SECA Core Technology Program Review

Onsite Fuel Processing R&D at the National Energy Technology Center

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Fuel Processing
Overview

- **Goal**
  – Provide SECA fuel cell developers with reliable, low cost fuel processors.
- **Objective**
  – Develop fuel processing technology for application specific fuel types (natural gas, gasoline, diesel,...).
- **Technical Challenges**
  – Deactivation of fuel reforming catalysts and fuel cell components are a principle technology barrier:
    - Sulfur-containing fuels poison reforming catalysts and fuel cell anodes, causing premature failure.
    - Carbon deposition on reforming catalysts, especially with the heavier hydrocarbon fuels, deactivate the reformer.

  – Large, complex, slow-response fuel processors problematic:
    - Many FC applications may require high power density design with “fast” response for transient operations.
- **Technical Approach**
  – Develop compact, modular processors that incorporate novel sulfur removal technology and/or sulfur/coke tolerant catalyst systems..

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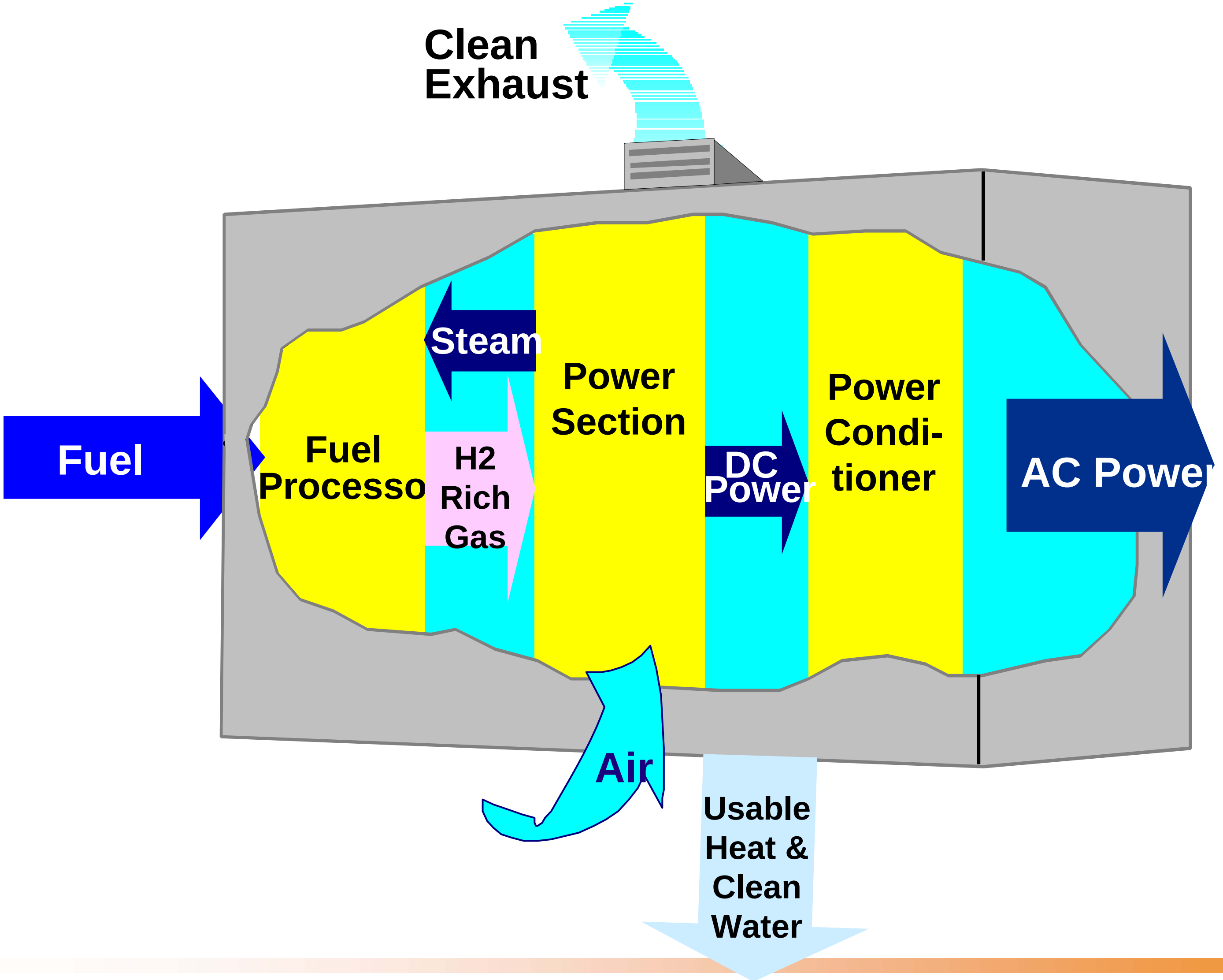
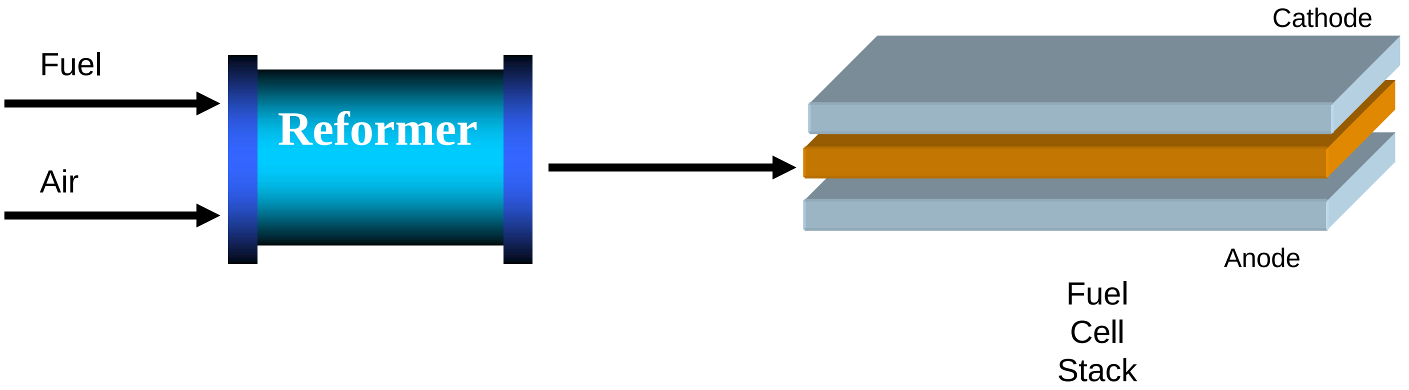
Fuel Processing

Simplified Fuel Cell System View



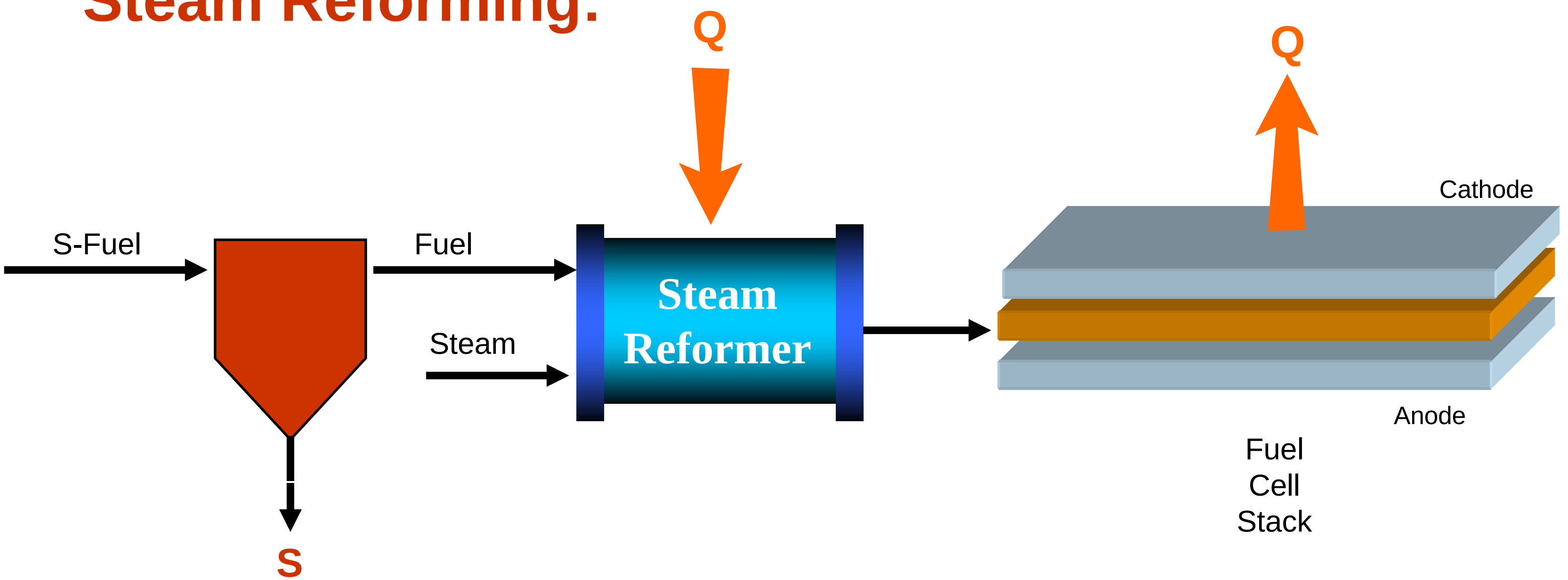
Fuel Processing - Introduction cont...

General Scheme:



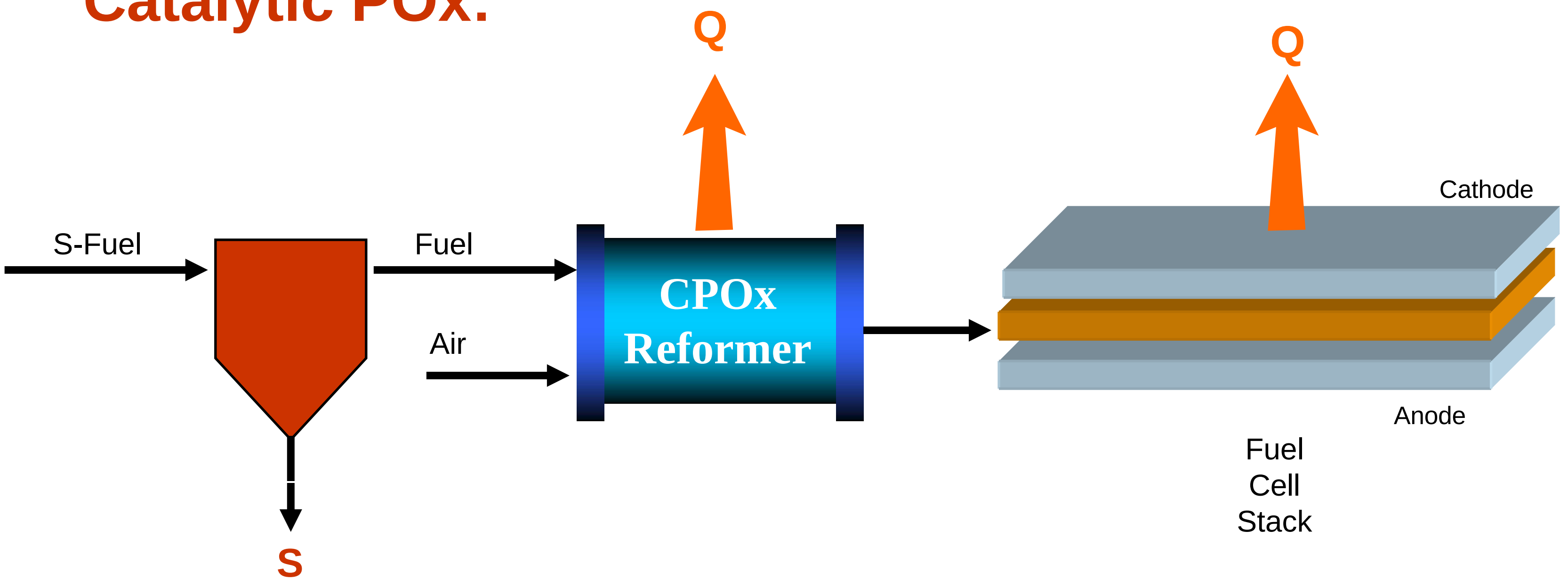
Fuel Processing - Introduction cont...

Steam Reforming:



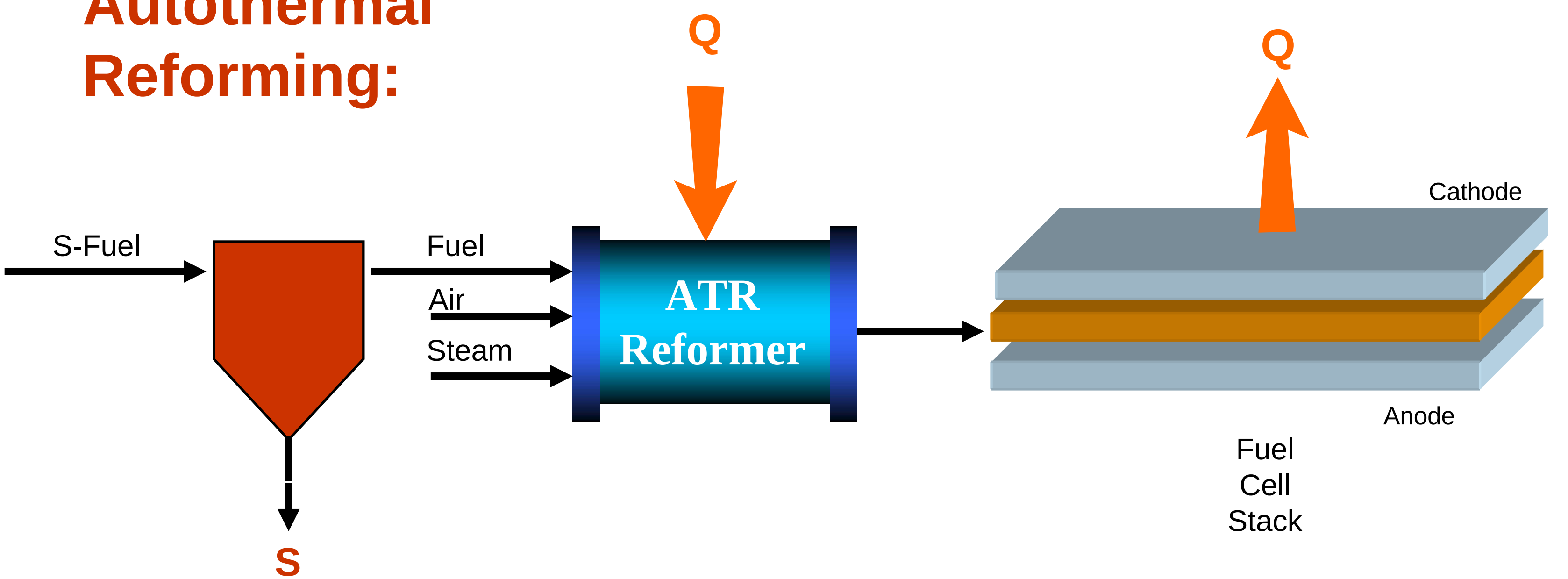
Fuel Processing - Introduction cont...

Catalytic POx:



Fuel Processing - Introduction cont...

Autothermal Reforming:



Fuel Processing for SECA
A variety of development issues

Sulfur poisoning

Coke Formation

High efficiency & thermal integration

Quick startup and transient response

SECA Development: Progressive Applications

2005

- $800/kW
- Prototype (β-Unit) 3 - 10 kW

2010

- $400/kW
- Commercial

2015

- Vision 21 Power Plants
  75% efficient plants
- Propulsion <$200?/kW

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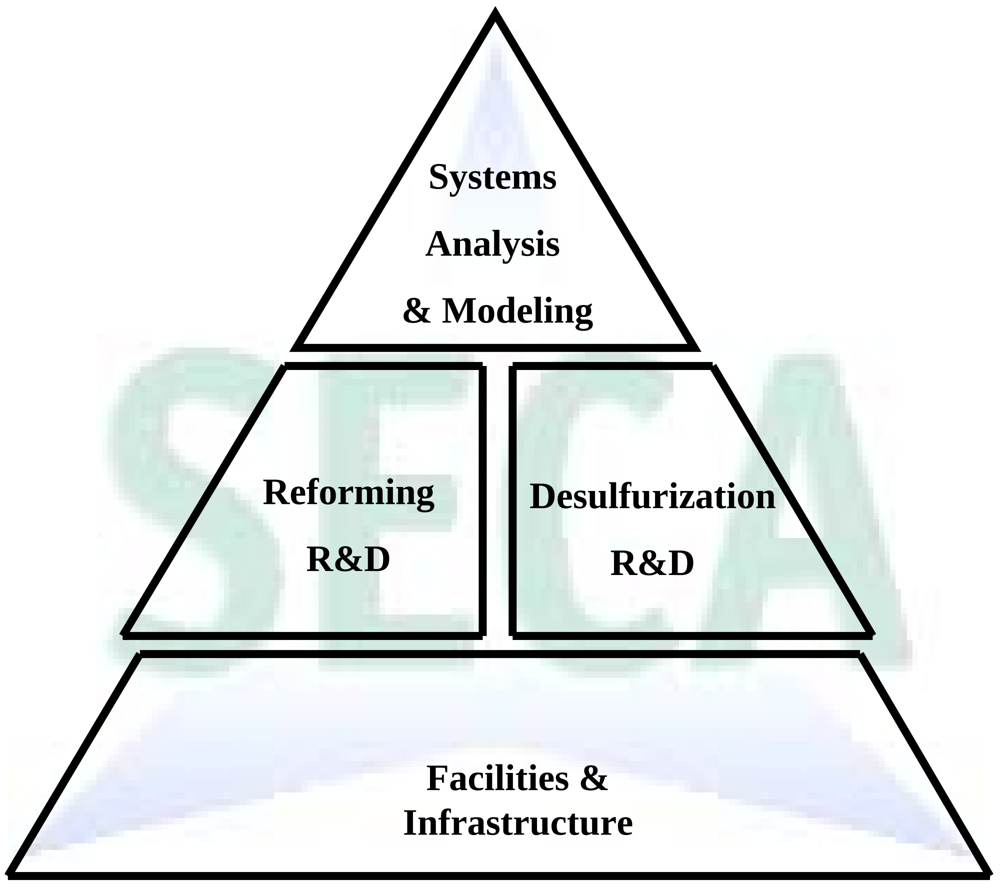
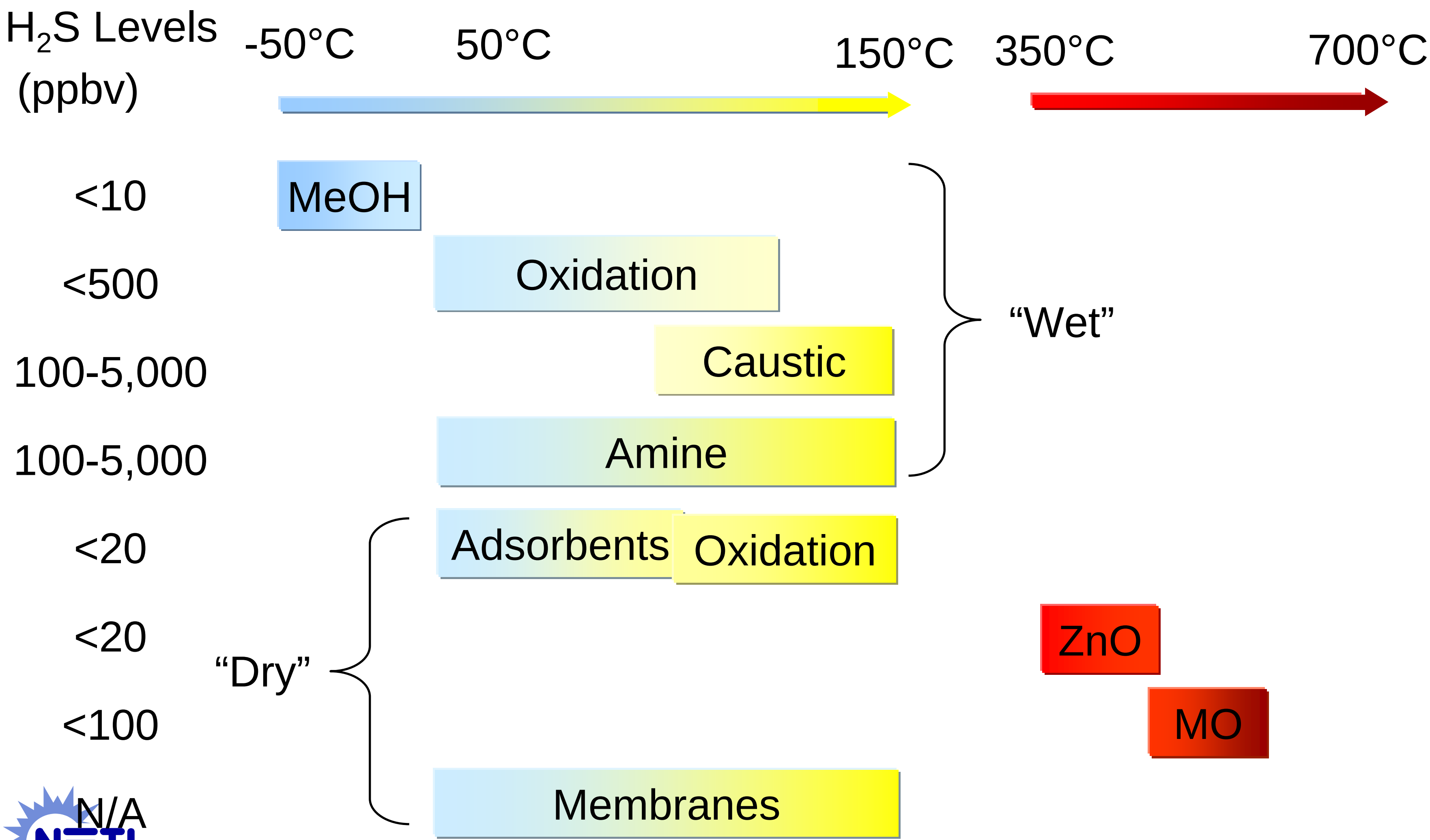
Approach to Program/Project Planning



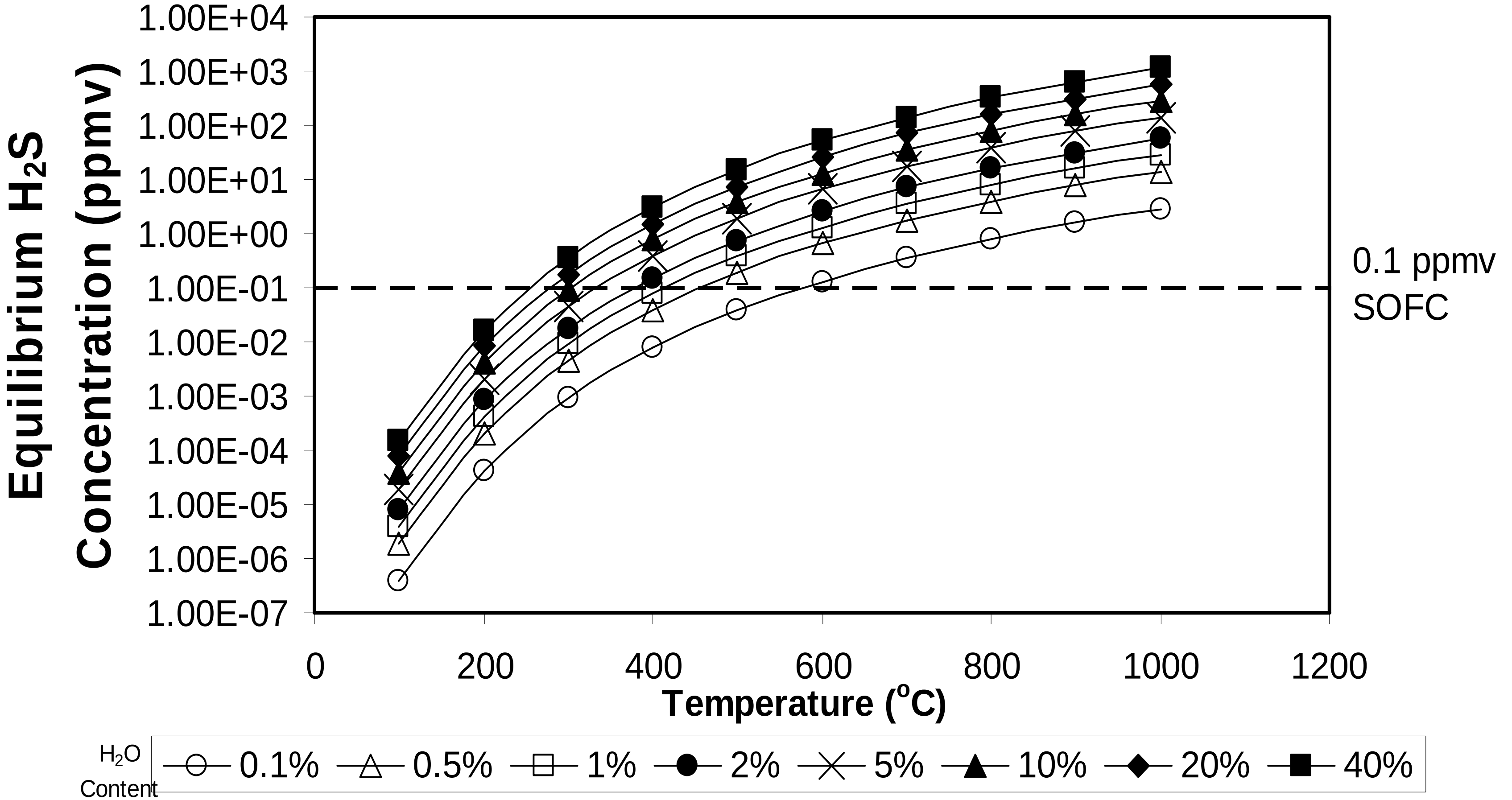
Natural Gas/Synthesis Gas Sulfur Removal Technologies



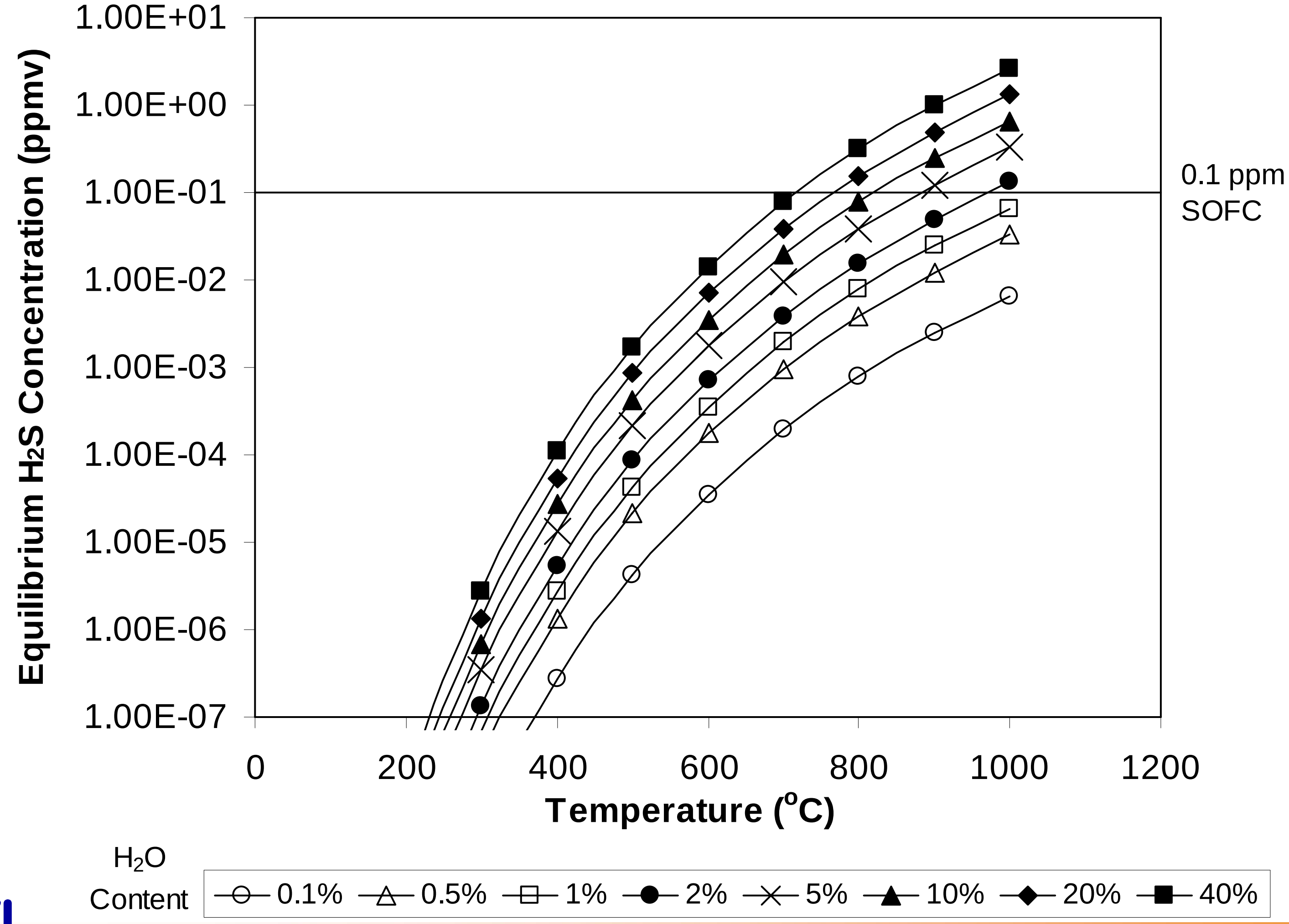
"High Temperature H_2S Removal"

- **Project Objective**
  - – Assess high temperature H_2S sorption/reaction technology as a method of removing sulfur in compact SOFC systems
- **Technical challenges**
  - High sulfur removal efficiency
  - Resistance to sintering, Ostwald ripening, etc.
  - Stability of silica "free" binder systems and matrix materials
  - Lifetime analysis, capacity, regenerability
- **Technical Approach**
  - – Perform thermodynamic study for suitable MO's
    - MO + H_2S **6** MS + H_2O
  - – Perform lab-scale screening of suitable catalysts, matrix materials and binder systems for high temperature H_2S sorption/reaction

Zn_2TiO_4 Equilibrium Sulfur Removal Efficiency



CuO Equilibrium Sulfur Removal Efficiency



"Selective Oxidation of Sulfur Compounds for Direct Sulfur Removal"

- **Project Objective**
  - Assess sulfur selective catalytic oxidation technology as a direct sulfur removal technology at low temperatures for SOFC systems
- **Technical Challenges**
  - High sulfur conversion/removal efficiency
    - H_2S, Mercaptans
  - High activity, high throughput, optimization
  - Lifetime analysis
- **Technical Approach**
  - Perform lab-scale screening of suitable catalysts and supports, e.g. removal efficiency, lifetime, SV
  - Kinetic measurements

"Selective Oxidation of Sulfur Compounds for Direct Sulfur Removal"

"H_2S Catalytic Partial Oxidation"

- $H_2S + {}^1/_2O_2 \rightarrow {}^1/_8S_8\downarrow + H_2O$
- $4RSH + O_2 \rightarrow 2RSSR\downarrow + 2H_2O$
- Sulfur product retained in activated carbon catalyst's micropores
- High sulfur loadings possible
- Thermal regeneration is necessary

"Sulfur Over Oxidation Possible"

- $H_2S + {}^1/_2O_2 \rightarrow {}^1/_nS_n + H_2O$
- ${}^1/_nS_n + O_2 \rightarrow SO_2$
- $4RSH + O_2 \rightarrow 2RSSR\downarrow + 2H_2O$
- Macroporous catalysts necessary
- High superficial velocities needed to 'wick' sulfur product away
- Metal oxide catalysts employed

"H_2S Complete Oxidation"

- $H_2S + {}^3/_2\, O_2 \rightarrow SO_2 + H_2O$
- Homogenous phase H_2S complete oxidation

100^{o}C 175^{o}C 250^{o}C

Temperature

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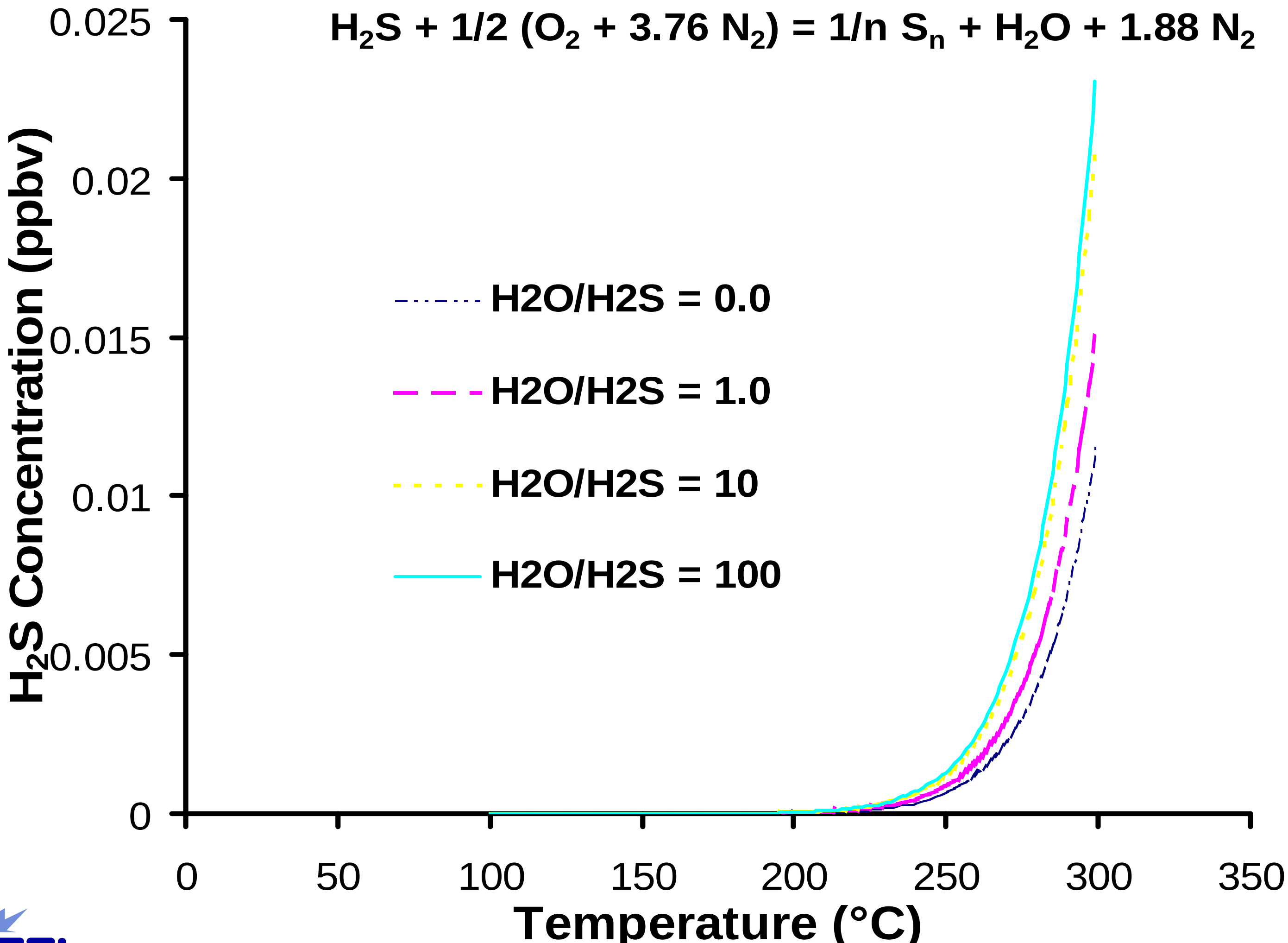
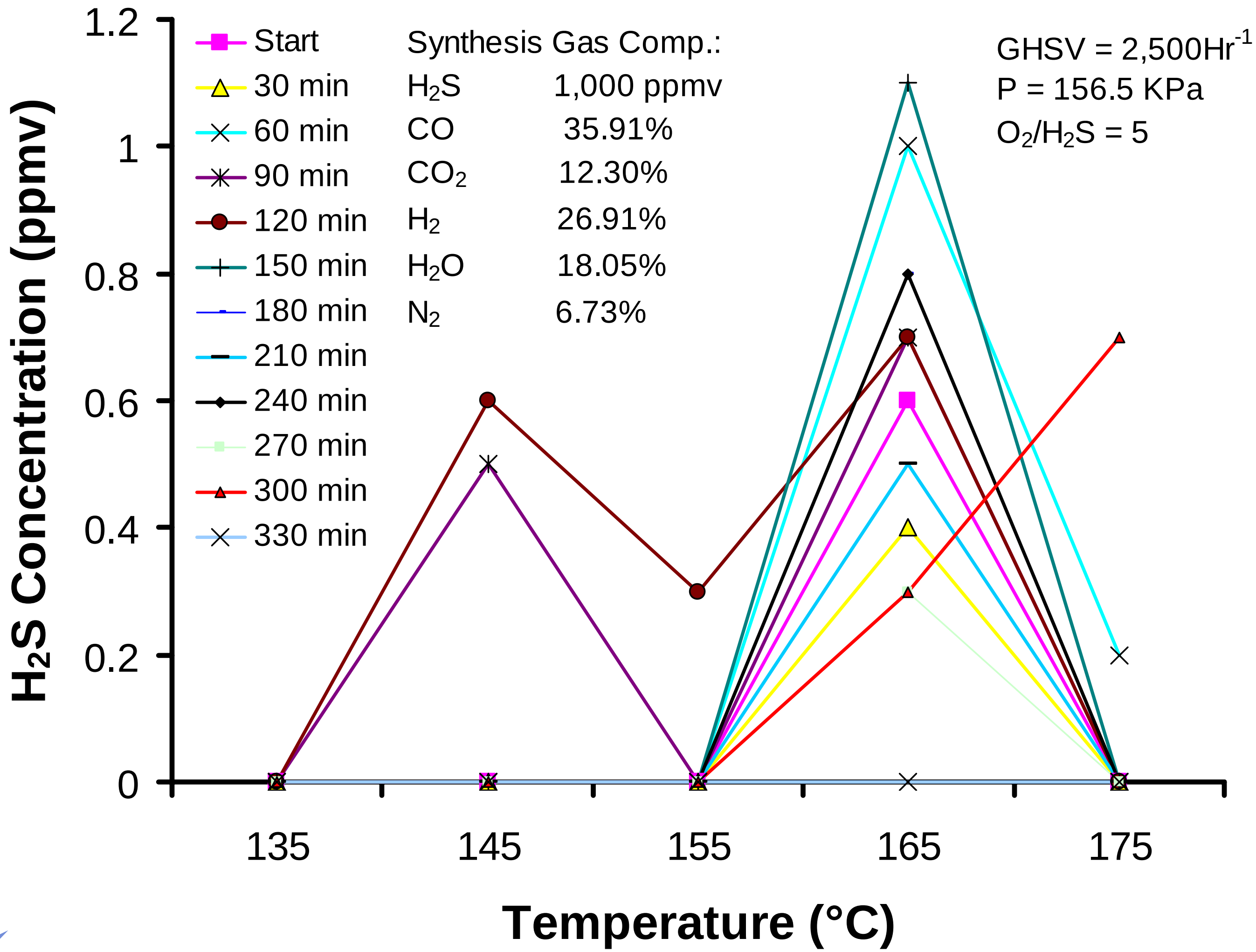
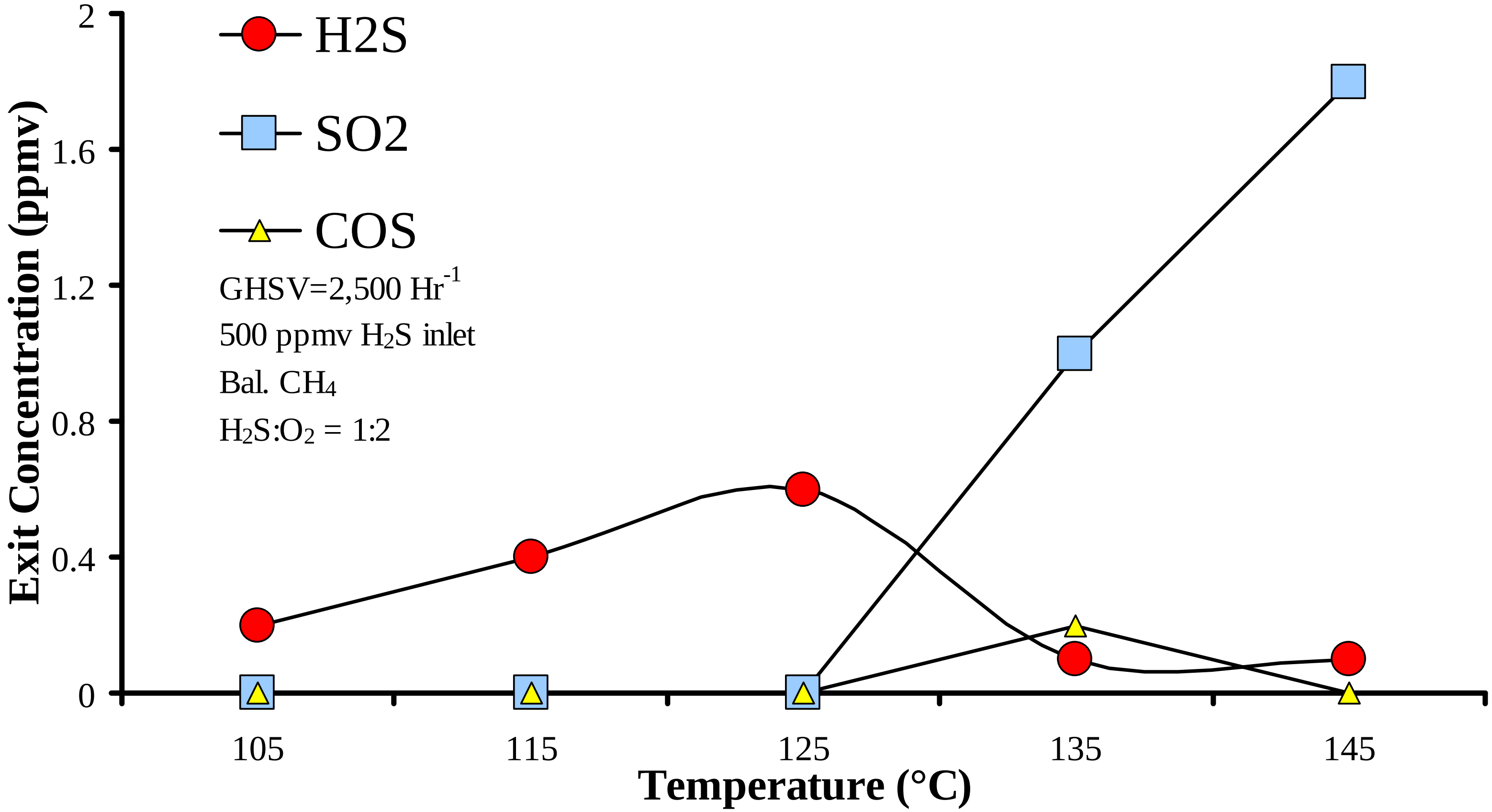
Equilibrium Removal Efficiency of the H_2S Partial Oxidation Reaction



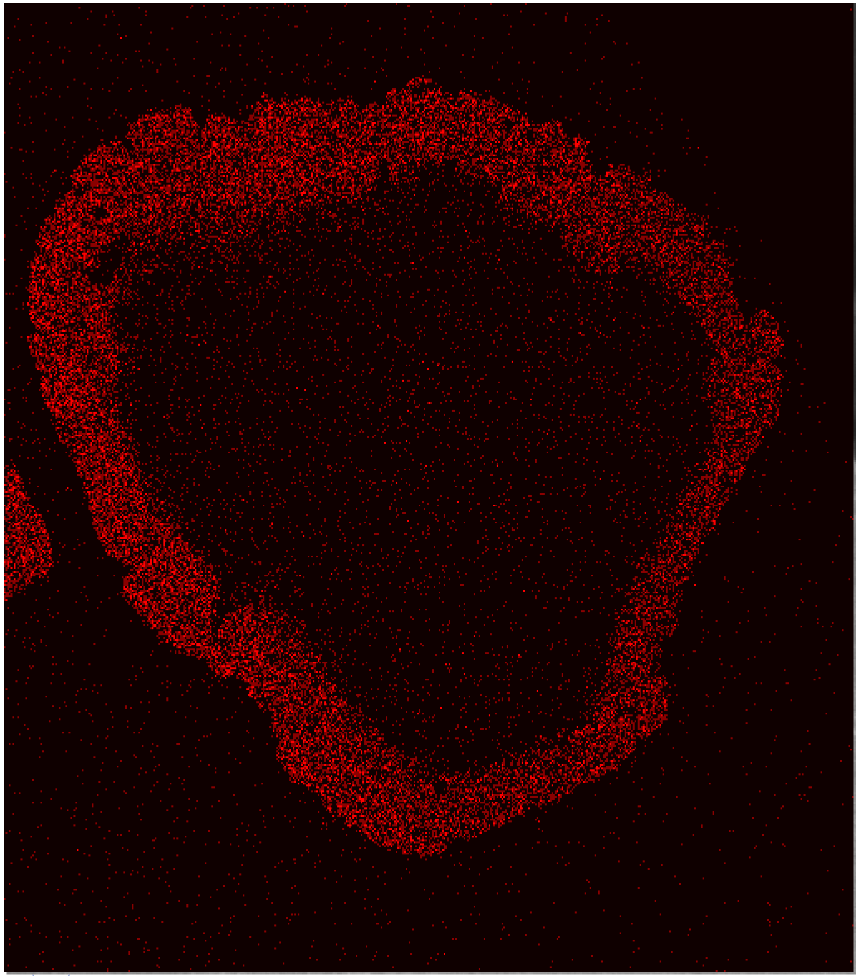
Effect of Temperature and Time on Stream on H_2S Removal Efficiency



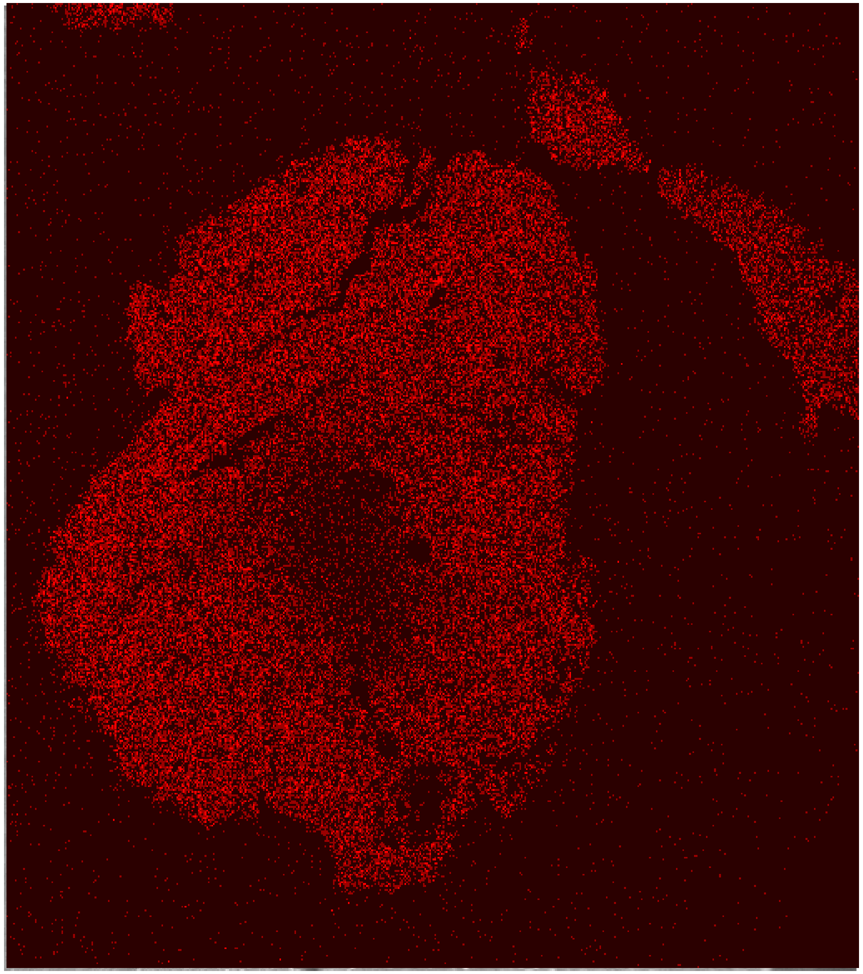
H_2S Partial Catalytic Oxidation Performance in Natural Gas



SEM/EDS Sulfur Profiles in Activated Carbon Catalyst Pellets

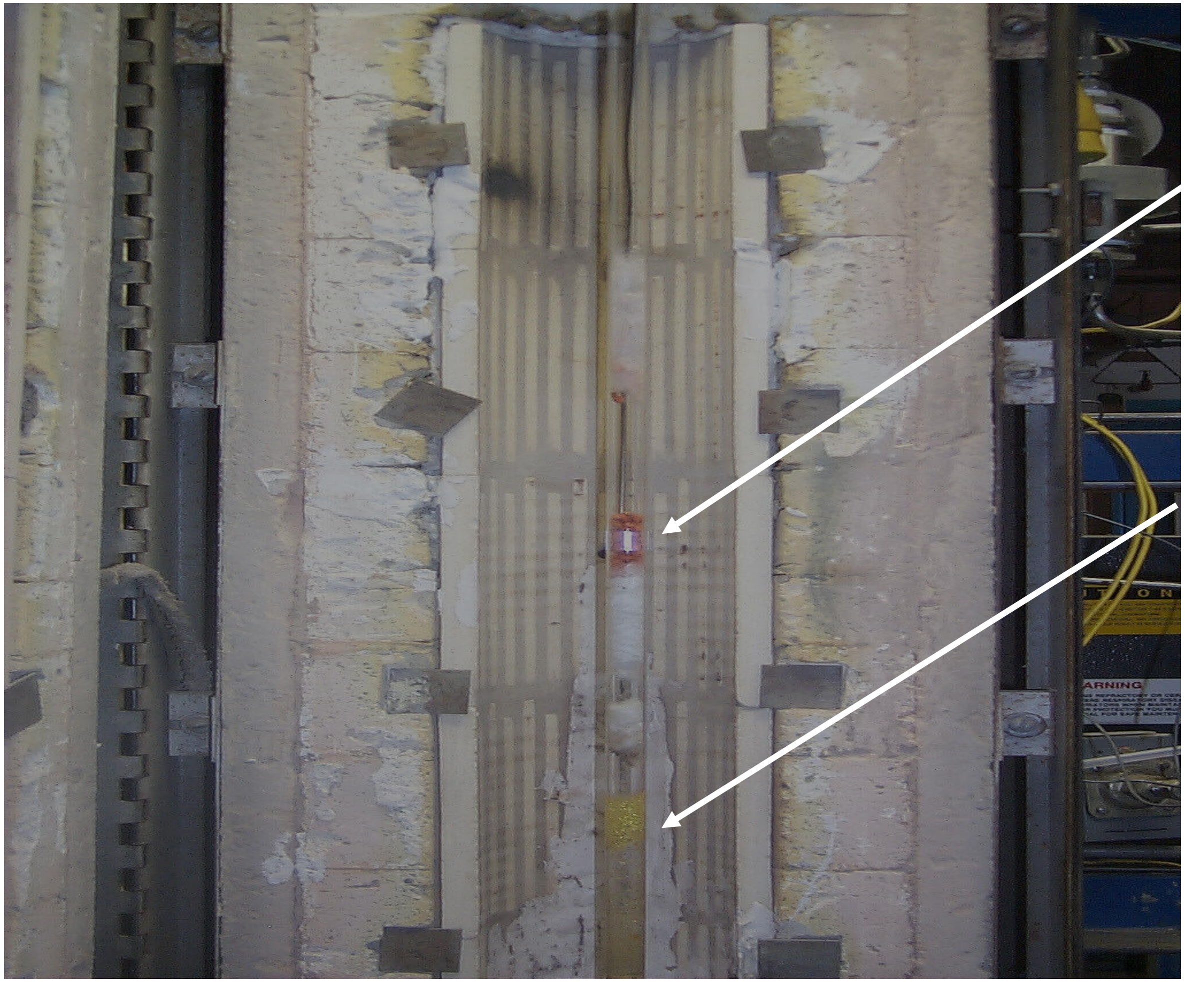


8 hours at 1,000 ppmv H_2S



16 hours at 1,000 ppmv H_2S

Continuous Catalytic Oxidation of H_2S



Metal oxide REDOX catalyst remained in oxide state

Sulfur product continuously Drips out

Facility/Infrastructure Overview

- **OBJECTIVES**
  - Provide adequate facilities to support RD&D for the SECA program.
    - Identify and understand fundamental mechanisms of concepts proposed for fuel processing applications
    - Explore R&D issues and demonstrate technology options at various scales.
    - Provide experimental validation of technology development
- **TECHNICAL CHALLENGES**
  - Fundamental issues must be studied at small scale with high analytical precision where all operating variables can be isolated and controlled.
  - Facilities must be economical to operate and flexible
  - Processes deal with high temperature (pressure) combustable and toxic gases
  - Effects of process scale must be understood.

Facility/Infrastructure Overview (cont.)

- **APPROACH**
  - Develop labscale facility to generate fundamental data for technology involving chemical reaction, separations, heat transfer, and mass transfer :
    - H_2S removal from Fuel Cell feedstocks
    - Kinetic rates for catalyst systems
    - Reaction Mechanisms (also failure mechanisms)
  - Provide mid-scale platform to:
    - Bridge the gap between lab scale and commercial components - minimize scaling issues.
    - Conduct validation testing and technology evaluation for program participants (testing of fuel processors in SECA program).

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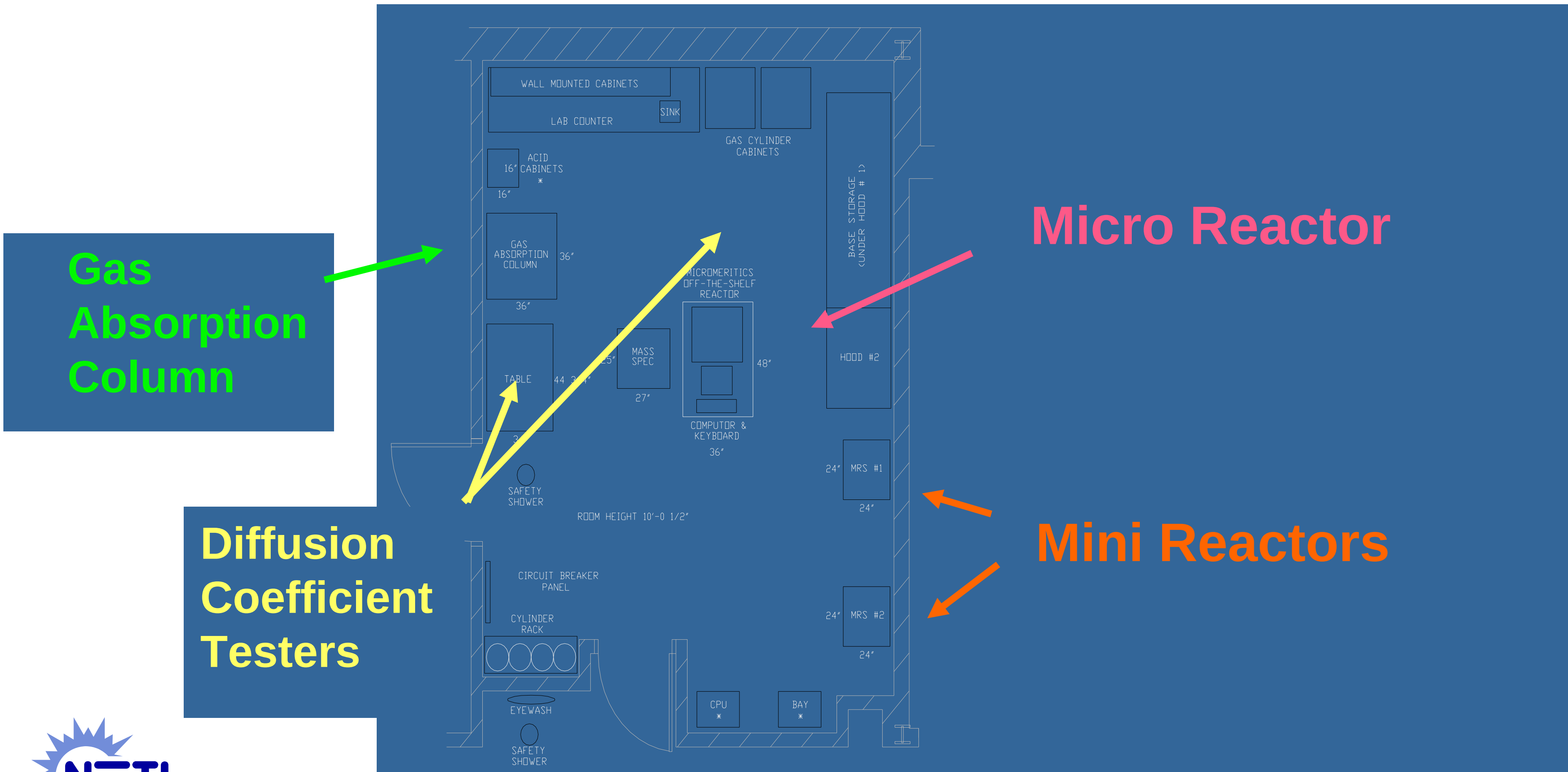
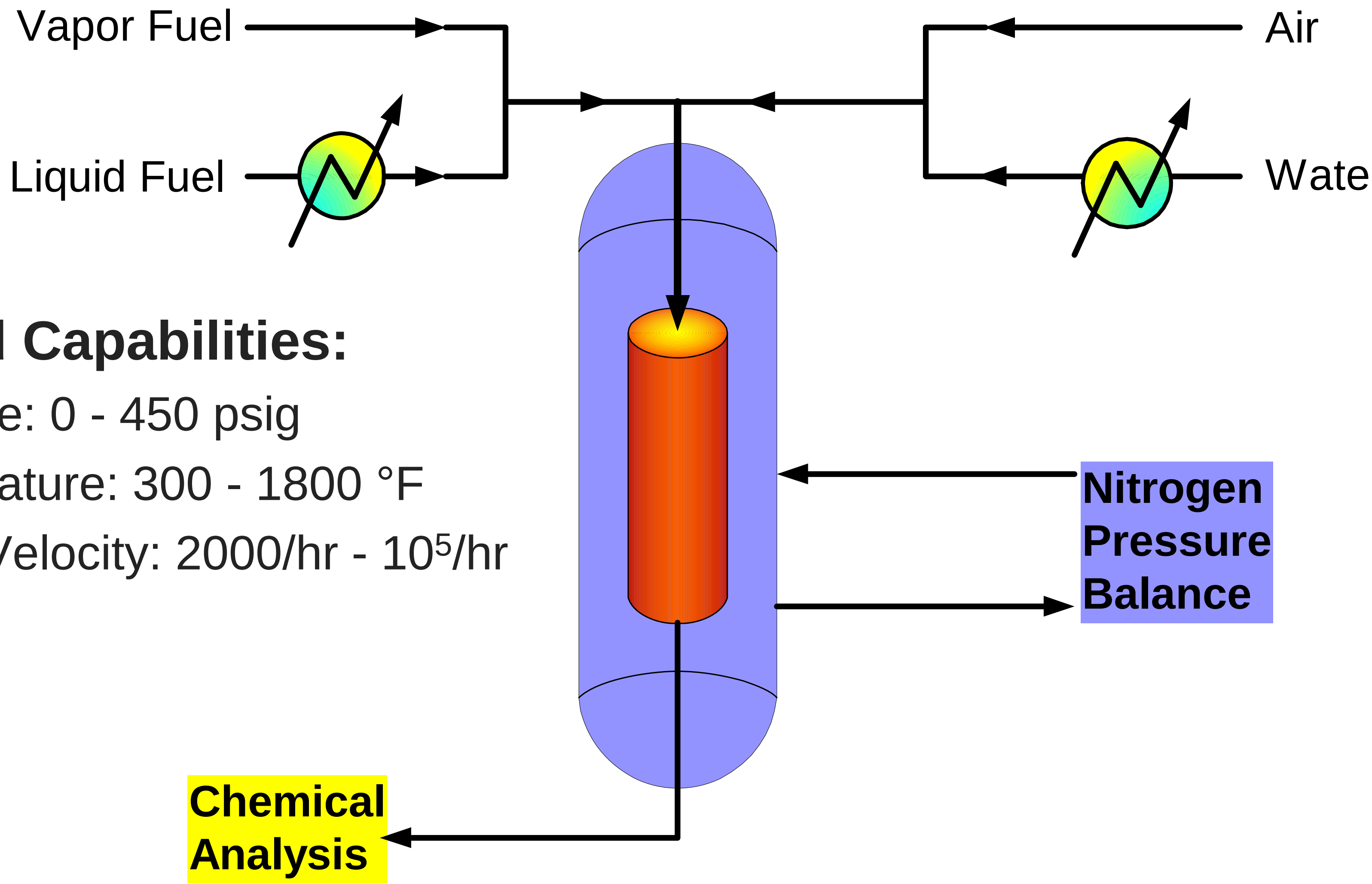
Fuel Processing Laboratory

Generate fundamental, design, and operational data for applications involving separations, heat transfer, and mass transfer :

- H_2S removal from Fuel Cell feedstocks
- Kinetic rates for catalyst systems
- Reaction Mechanisms (also failure mechanisms)



Miniature Reactor System
B25 Fuel Processing Laboratory

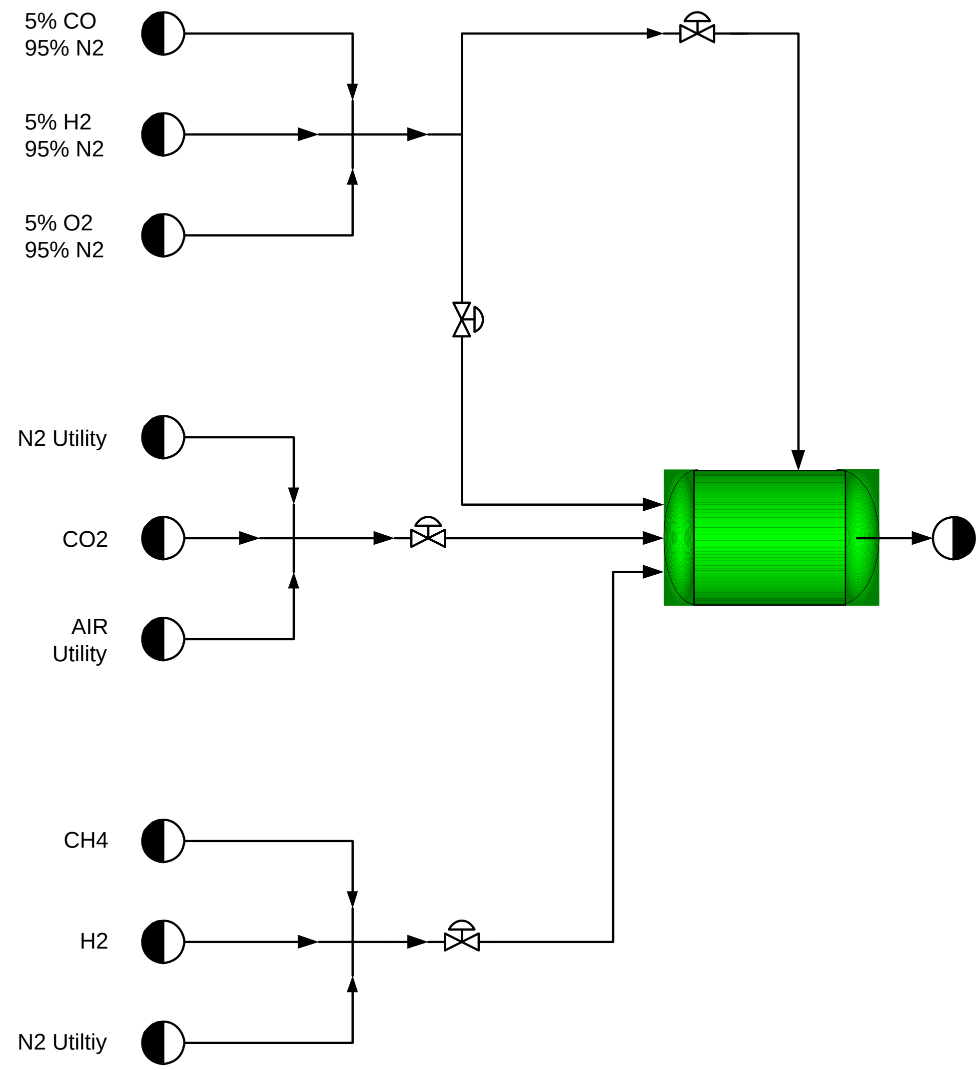


Test Bed Capabilities:

- Pressure: 0 - 450 psig
- Temperature: 300 - 1800 °F
- Space Velocity: 2000/hr - 10^5/hr

Fundamental Studies Microreactor
B25 Fuel Processing Laboratory

- **System Volume = 0.8 cm^3**
- **Sample can participate in reaction, be isolated quickly, and be subjected to Temperature Programmed Studies**
- **Instrument Capabilities:**
  - Temperatures from -100 to 1100 °C
  - Operates near ambient Pressure
  - Flowrates up to 75 sccm

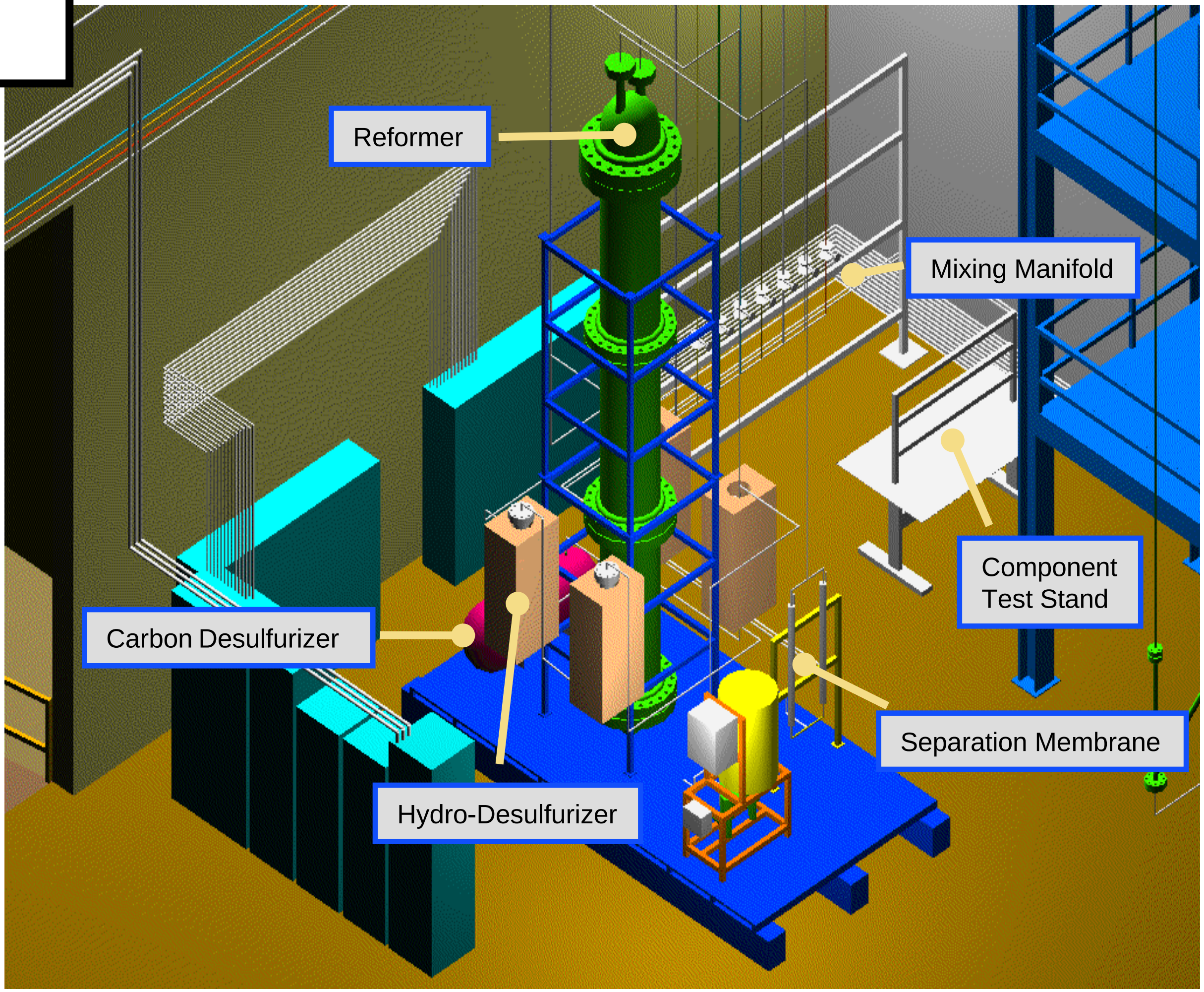


Fuel Processing Research Facility

- ✓ Explore R&D issues that demonstrate technology options for fuel-gas processing at a significant mid-scale level
- ✓ Address coal gas cleanup technology development as it relates to fuel cells and Vision 21

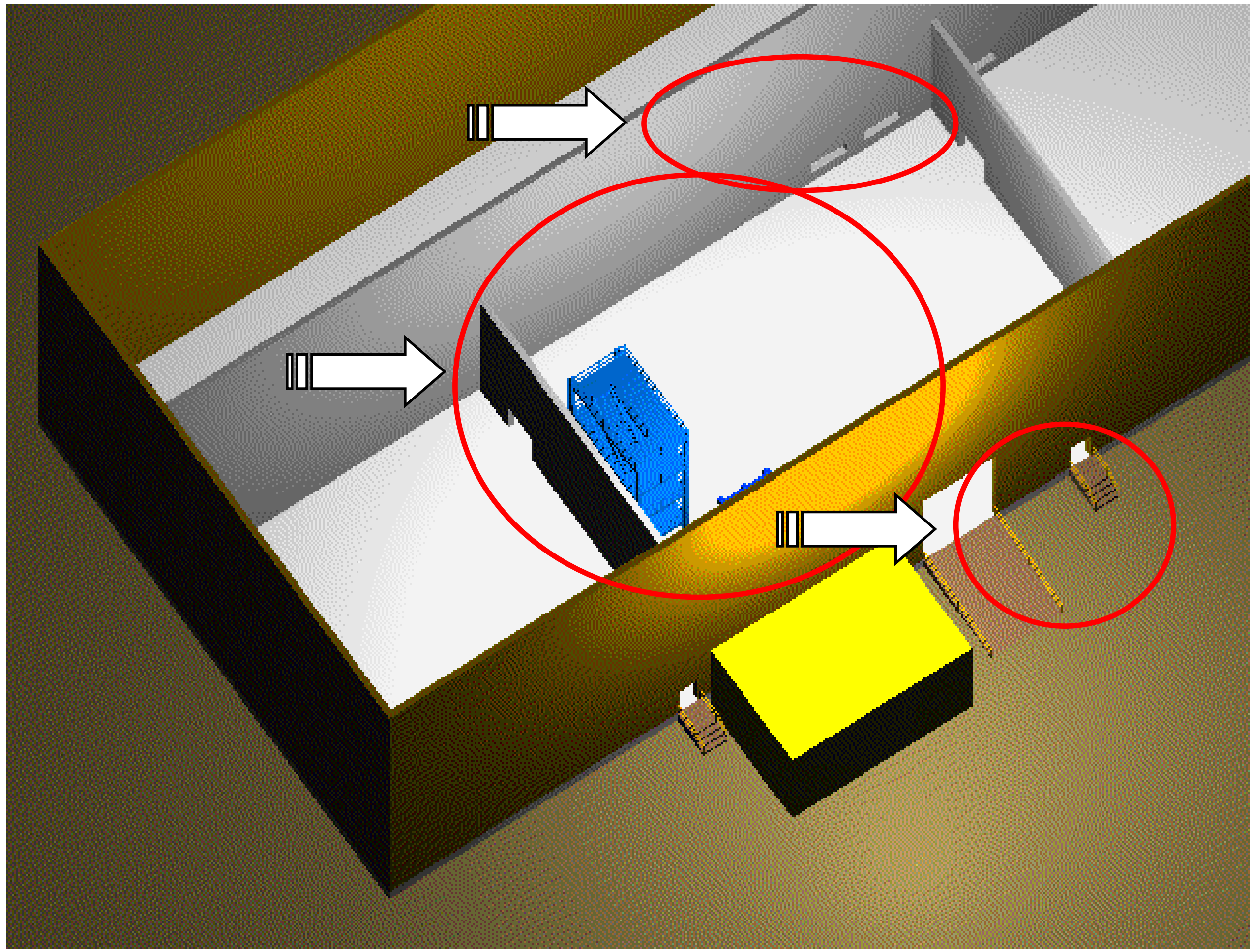
CAPABILITIES:

- 2000 SCFH of tailored synthesis gas
- 900 °C
- 30 atmospheres
- Reformer Modes:
  - Partial Oxidation
  - Steam
  - Auto-thermal
- Multiple unit operations for fuel gas processing



Facility Layout

- **Located on the NETL-MGN Site**
- **Areas:**
  - 2200 SQFT of Research Area
  - 1600 SQFT of Remote Operations Area
  - 350 SQFT of Gaseous and Liquid Fuels Storage Area



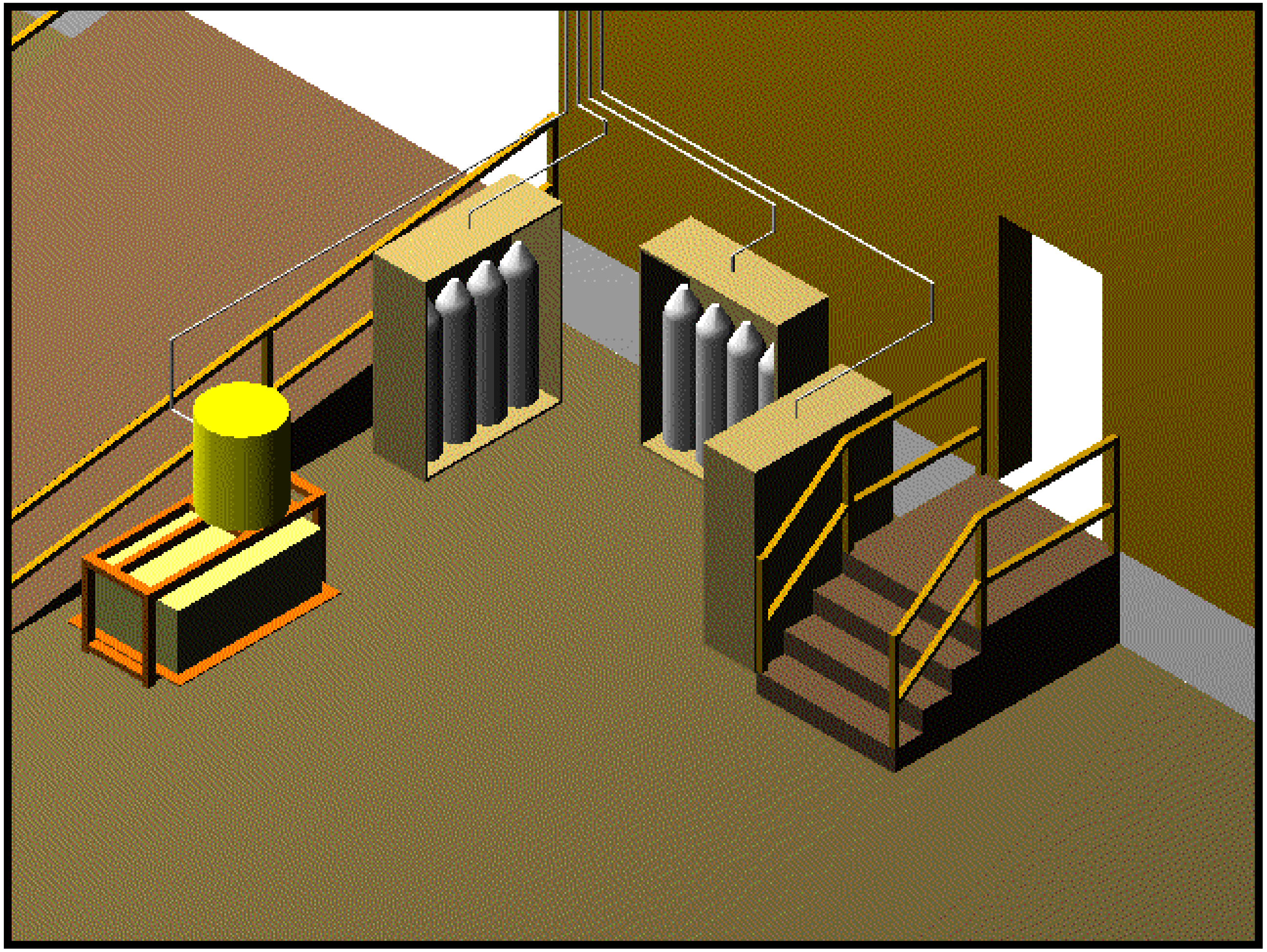
FPRF Fuel Storage Area

Gaseous Fuels Storage

- Hydrogen
- Carbon Monoxide
- Hydrogen Sulfide
- Others if needed

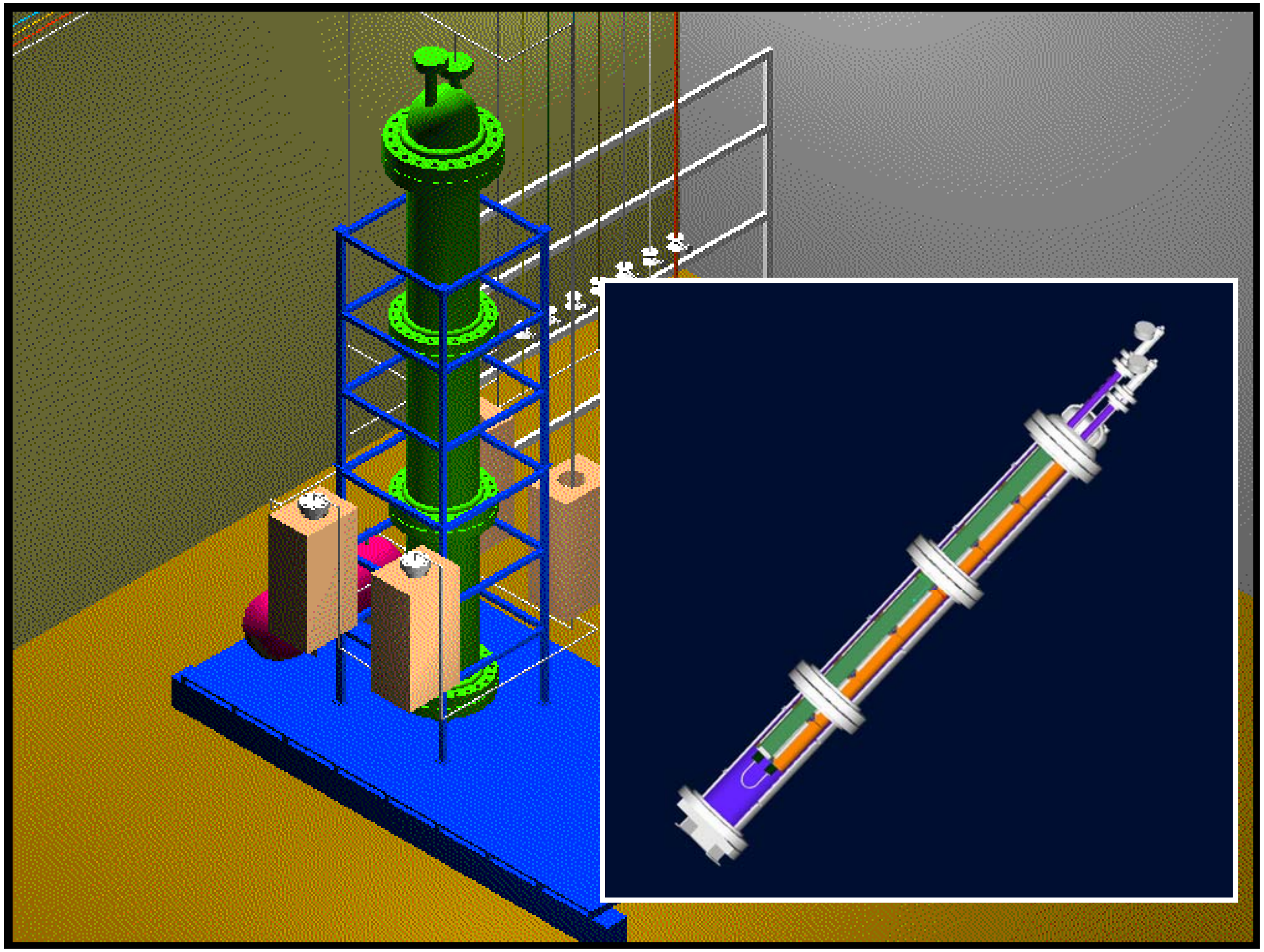
Liquid Fuels Storage

- Diesel Fuel
- Others if needed



FPRF Process Area

- Manifold Rack
- Carbon Desulfurizer
- Preheater (H-100)
- Hydro-Desulfurizer
    - Preheater (H-200)
- Zinc Oxide Bed
    - Preheater (H-300)
- Preheater (H-400)
- Reformer



FPRF Process Area Continued

- Hydrogen Separation Membrane
  - UOP CRADA
- Water Tank
- Preheater (H-500)
- Circulating Transport Reactor
- Support Equipment
- Waste Incinerator
- Prototype FP Test Bay