Emissions Reduction with Oxyfuel Combustion

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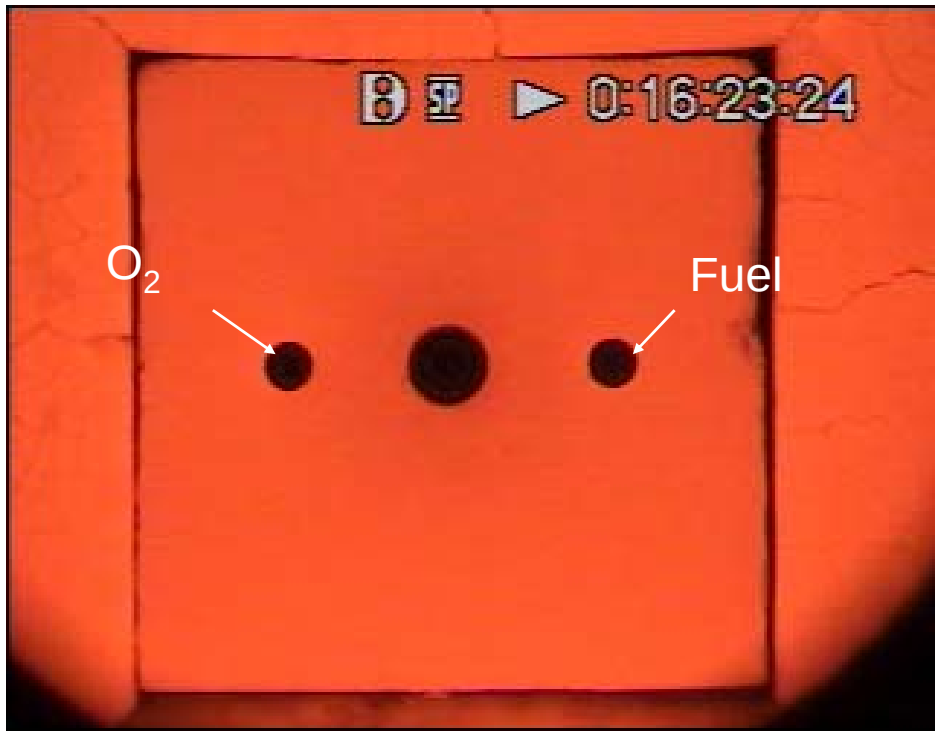
Ultra-low Emissions Oxyfuel Burner

By engineering the mixing process we can create:

- Low temperature
- Low emission
- Highly efficient
- Oxyfuel flames

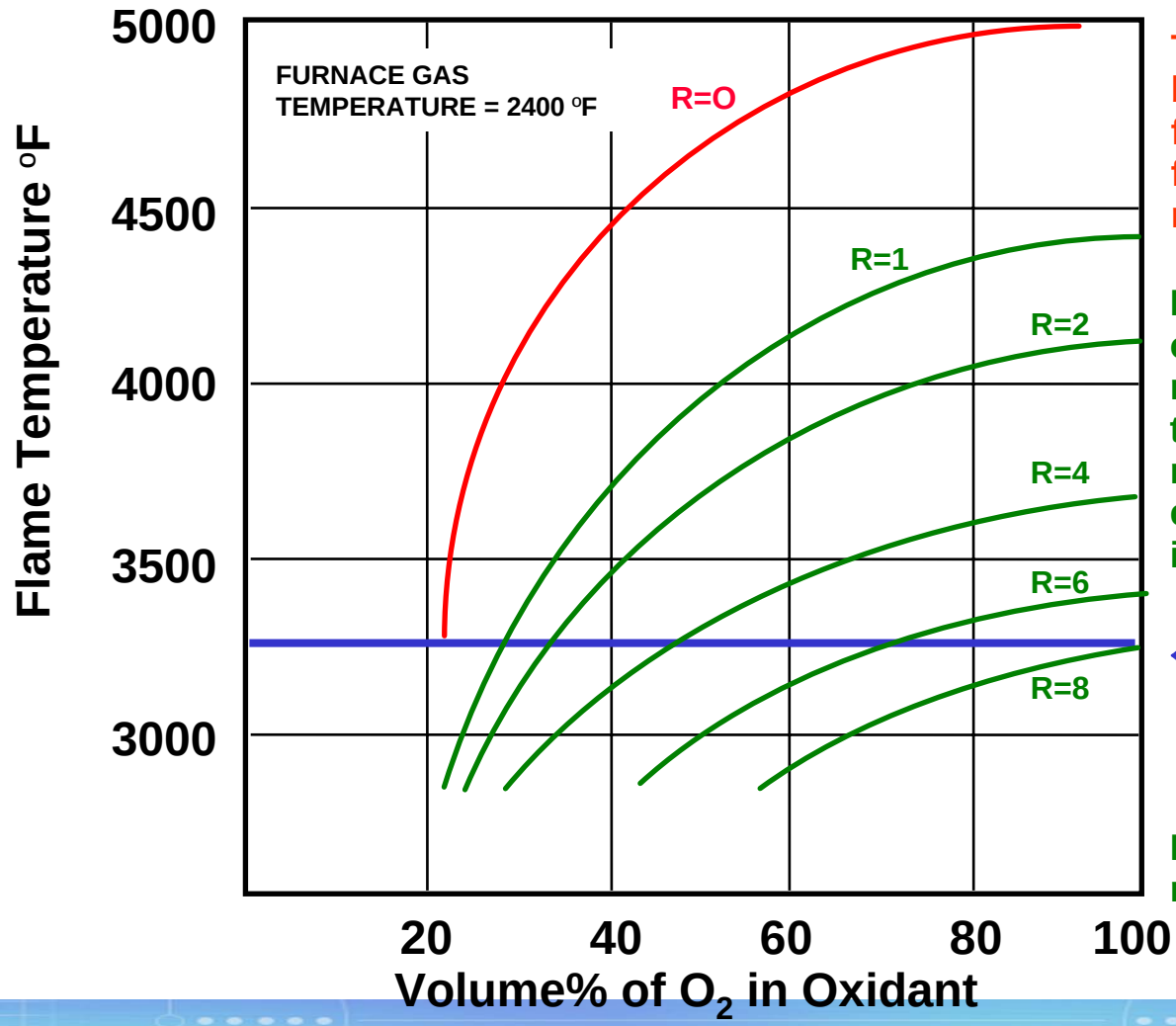


Praxair's Dilute Oxygen Combustion Burner
Combustion with no visible emissions (luminosity)

Agenda

- Common Perceptions of Oxyfuel Combustion
  - Very high temperature combustion process
  - High NOx emissions
  - If air is free, why would/should I pay for oxygen
- Emissions Reduction with Oxyfuel Combustion
  - Yesterday – Glass Furnace
  - Today – Coal Fired Boilers
  - Tomorrow – Onsite Mercury Sorbent Generation
  - Day-after-tomorrow – Oxycoal Combustion

Flame Temperature For Natural Gas



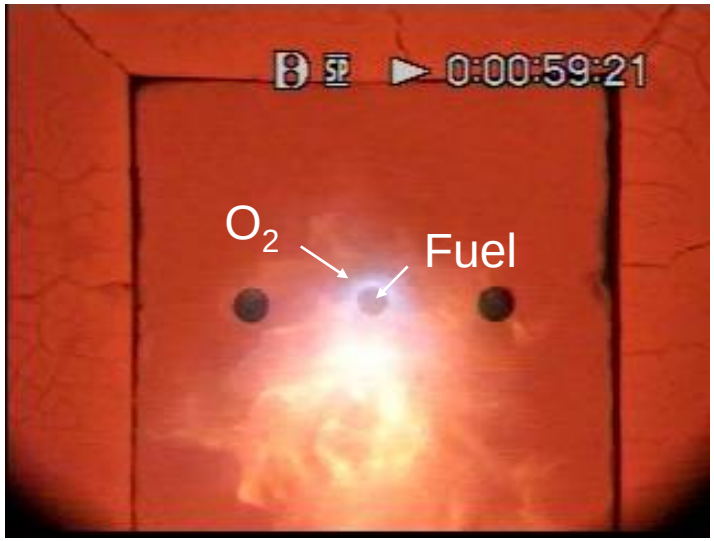
Traditional oxy-fuel burners use high flame temperature for welding and melting.

Praxair's advanced oxy-fuel burners reduce flame temperature and reduce NOx emissions in industrial furnaces.

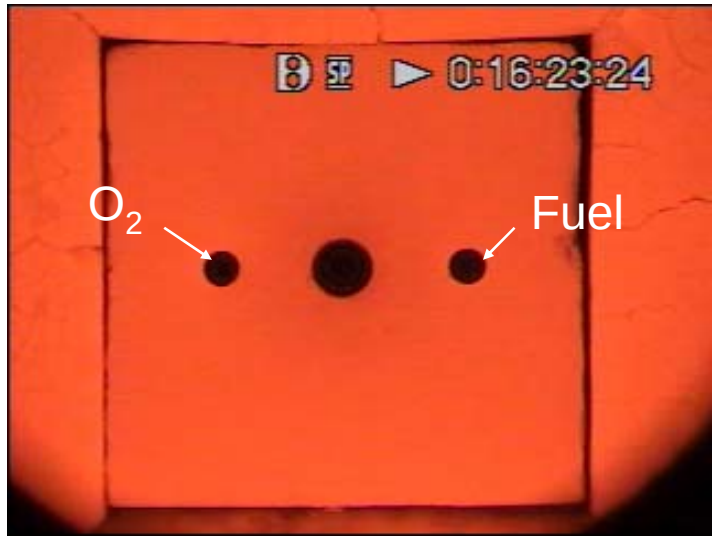
← Flame Temp of Natural Gas/air mixture

R=Flue gas recirculation ratio

Oxyfuel Burners in Lab Furnace



Typical Oxyfuel Burner
NOx emissions 0.25-0.4 lb/mmbtu



Dilute Oxygen Combustion
NOx emissions 0.003 lb/mmbtu

- Mixing is key design feature of all Praxair burners
  - Dilution of fuel and/or oxygen with POC is critical
  - Controlled mixing provides
    - Peak temperature control
    - NOx emissions control

Enirvonmental Related Awards

2001 Indiana Governor's Award For Pollution Prevention

1998 Eighth Annual National Award for Environmental Sustainability from Renew America

1996 DOE National Energy Award

1995 DOE-OIT Commercialization Award

1989 Kirkpatrick Chemical Achievement Award

If Air is Free……

- Economic Benefits of Oxyfuel Combustion
- Reduced Emissions
  - NOx, Particulates, CO
  - CO2 (through energy efficiency)
- Increased Throughput
  - Improved heat flux distribution
- Fuel Savings
- Equipment Cost Savings
  - Smaller flue gas cleanup equipment (due to lower gas flows)
  - Elimination of regenerators and recuperators

Oxyfuel combustion typically provides multiple benefits

Emissions Reduction with Oxyfuel Combustion

Yesterday – Glass Furnaces
Today – OEC for Coal Fired Boilers
Tomorrow – Onsite Production of Hg Sorbents with Hot Oxygen
Day After Tomorrow – Oxy-Coal Combustion

Oxy-Fuel Fired Glass Melting Furnaces

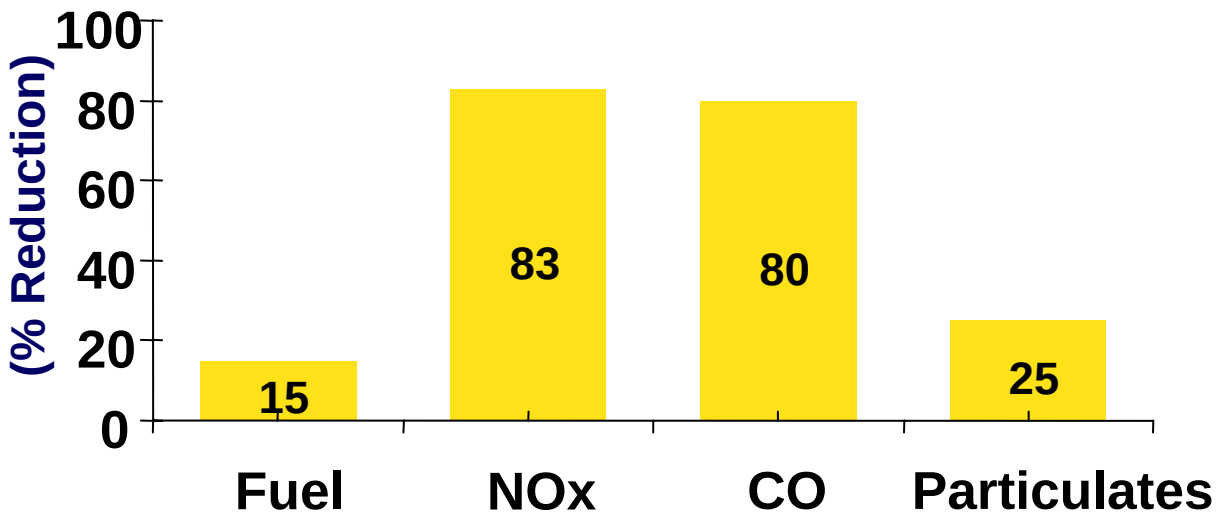
- Praxair Demonstrated the First Oxy-Fuel Fired Container Glass Furnace in 1991
- About 10,000 tpd of O_2 used today in the U.S.
- 85+ Glass Furnaces converted to Oxy-Fuel by Praxair
- Hold over 50 Patents in Glass Applications

- Main Benefits
  - Emissions Reduction (NOx, CO, Particulate)
  - Fuel Savings
  - Elimination of Regenerators
- About 30% of glass furnaces in the USA have been converted to oxy-fuel firing.

Reduction of Energy and Emissions

Praxair Awards for Developments in Glass Industry:

- **Technology Commercialization Award DOE-OIT 1995**
- **National Energy Award DOE 1996**
- **Eighth Annual National Award for Environmental Sustainability RENEW AMERICA 1998**



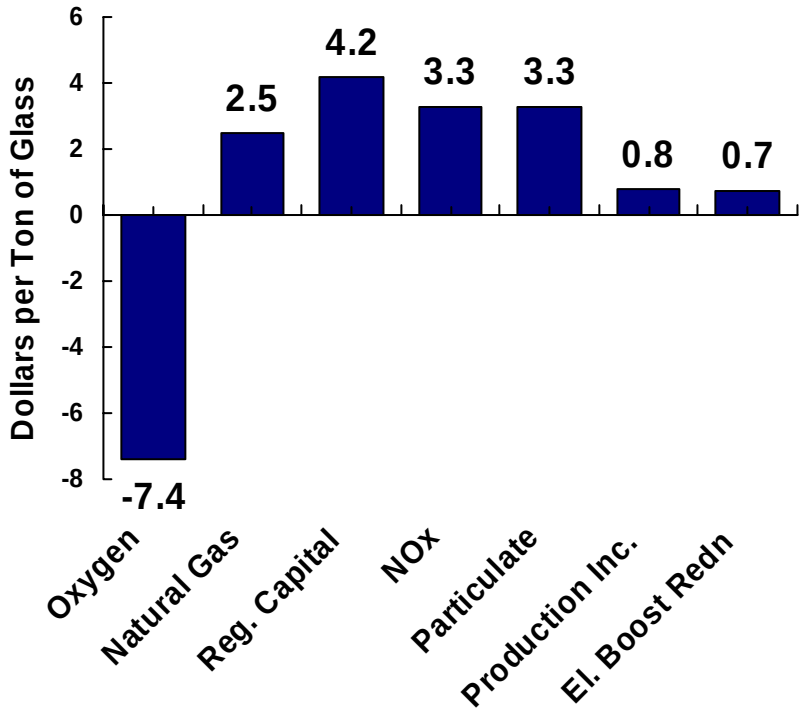
300 TPD Container Glass at Gallo Glass

Economic Benefits of Oxygen Combustion for Glass Melting

Multiple Benefits:

- Fuel Savings
- Capital costs reduction
  - Elimination of regenerators, smaller furnace, etc.
- Production Rate Increase
- Reduction of NOx and particulates emissions
- Product quality improvement

Example: 300 TPD Container Glass Furnace



Significant net benefits of oxyfuel conversions have resulted in conversion of ~30% of all US glass furnaces

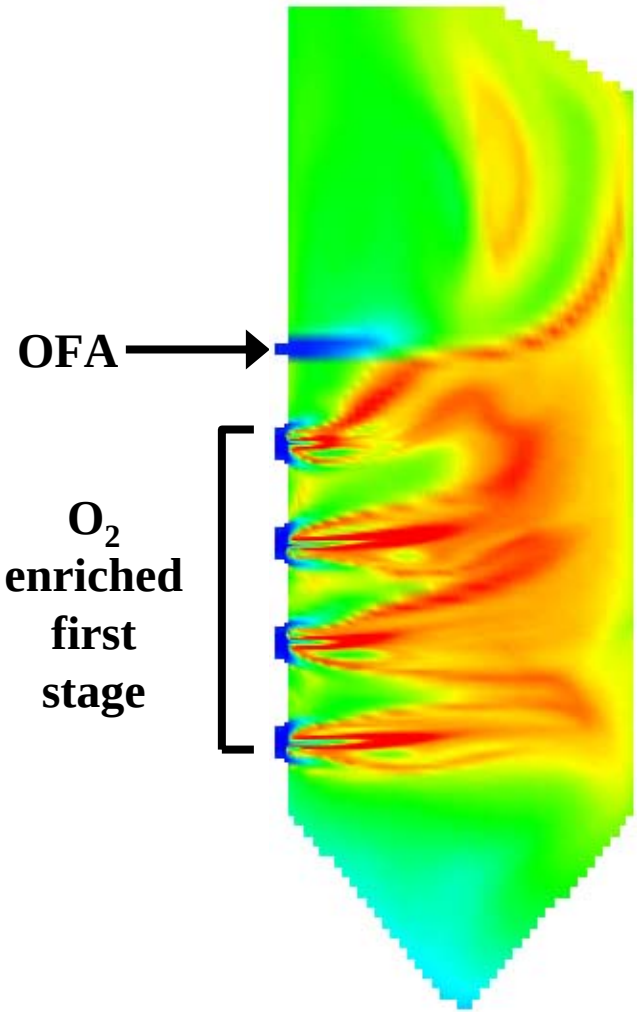
Oxygen-Enhanced Combustion (OEC) in Coal-Fired Boilers

Need:

- Cost effective NOx reduction technology for coal-fired boilers <300 MWe

Solution:

- Strategic injection of oxygen (<5% of required O2)
  - Enhances volatile yields
  - Anchors coal flame
  - Increases first stage temperature
- Facilitates deeper staging
  - Makes gas stage more fuel rich
  - Enhances conversion of Fuel N to N2
  - Modifies reaction kinetics to significantly reduce NOx formation
  - Reduces char yields
  - Typically reduces LOI and opacity

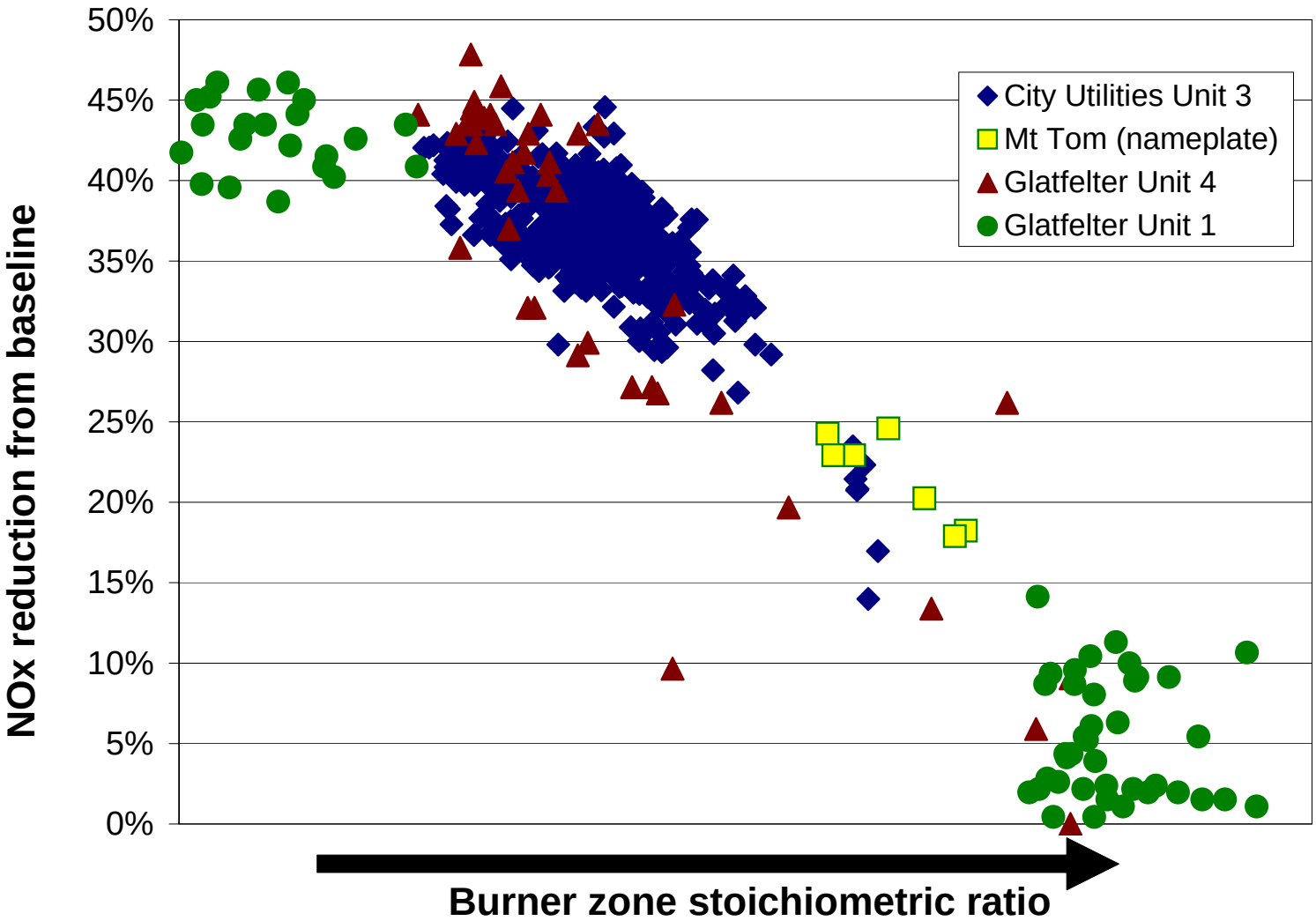


Developed with co-funding by DOE-NETL

Commercial Experience with OEC

- OEC demonstrated from pilot to utility boiler scale
  - 3 seasons at Mt. Tom Station in Holyoke, MA (150 MW)
  - 2 seasons at P.H. Glatfelter's Spring Grove, PA facility (2 industrial boilers 200k & 275k pph steam)
- At commercial scales utilities have seen:
  - Significant NOx reductions
  - Improved flame stability
  - LOI reduced even at deeper staging
  - CO - little or no change
  - Reduced flue gas volume
  - Restored generating capacity

Comparison with Prior Results



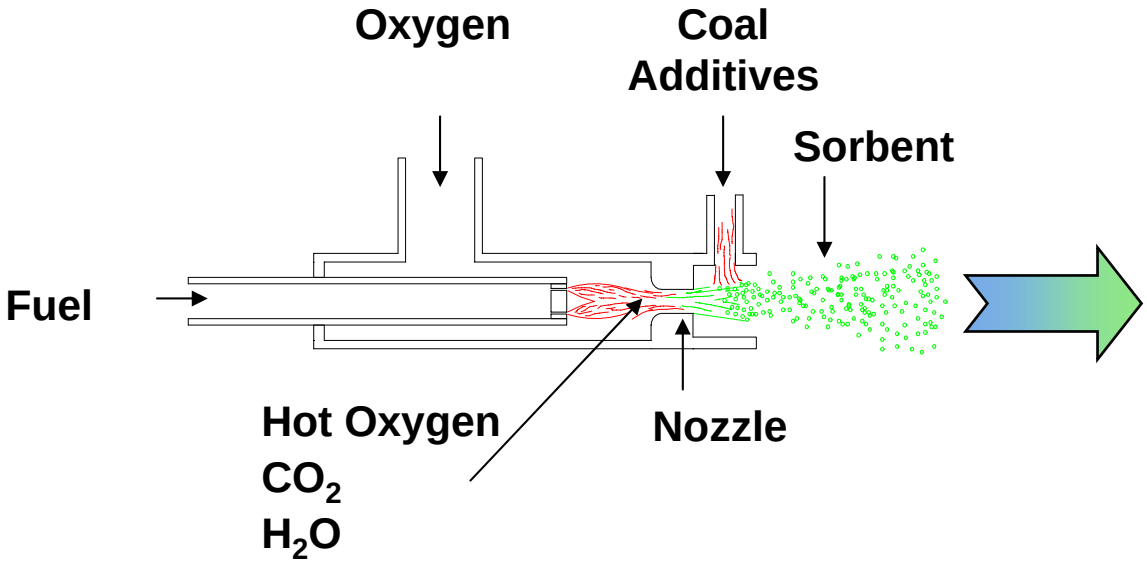
Summary – Coal NOx

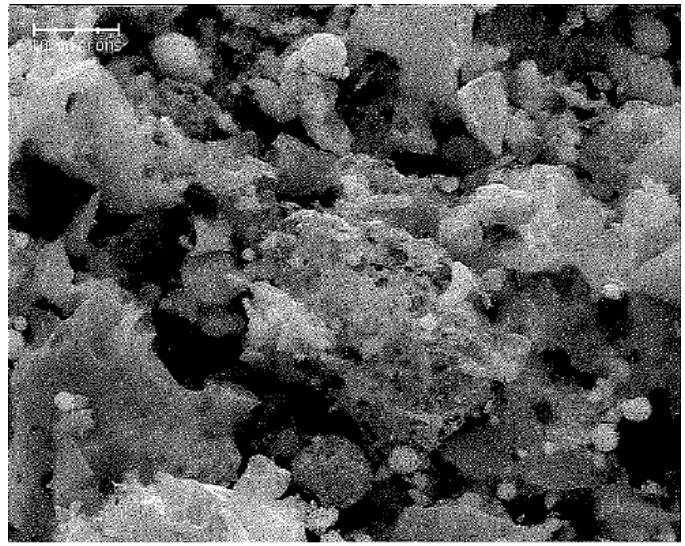
- Strategic injection of small quantity of oxygen provides
  - Lower NOx emissions
  - Improved flame stability
  - Little or no impact on LOI from basecase
- System characteristics
  - Very robust
  - Operators very comfortable with system
  - Rapid installation (order to start-up in as little as 6 months)
  - Possible to install without unit outage
- NOx emissions reductions are similar across scales
  - Allows good prediction of benefits before starting project

Onsite Production of Mercury Sorbents

- Powder Activated Carbon (PAC) effective flue gas mercury sorbent
  - Doped varieties used in PRB flue gas
  - Suitable for in-flight and filter configurations
  - PAC currently produced off-site and shipped to plant location
- Mercury sorbents have direct and indirect impact on economics
  - Cost of sorbent
  - Sorbent can negatively impact ash characteristics for cement replacement
- Praxair has developed a process to produce PAC on-site from customer's own coal

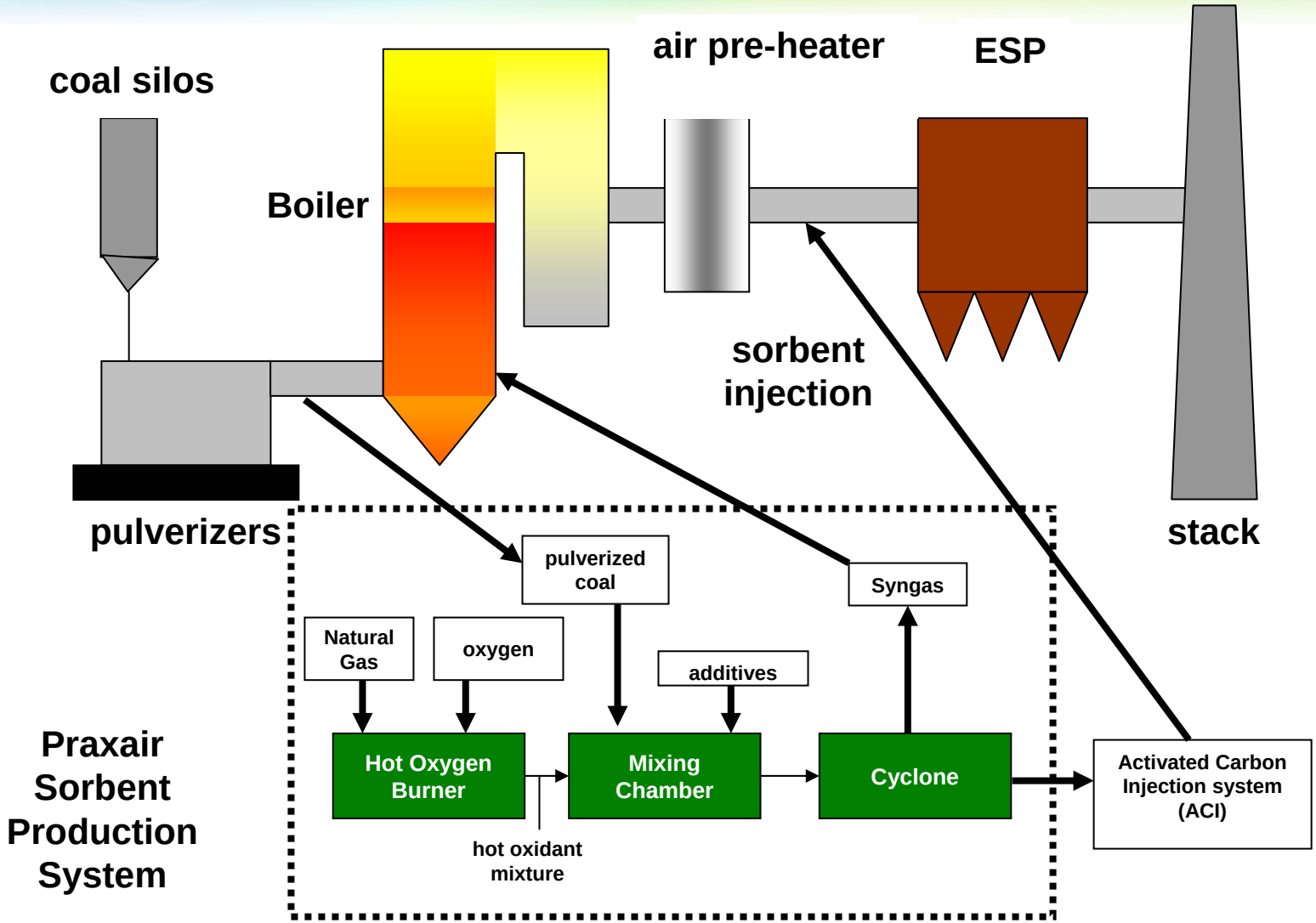
Sorbent Production with Hot Oxygen





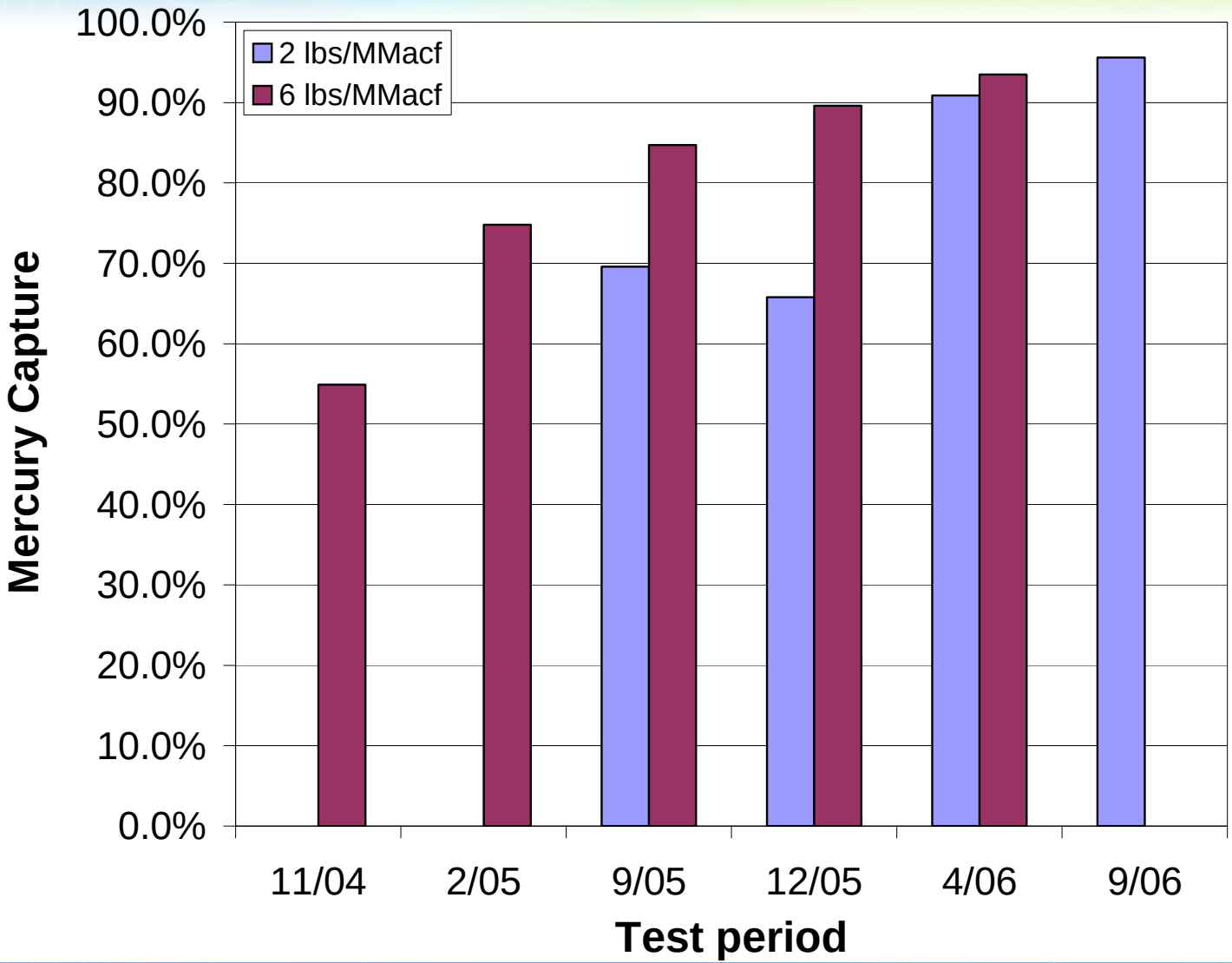
- Fraction of O_2 burned to heat O_2 stream
- High velocity, hot gas mixes with coal and additives
- Coal particles are rapidly devolatilized
- Doped activated carbon product is formed

Integration of Sorbent System with Boiler

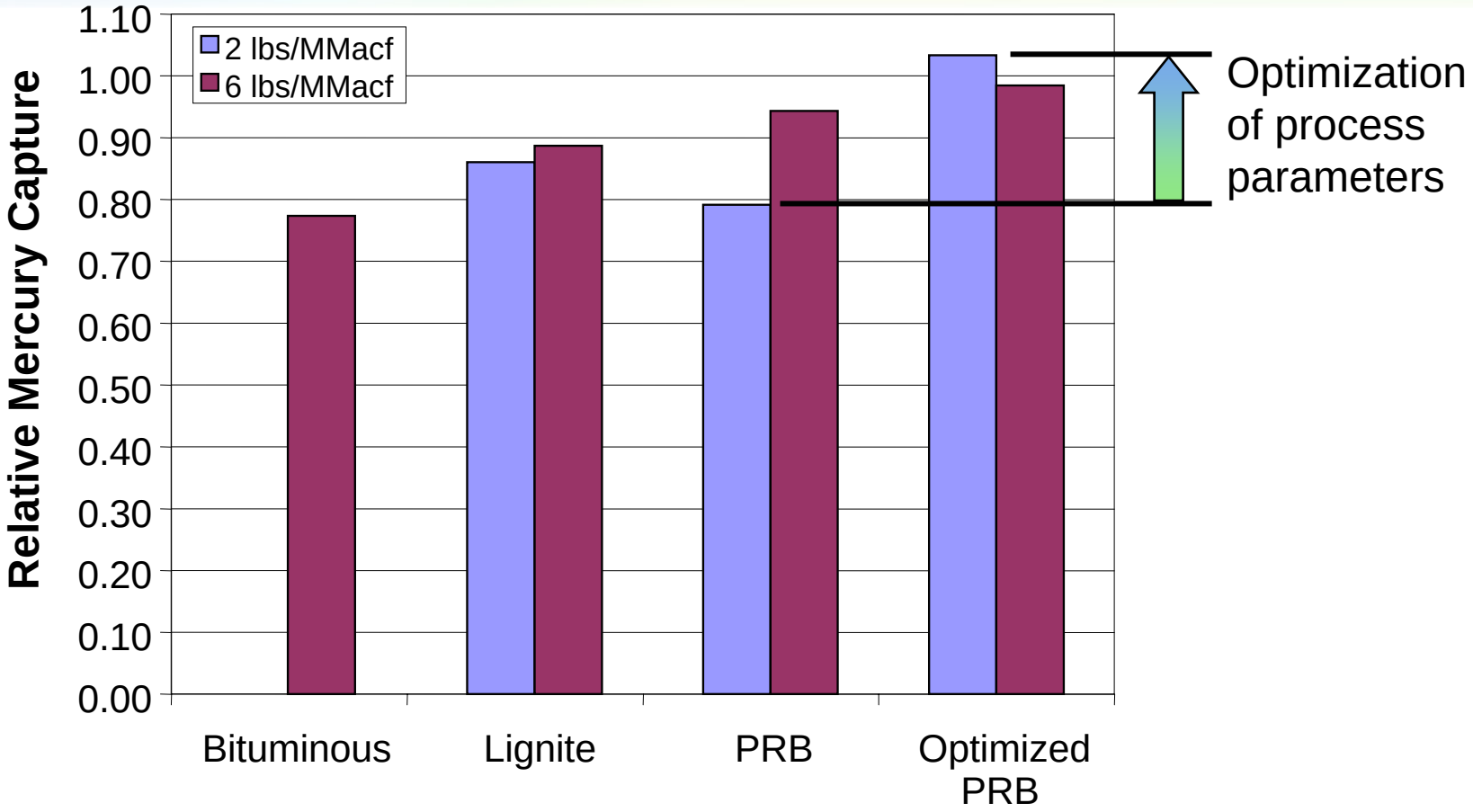


Simple, flexible, automated process

Successful Product Optimization



Performance vs. Coal Type



Expect improved performance from lignite and bituminous coals after further optimization

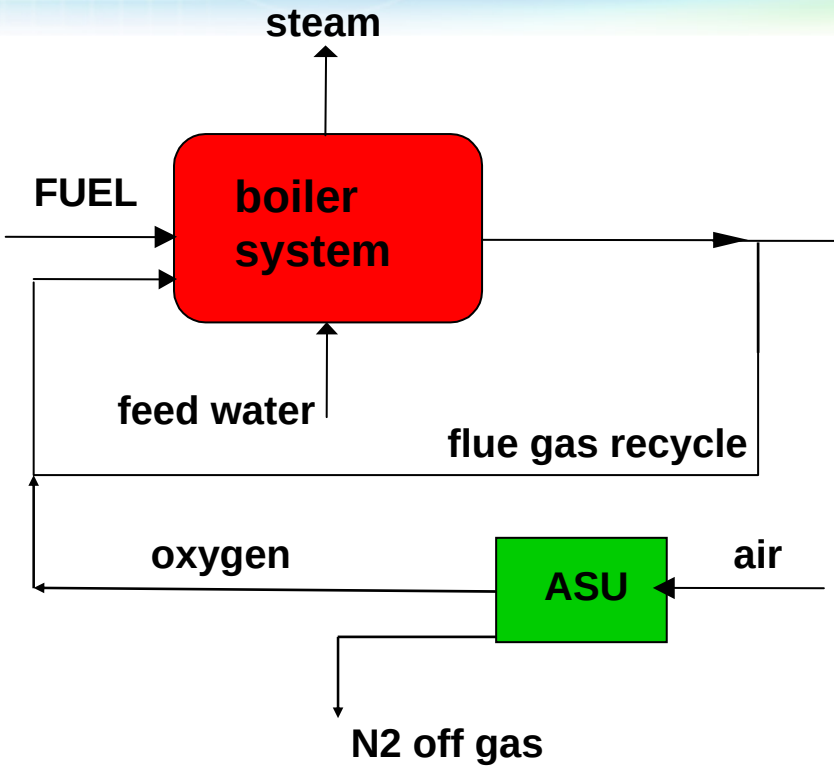
Cement Compatibility and Stability

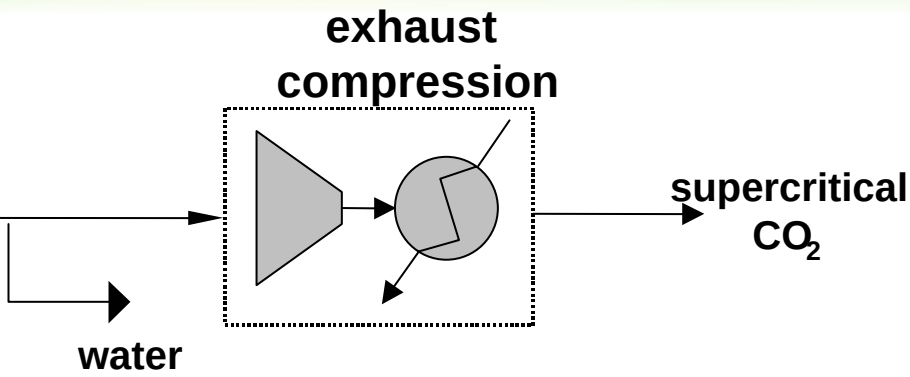
- Promising results indicated for cement compatibility
  - Process underway as part of DoE co-funded program
  - Acceptable limit for foaming index is 25
  - Foaming index tests of approx 15 to 35 have been achieved (ref. 80 – 100 for Norit FGD, 35 for Darco Hg-LH)
  - Optimization work underway
- Product does not have degradation after storage
  - Sample from same batch tested twice (six months apart) at Xcel's Comanche station
  - No special storage techniques employed
  - No difference in mercury capture between two samples

Summary – Mercury Sorbent

- Extremely flexible oxygen-based process
  - Suitable for use with multiple coal types
  - Optimized material provides excellent capture
  - Capable of providing local or regional sorbent production
- No product degradation during storage
- Process technology to minimize impact on ash compatibility with cement
  - Preliminary results are promising
- Cost to remove is 40% less than estimates of current commercially available doped PAC

Oxy-PC Firing of Existing Boilers with FGR for Retrofit Applications





- Many international studies
- Technically feasible
  - Oxy-coal firing tested in multiple pilot studies
  - 30 MW demo projects announced
    - Vattenfall 30 MWt pilot (Germany)
    - CS Energy 30 MWe unit (Australia – Japan/Australia)
- ASU Challenges
  - For boiler with ~10,000 Btu/MWe ASU consumes ~17% of power output

Direct Oxy-PC Fired Utility Boiler Design Options for New Installation

- No fundamental technical barriers to use direct oxy-pc firing without FGR
  - Heat flux can be controlled by burner/boiler design
  - Tube surface temperatures can be maintained at the same levels as the current designs, if desired.
- There are many design options and opportunities to optimize the boiler design specific to direct oxy-pc firing.
  - Radiant superheaters
  - Separately fired superheater furnace (e.g., Albany Reseach/Jupitor)
- Path forward
  - Fundamental oxy-coal combustion studies are needed to develop future generation advanced oxy-coal fuel fired boilers
  - For new direct oxy-fuel fired boilers many design innovations appear possible and need further evaluation and development.

Summary

- Oxyfuel Combustion is a multi-benefit technology
- Benefits typically include:
  - Reduced emissions (NOx, CO, Particulates, CO_2)
  - Increased throughput
  - Improved fuel efficiency
  - Reduced capital
- Although “air is free” the benefits of O_2 often outweigh the cost
- Oxygen can be the most cost effective solution for achieving environmental compliance without sacrificing plant performance
- Praxair continues to expand into markets that can benefit from oxygen but may not be familiar with its use/handling