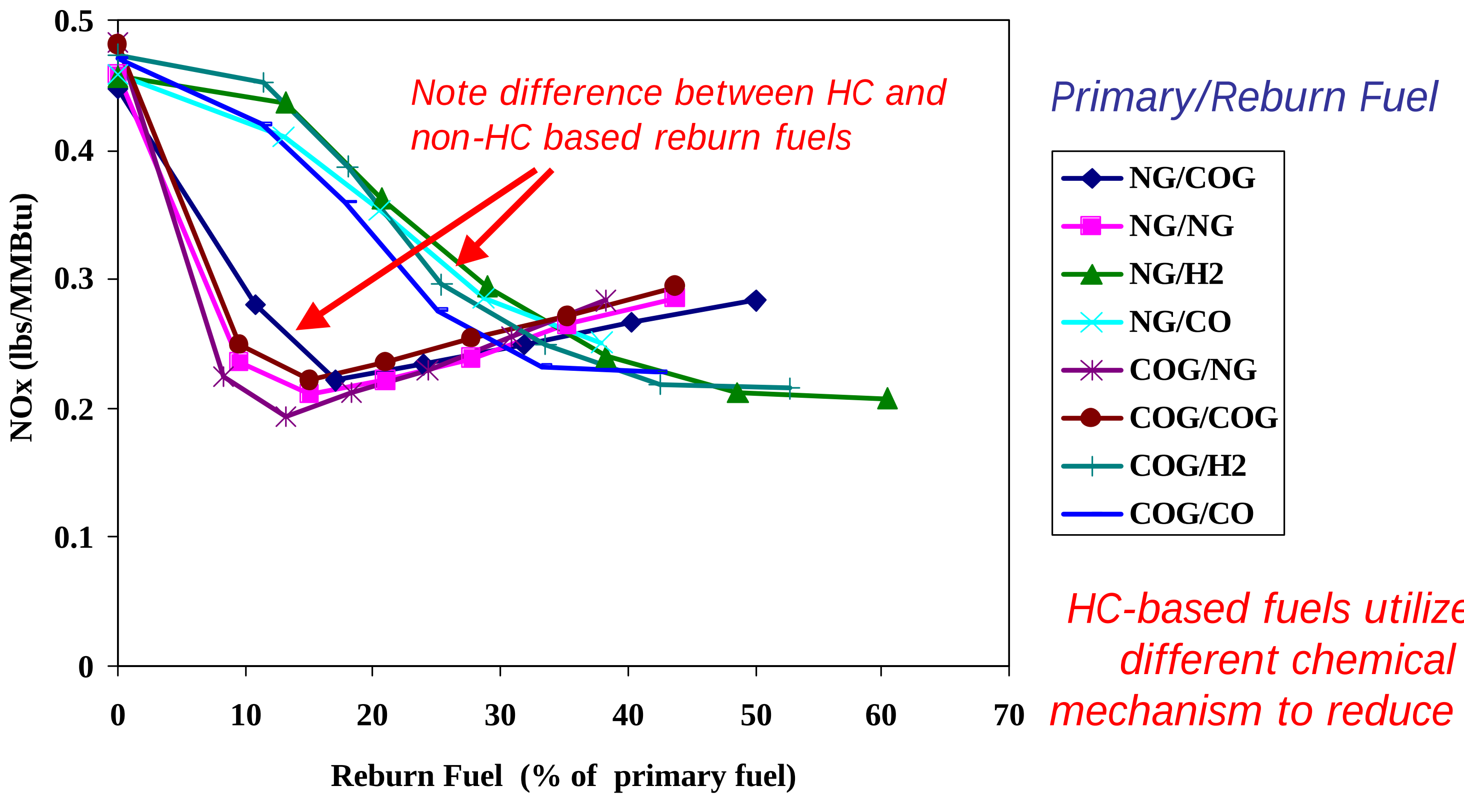
Natural Gas Reburning

- Traditional approach
  - HC injection to create fuel-rich region and HC's react with previously formed NO and convert to HCN
  - HCN decays to N_2 under fuel rich conditions given sufficient residence time/temperature
  - Subsequent air addition to consume rich products
- Proven – can provide 50-60% or greater NOx reduction
- Optimal fuel-rich injection stoichiometry due to thermochemical considerations
  - NO formed if too lean – not much different from main combustion zone
  - Equilibrium favors fixed nitrogen species (HCN, NH_3) at richer stoichiometries
    - Fixed nitrogen species are re-oxidized to NO with burnout air addition



Gas Reburning Experiments

Primary Zone - 100,000 Btu/hr*
Injection Temperature – 1422 K (2100ºF)



HC-based fuels utilize a different chemical mechanism to reduce NO

**University of Utah – Bench-scale test furnace*

Fuel-Lean Gas Reburning (FLGR)

- Injection into overall lean combustion products
  - Sufficient excess air to consume all reburn fuel and retain appropriate exhaust O_2 level
  - Avoids expense of installation of overfire system
- Fundamental kinetics would indicate “lean” reburning not possible
  - In practice, approach relies upon delayed mixing to promote rich pockets or diffusion flamelets
    - Traditional gas reburning can then occur in these rich zones
  - Mixing eventually brings lean and rich zones together to achieve overall level of excess oxygen
- Optimization issue: maximize NO reduction while minimizing CO emissions

Amine-Enhanced Fuel-Lean Gas Reburning (AEFLGR)

- Co-injection of natural gas and amine-producing agent (e.g., urea)
  - Similar levels of NOx reduction to conventional gas reburning
  - Reduced cost due to
    - Elimination of overfire air system
    - Reduced natural gas usage (typically < 10% of total heat input)

Pulverized Coal Reburning

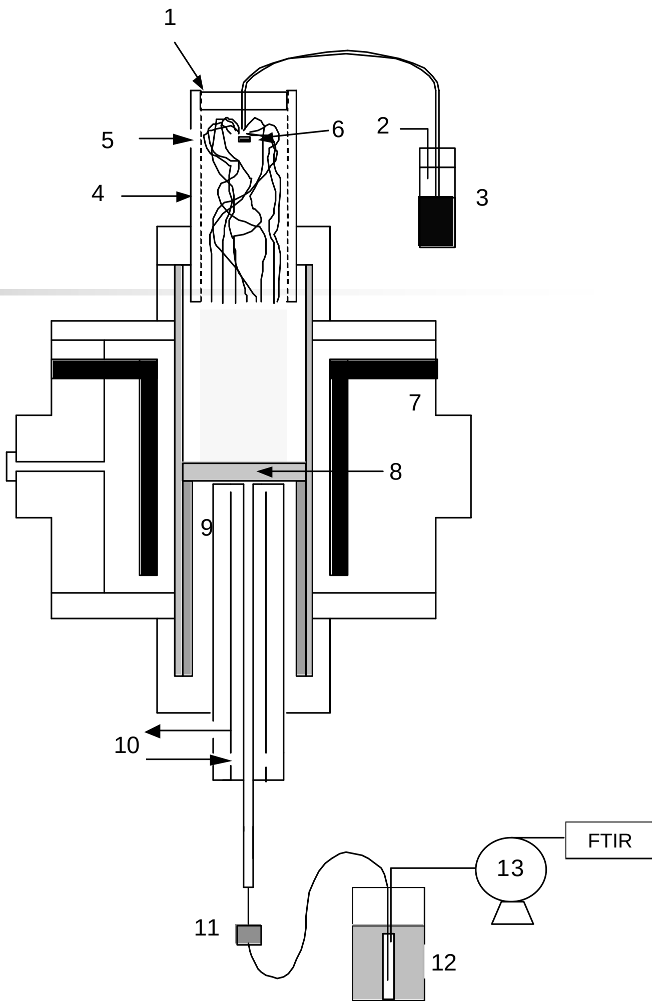
- Would like to use coal
  - Cost, accessibility to reburn fuel, abundancy
- Coal can be used to produce HC's necessary for reburning of NO
- Additional considerations
  - Addition of more fuel nitrogen (-)
  - NO reduction by residual char (+)
  - Burnout of residual char (-)
- DOE CCT demo (NYSEG/Milliken) – using micronized coal (80% < 325 mesh)
  - Achieved 29% NO reduction beyond LNCFS III system, LOI < 5%
  - Successful, but high energy penalty associated with micronizing
- Greater understanding of controlling mechanisms could lead to technology enhancements

Coal Reburn – Reduction Mechanisms

- In traditional coal reburning, coal is injected creating a fuel-rich zone where NO is reduced by two mechanisms:
  - I – homogeneous reaction with volatiles released after coal injection
  - II – heterogeneous reaction with char
- Evidence of a third mechanism for NO reduction during reburning
  - III – NO reduction by nitrogenous species released from char under oxidizing conditions

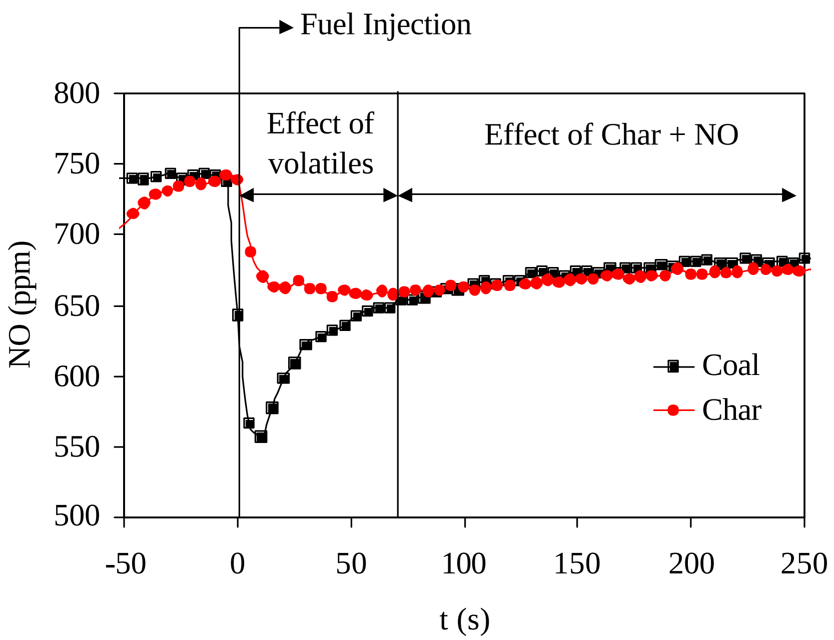
Experimental

- Electrically heated, laminar-flow, drop-tube reactor
- Conventional setup of the drop-tube was modified to allow the implementation of batch experiments with in situ char formation
- After injection, the fuel spreads uniformly over the entire cross-sectional area
- The solid stream is then collected over an alumina/silica non-woven fabric



1. Quartz window
2. Carrier gas input
3. Feeding system
4. Distributor
5. Distributor radial gas
6. Disk input
7. Heating element
8. Alumina/silica non-woven fabric
9. Collection Probe
10. Cooling Water
11. Filter
12. Cold trap
13. Vacuum pump

Inert Atmosphere

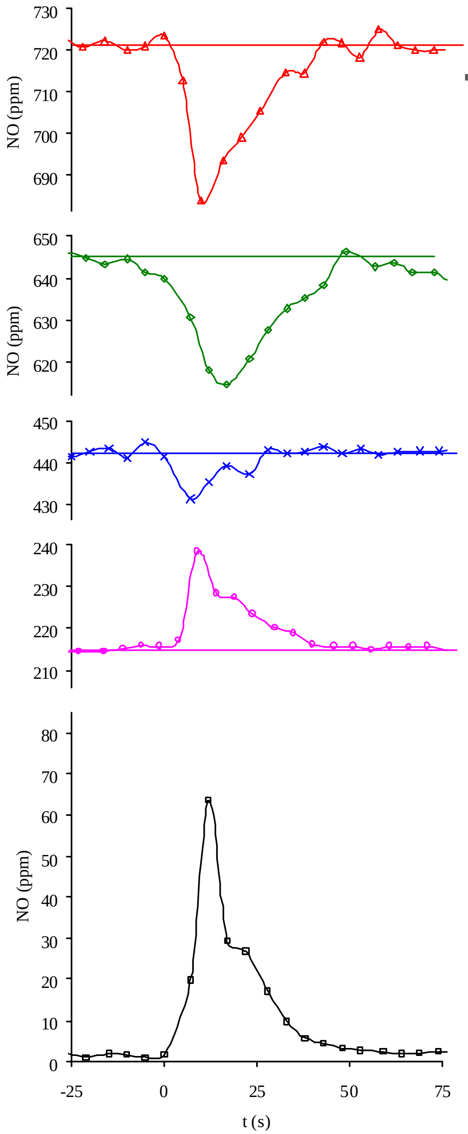


This experimental approach allows evaluation of effects I and II under different atmospheres

- NO profiles after fuel injection at t = 0 s
- 750 ppm NO/He. T = 1293 K
- Identical mass of coal and char at t = 250 s
- The plot shows the existence under inert atmospheres of effects I and II

Oxidizing Atmosphere

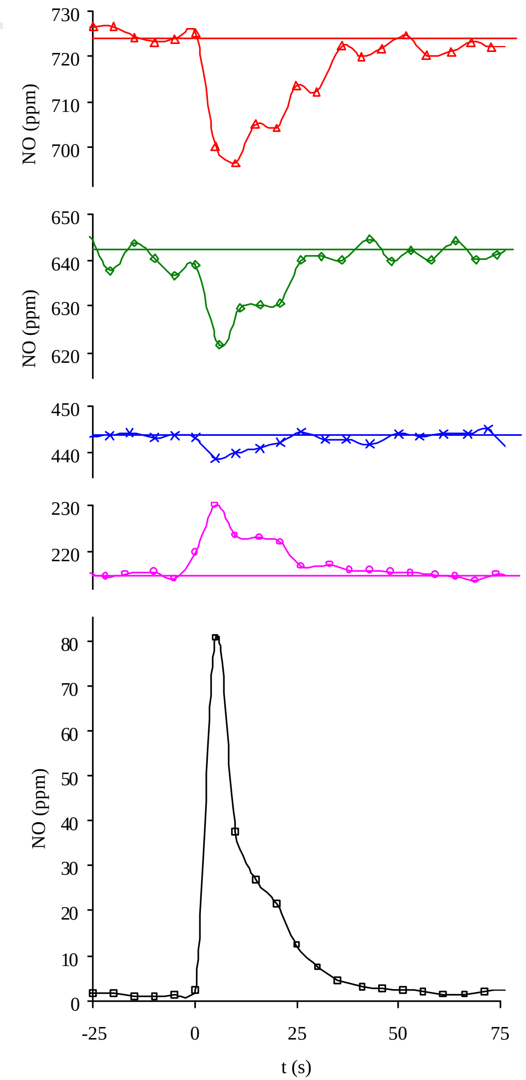
Coal



- NO profiles after fuel injection at t = 0 s
- 4 % O_2 in He, T_g = 1698 K
- Background NO changes with vertical axis
- As the background NO increases, the amount of NO produced decreases
- At NO > 400 ppm the fuel reduces background NO
- The effect is very similar for coal and char

⇒ **Reduction appears to be result of char, or char products, under oxidizing conditions. Which is it?**

Char



Comparison of Kinetic Constants

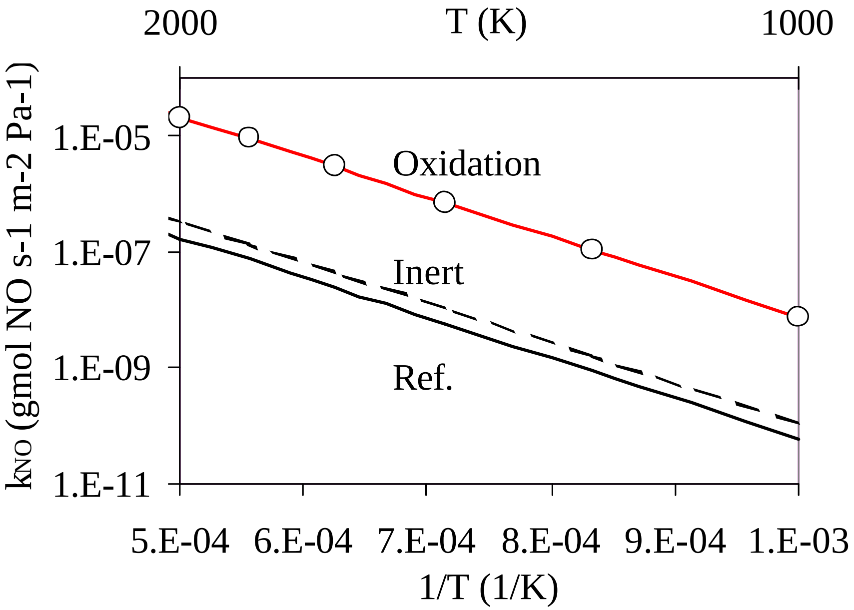
- Figure compares Arrhenius plots for the rate of nitric oxide reduction:

  Bold line: Data from Aarna and Suuberg (Fuel 1997, 76, 475) (Char/NO kinetics are found to depend on char type and vary by about an order of magnitude around the values reported by Aarna and Suuberg)

  Dashed line: Inert atmosphere

  Circles: Oxidizing atmosphere (4 % O_2 in He, T_g = 1698 K)

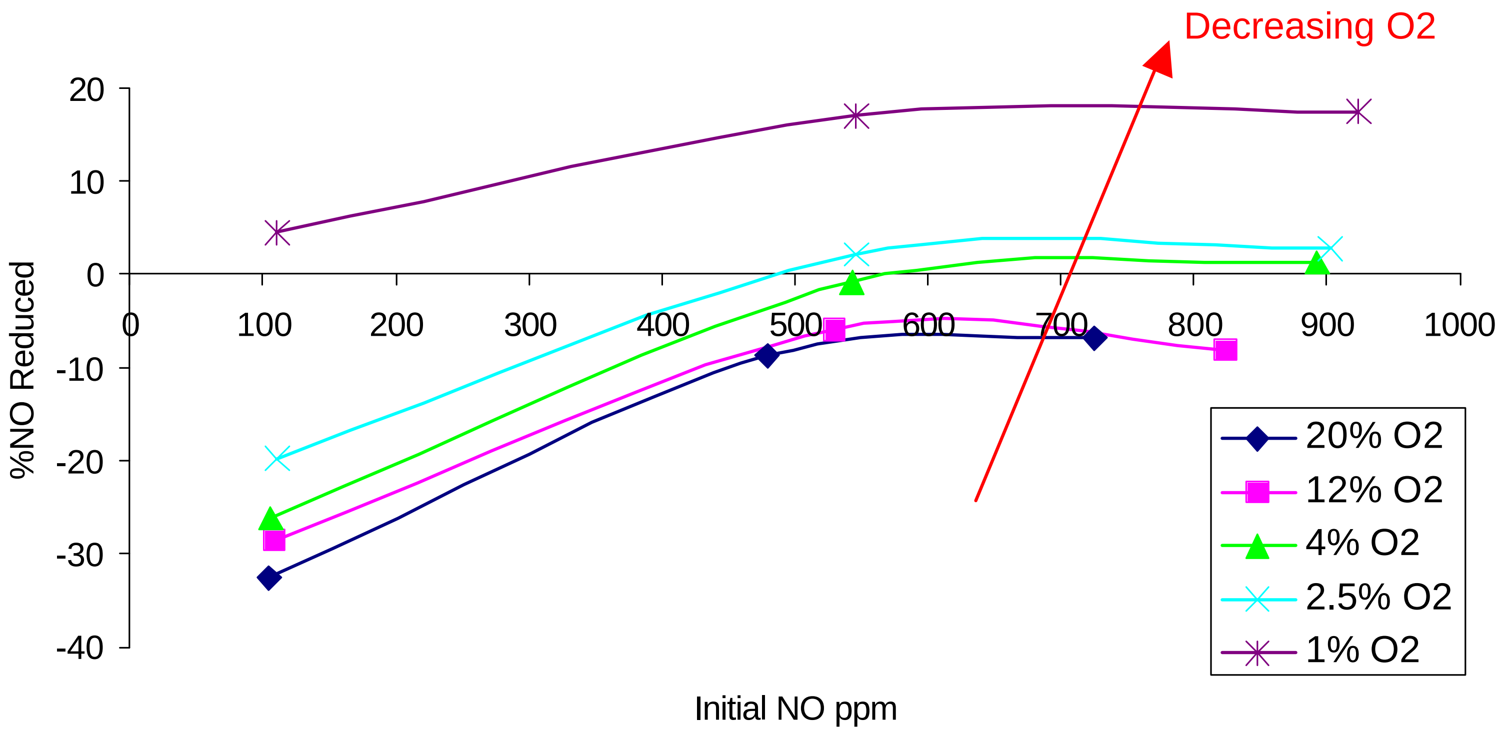
- Results suggest that the rate of NO reduction under oxidizing atmosphere is ~ two order of magnitude higher than the one found under inert conditions



Why not try it out?

Increased reduction under oxidizing conditions also noted by Jensen et al (2000) and Tomita (2001).

Continual Feed Drop Tube Experiments



Continual Feed Experiments (1 g/hr), Ohio Coal
Reactor T = 1650 K
Variable initial NO and O_2 concentration

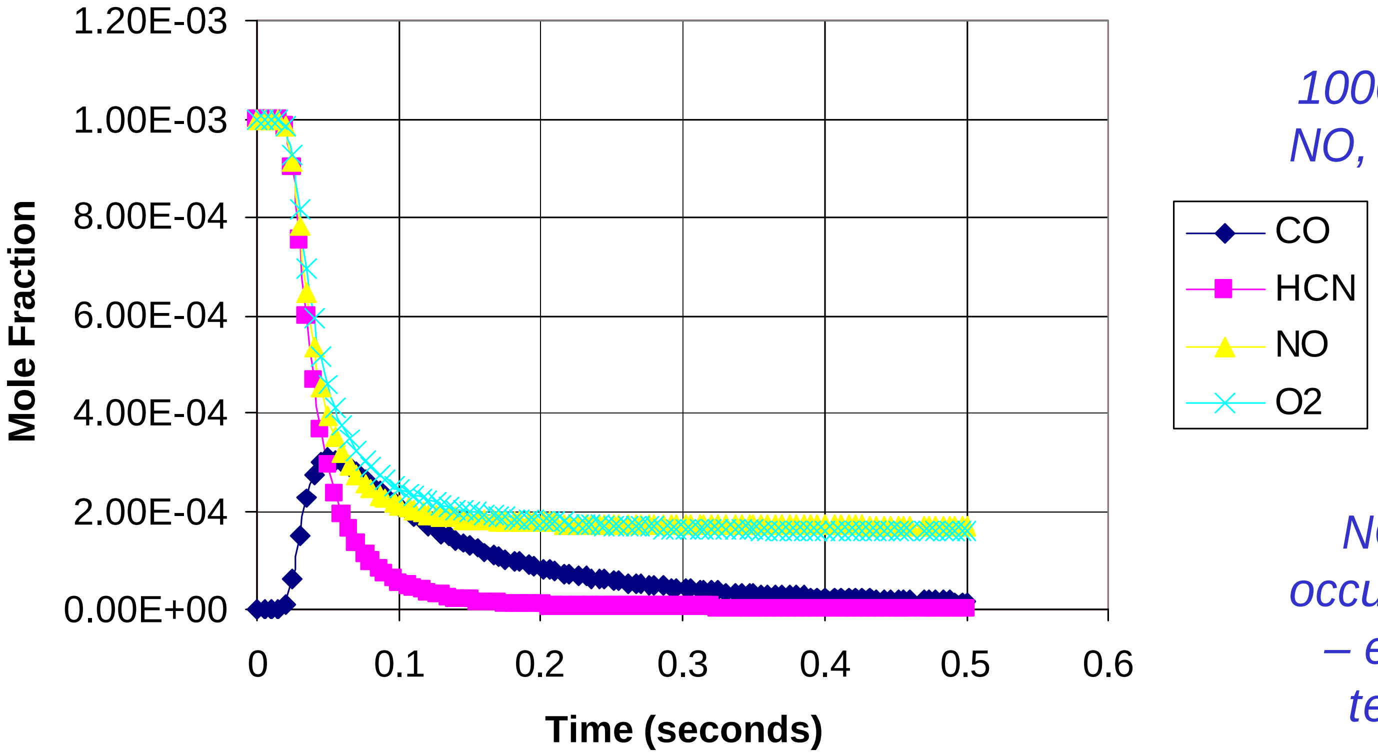
Preliminary Reburn Tests

- Initial experiments showed limited NO reduction
  - Not yet identified optimal conditions
  - Need to understand what is controlling
- Comparison of kinetic rates indicated it is likely char oxidation products (not char) that are responsible for 100X increase in reduction rate
- What char product could be reducing NO?
  - Small amounts of HCN detected that increased with increasing sample size
  - How effect could this be?

Homogeneous Reactions Between HCN and NO

- HCN can be readily oxidized to NO under combustion conditions (Fuel N conversion)
- Reduction known to occur under SNCR conditions
  - Gas phase cyano compounds evolved from urea, cyanuric acid
  - Exhibits SNCR temperature “window”
- Reduction of NO by HCN will clearly be function of
  - O_2, Temperature, perhaps initial NO concentration?
- Can evaluate using detailed kinetic modeling

Kinetic Calculations*

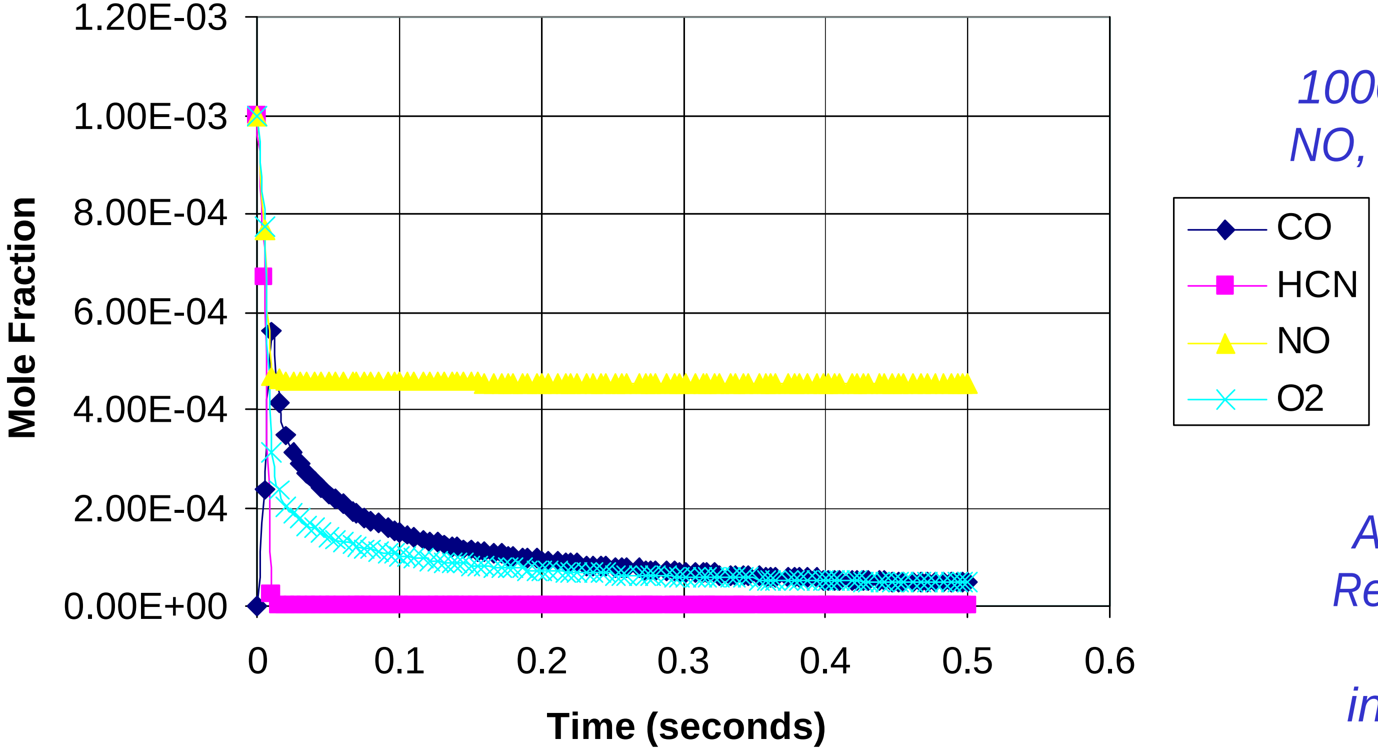


PFR Calculation
1273 K
1000 ppm each of NO, HCN and O_2 in Ar

NO Reduction occurs very rapidly – even at lower temperatures

**PFR Calculations based on GRImech 3.0 (53 species, 325 reactions) and Chemkin II*

Kinetic Calculations*



PFR Calculation
1698 K
1000 ppm each of NO, HCN and O_2 in Ar

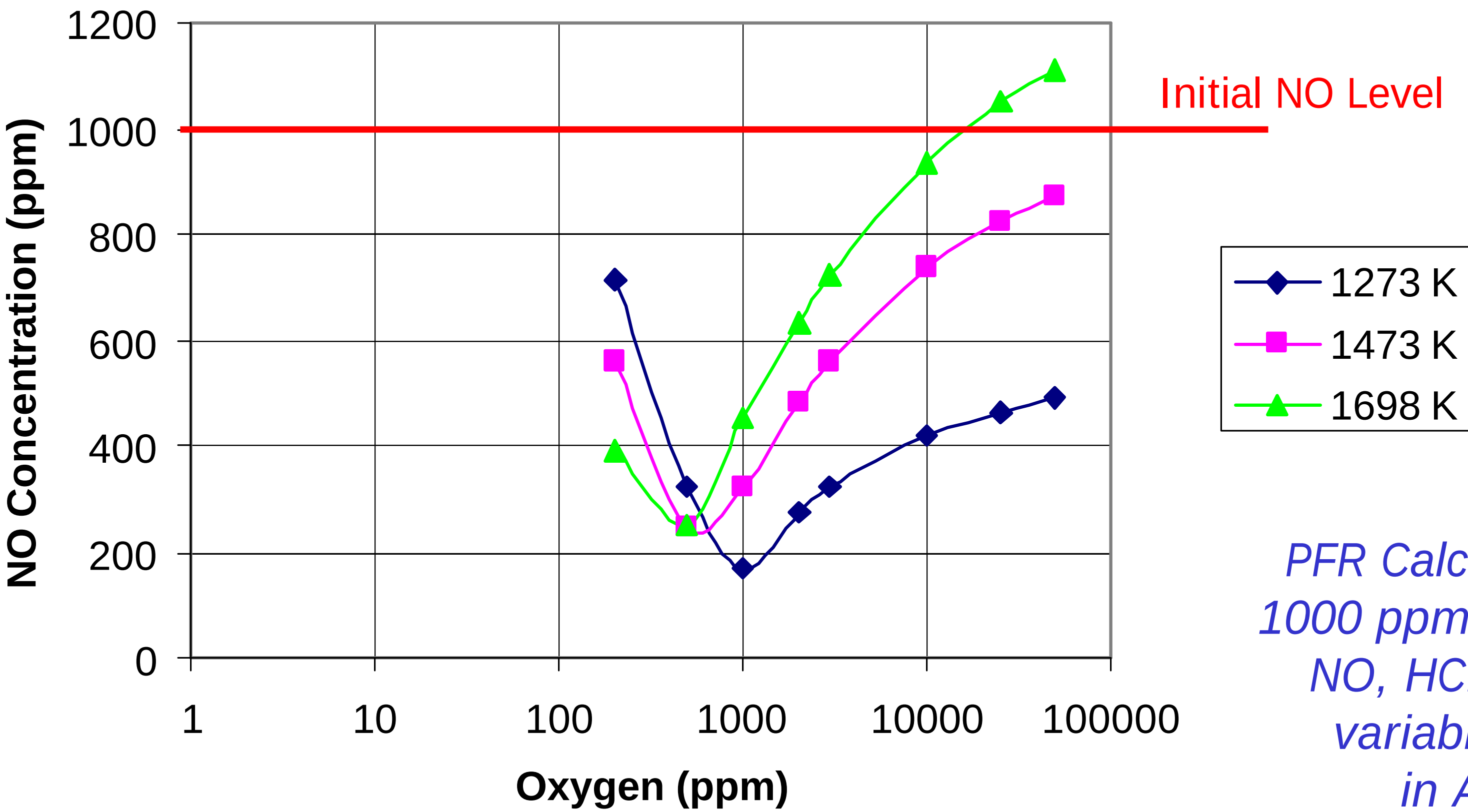
At higher T NO Reduction occurs almost instantaneously

Equilibrium NO level is higher for higher T

**PFR Calculations based on GRImech 3.0*

Homogeneous Calculations* - Oxygen Sensitivity

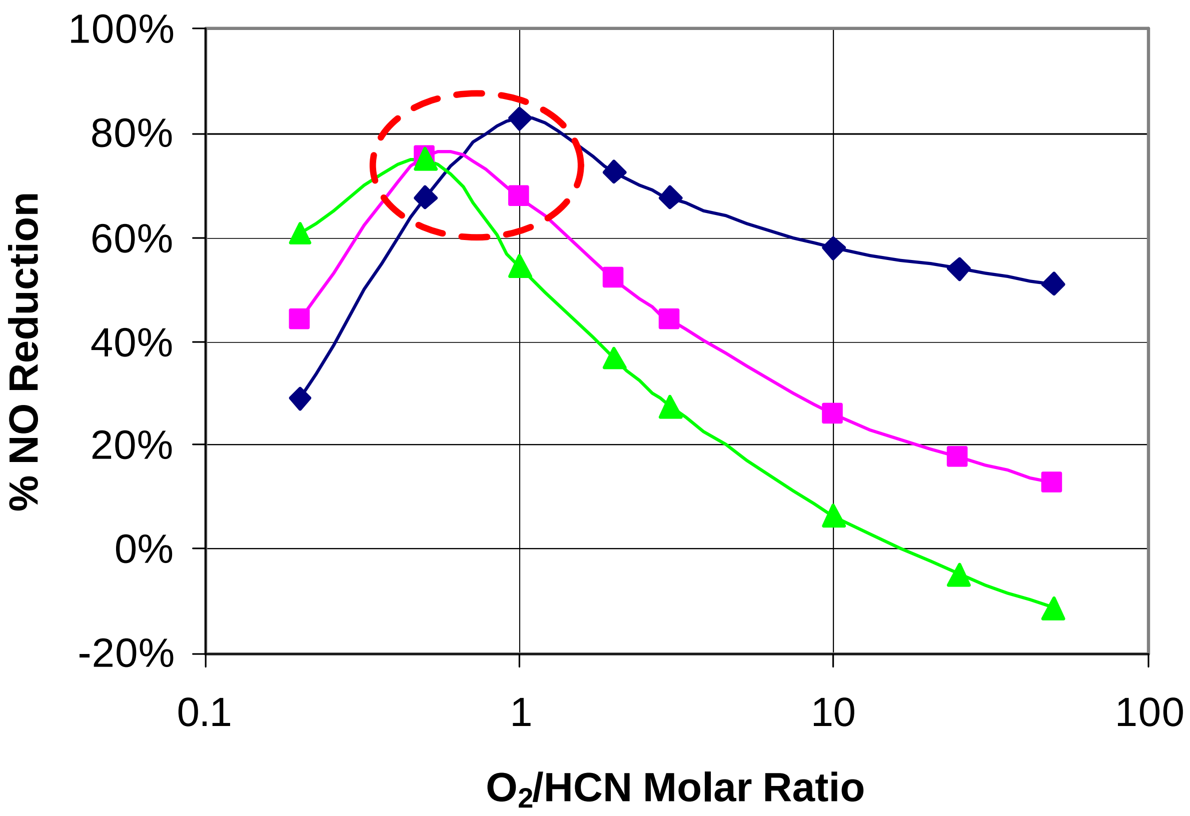
Plot of exit NO values



PFR Calculation 1000 ppm each of NO, HCN and variable O_2 in Ar

**PFR Calculations based on GRImech 3.0*

Homogeneous Calculations* – Oxygen Sensitivity



PFR Calculation
1000 ppm each of NO, HCN and variable O_2 in Ar

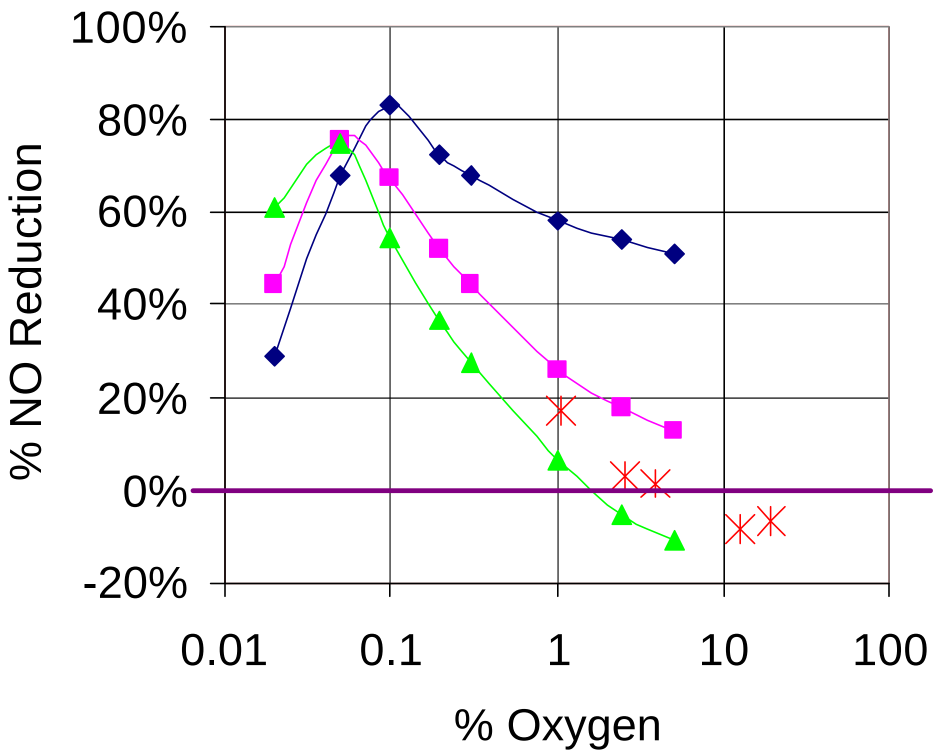
Appears we want to be near stoichiometric w.r.t. evolved HCN.

**PFR Calculations based on GRImech 3.0*

Summary of Kinetic Calculations

- Preliminary homogeneous kinetic calculations indicate:
  - If HCN is present in pores and boundary layers as product of char oxidation (w/limited O_2)
    - Potentially very effective reducing agent for NO under certain T, O_2 conditions
- Real situation more complex
  - Also have hetergeneous effects to consider
- Results are encouraging

Comparison of Initial Reburn Results with Calculations



Continual Feed Experiments
Ohio Coal
Reactor T = 1650 K
Background NO = 700 ppm

Lots of uncertainties with these comparisons; however, the general trend is comparable and results indicate just need to run at lower oxygen levels or lower temperatures.

Concluding Comments

- Experimental results indicate
  - 3 potential mechanisms for NO reduction after coal injection
- First two mechanisms (reaction with volatiles and char)
  - are typically utilized during conventional coal reburning
- Proposed third mechanism (reaction of NO with nitrogenous compounds released during char oxidation)
  - has a greater magnitude for reduction rate than char reduction
- Kinetic calculations and experiments indicate
  - coal reburning may be most efficient under slight oxidizing conditions
- Optimization and development for industrial application still remains
  - to evaluate suitable operating conditions to maximize NO reduction and minimize unburned carbon in fly ash
  - Key will be to design system to control oxygen introduction