Integrated Ceramic Membrane System for H_2 Production

Cooperative Agreement: DE-FC36-00GO10534

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DOE Annual Merit Review Meeting
May 19, 2003

Praxair Hydrogen

- **Only U.S. Hydrogen Supplier in All Sizes (Cylinders to Liquid to Pipelines)**
  - First industry-financed liquid hydrogen facility (1959)
  - Six large LH_2 plants designed, constructed, and operated
  - Largest capacity single-train LH_2 production system (60 t/d)
  - Four LH_2 plants currently in operation
  - Smallest industrial SMR-based product line (HGS)
- **Over 500 Million SCFD Capacity**
- **Current Distribution Network:**
  - Over 600 GH_2 and LH_2 customers
  - 50 LH_2 trailers, 16 LH_2 rail cars
  - Over 250 miles of GH_2 pipeline
  - 150 GH_2 tube trailers
- **First PSA H_2 Unit (Over 300 Designed and Built)**

Outline - Integrated Ceramic Membrane System for H_2 Production

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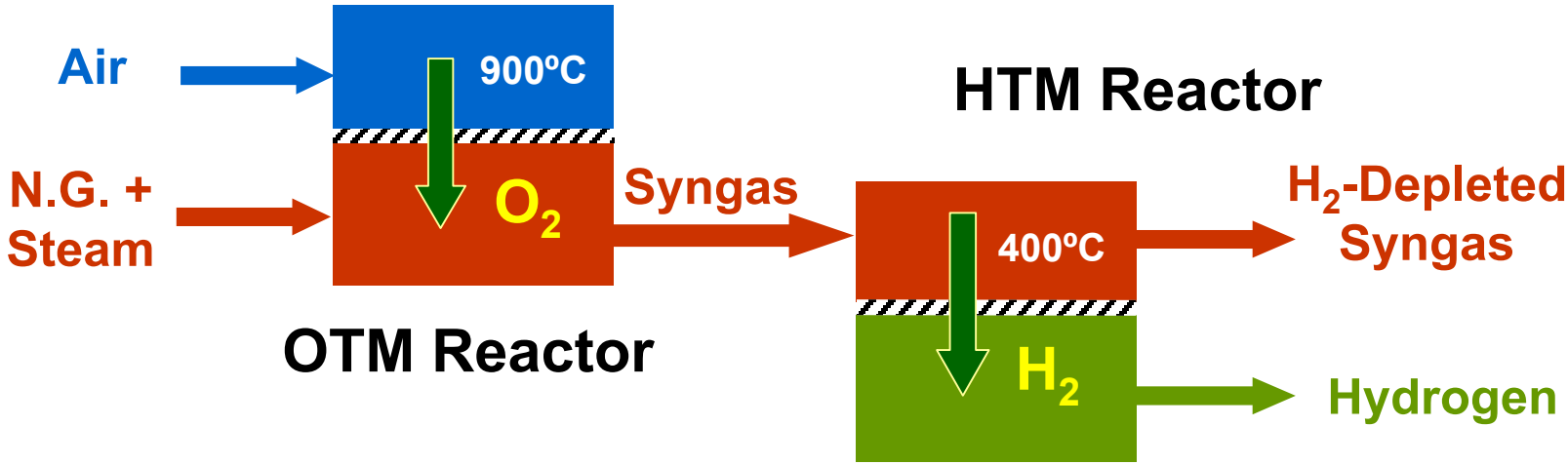
- Concept Review
- Team Structure
- Relevance and Objectives
- Approach
- Project Timeline
- Program Plan
- Accomplishments and Progress
- Responses to 2002 Questions

OTM/HTM Concept
Preferred Process - Sequential Reactors



OTM Reactor

Synthesis gas generation

$CH_4 + ½\ O_2 \rightarrow 2\ H_2 + CO$

$CH_4 + H_2O \rightarrow 3\ H_2 + CO$

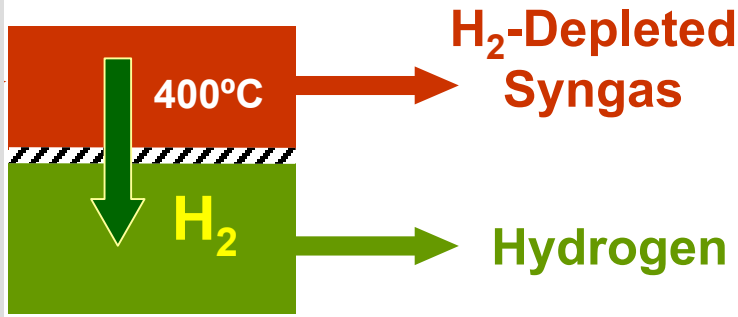
HTM Reactor

Water-gas shift reaction

$CO + H_2O \rightarrow H_2 + CO_2$

Hydrogen Separation

HTM Concept
Preferred Process - Sequential Reactors



HTM Reactor

- Water-gas shift reaction
  $CO + H_2O \rightarrow H_2 + CO_2$
- Hydrogen Separation

Team Structure

- **Praxair**
  - Overall Lead
  - Substrate Development
  - Process Economics
- **Research Triangle Institute**
  - Membrane Development
    - Palladium coating
  - Membrane Testing
- **Joint**
  - Membrane Production
    - Unique opportunity to integrate substrate and alloy development
    - Iterative process
  - Reactor Design

Relevance and Objectives

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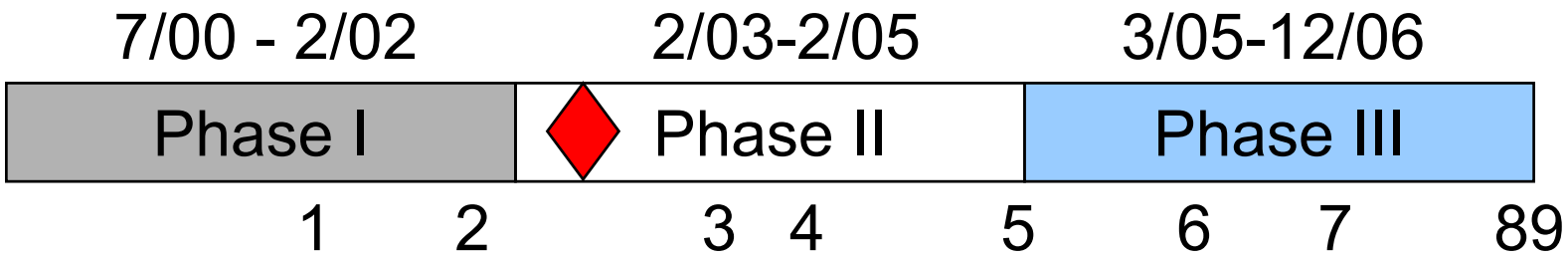
- **Relevance**
  - Low-Cost On-Site Hydrogen Production
    - Use existing natural gas infrastructure
    - Pd layer is thin - small component of overall cost
  - High Thermal Efficiency
  - Transportation & Industrial Markets
    - 1000 - 5000 scfh
  - Low-Cost Hydrogen Separation and Purification
- **Phase IIA Objectives**
  - Develop Cost-Effective Hydrogen Membrane
    - Supported Pd alloy
    - Syngas tolerance
    - Single-tube testing
  - Review Phase I Technoeconomic Study

Program Approach

- **Phase I**
  - Technoeconomic Feasibility Study
  - Define Development Program
- **Phase II**
  - A Develop and Test HTM Alloy and Substrate
  - B Integrate HTM and WGS in Single Tube Tests
- **Phase III**
  - Pilot Scale Demonstration
  - Define Mass Production Methods

Program Timeline



- **Phase I - Feasibility**
  - 1 Selected Two-Stage Process with Pd Membrane
  - 2 Assessed Economics Vs. Current Options
- **Phase II - Hydrogen Membrane Development**
  - 3 Select Alloy and Substrate
  - 4 Membrane Production and Testing
  - 5 Verify Reactor Performance and Update Process Economics
- **Phase III - System Design and Testing**
  - 6 Design (DFMA Focus) and Fabricate Multi-Tube Pilot Unit
  - 7 Operate Pilot Unit
  - 8 Verify System Performance and Update Process Economics
  - 9 Develop Commercial Offering

Phase IIA Plan

- **Select Substrate**
  - Strength, Thermal Expansion Match
  - Metal or Ceramic
- **Select Alloy**
  - Flux, Life, Cycling, Contaminant Resistance (S, CO, …)
- **Membrane Testing**
  - Confirm Performance in Simulated Syngas Environment
- **Process Economics**
  - Confirm Membrane is Cost-Effective
- **Phase IIB and Phase III Plan**

Phase IIA Tasks

- **Schedule**
  - Start: Kickoff Meeting February 2003
  - End: February 2004
- **Task 1 - Update Literature Review**
- **Task 2 - Substrate Development**
- **Task 3 - Membrane Development**
- **Task 4 - Membrane Tube Testing**
- **Task 5 - Process Economics**
- **Task 6 - Program Management**

Phase IIA Schedule

Task	Description	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan
1	Update Literature Review												
2	Substrate Development												
3	HTM Development												
4	Membrane Tubes												
5	Process Economics												
6	Program Management												

- Task 1 Complete
- Tasks 2, 3, and 4 Underway
- Task 5 Later

Phase I Review

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Defined Optimum Process

- Two-stage process with OTM followed by HTM
  - Pd membrane over ceramic proton conductor
  - Higher flux
  - Lower capital cost - smaller high T reactor
  - Higher energy efficiency
  - Shorter development time
  - Better reliability
  - Lower technical risk

Technoeconomic Analysis

- Low hydrogen cost gives this process the potential to be a preferred approach compared to other small-scale methods

Accomplishments and Progress

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- **Phase IIA**
  - Substrates Discovered with Suitable Thermal Expansion
    - Pd CTE = 11.9 ppm
    - CGO CTE = 12.5 ppm
    - YSZ CTE = 10 ppm
  - Alloys Identified
    - Pd-Cu, Pd-Ag, Pd-Au
  - Substrate Tubes Produced and Coated Starting in March
- **Progress**
  - Program is On Schedule
  - Membrane Fabrication and Testing Underway

Porous Tube Production

- **Tubes Made by Isostatic Pressing**
  - Isopressing Mold and Mandrel

Porous Tube Production

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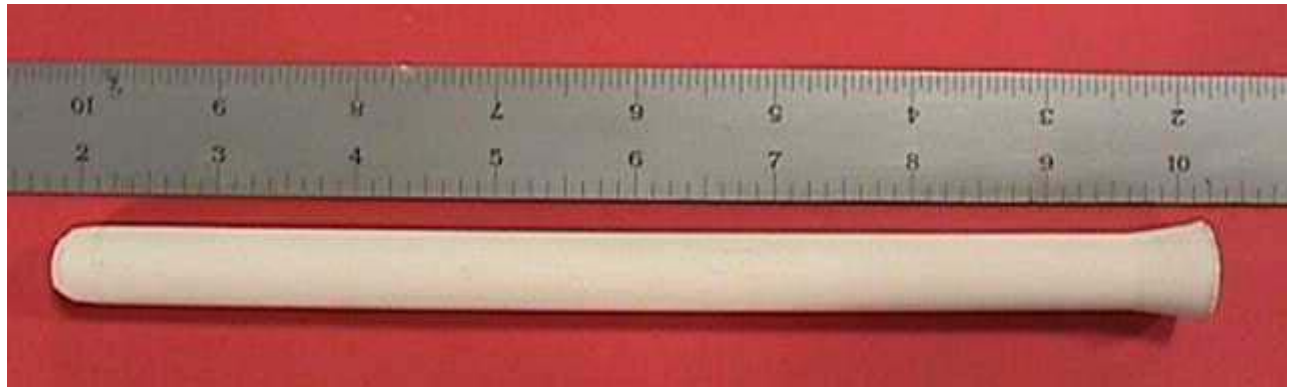
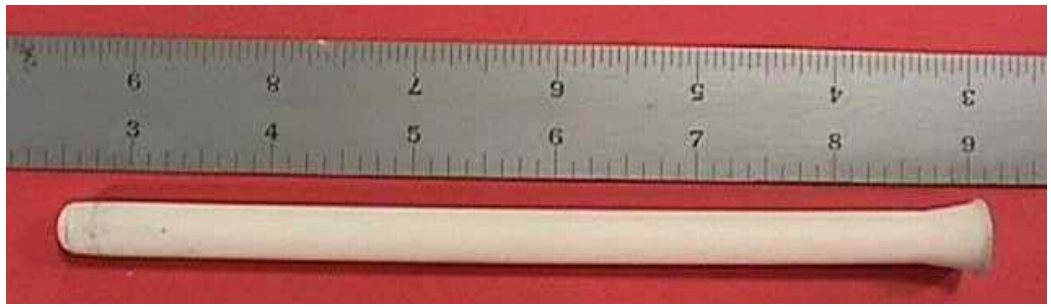
Green



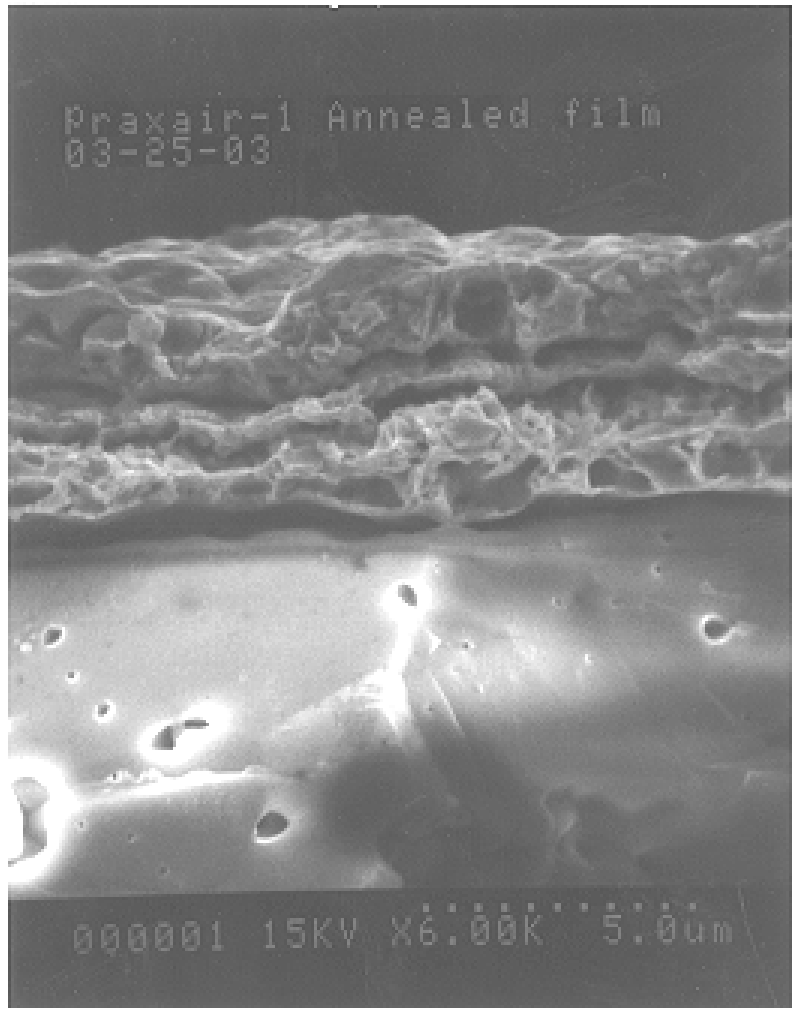
Sintered



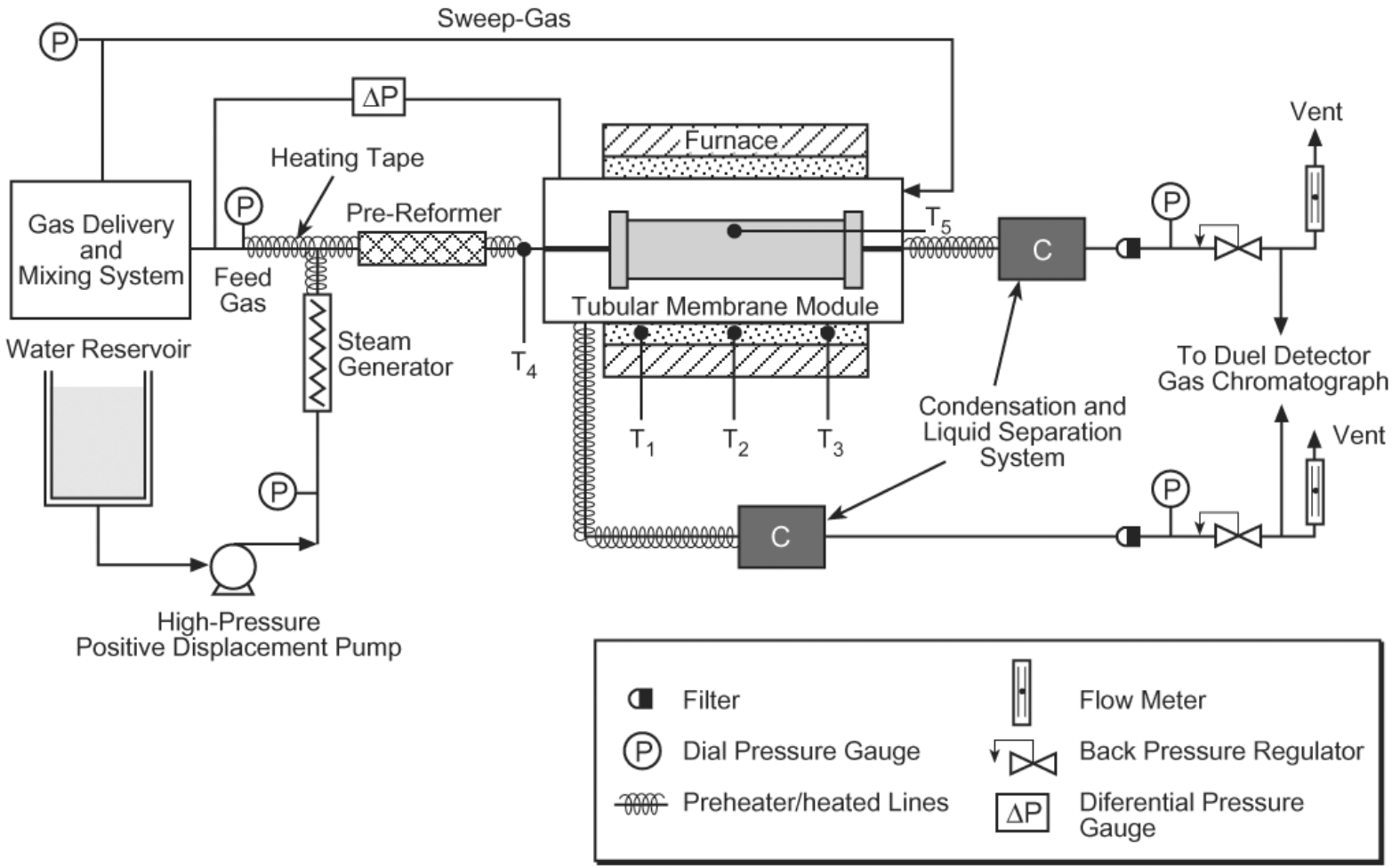
- Sintering causes shrinkage of about 20%

Tube Coating

- **Coated Tube**
  - Pd film is about 4 μm
  - Surface roughness led to holes in the film
  - Substrate needs to be smoother and more consistent
  - Pore size needs to be reduced



Test Apparatus



2002 Questions

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- **Panel's Main Concern was Lack of an Experimental Program**
  - Focus of Phase I was technoeconomic evaluation and process definition
  - Focus of Phase II is membrane development and experimental validation - Began in 2003
  - Information about experimental program presented
- **Communication and Cooperation with Others**
  - RTI is an essential team member
    - No contract in place last year - could not discuss
  - Results presented in upcoming DOE reports
  - Will present external paper(s) when we have test results

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Questions?

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