Autothermal Cyclic Reforming Based Hydrogen Generating & Dispensing System

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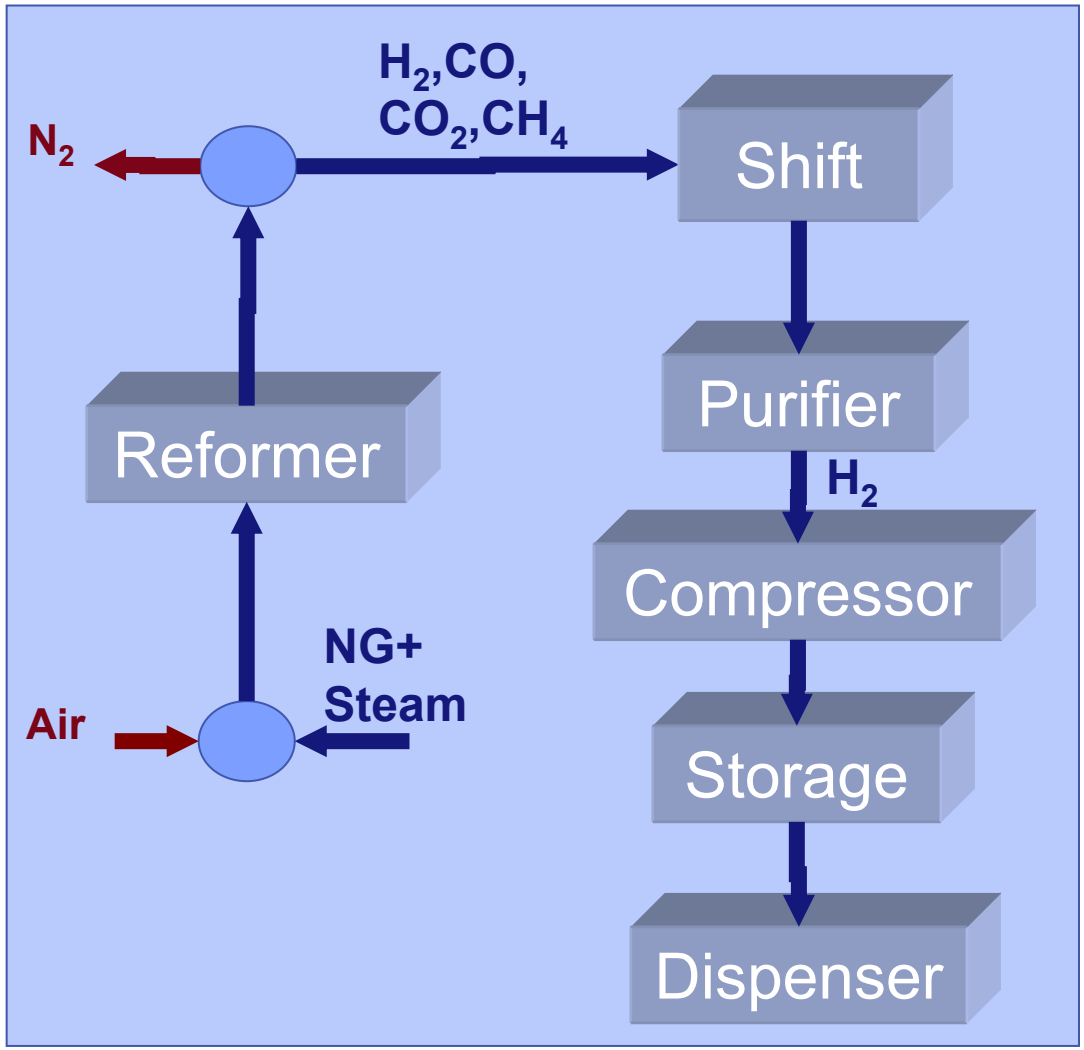

Project ID # PD3

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Overview

Timeline

- Start - Jan 2002
- Finish - Dec 2005
- 85% Complete

Budget

- Total project funding
  - DOE - $2,382K
  - Contractor - $1,812K
- Funding received in FY04
  - $650K
- Funding for FY05
  - $650K
- Funding reduced - Fabrication & operation of H2 compressor, storage & dispenser removed from scope

Barriers

- Barriers
  - > A. Fuel Processor Capital Costs
  - > B. Fuel Processor Manufacturing
  - > C. Operation & Maintenance
  - > E. CO_2 Emissions
  - > F. Control & Safety
  - > L. Durability
  - > M. Impurities
- Targets - production & dispensing

	2003	2005	2010
Efficiency (LHV)	65	65	75

Partners

- Praxair - Purifier
- University of California at Irvine – Host Site

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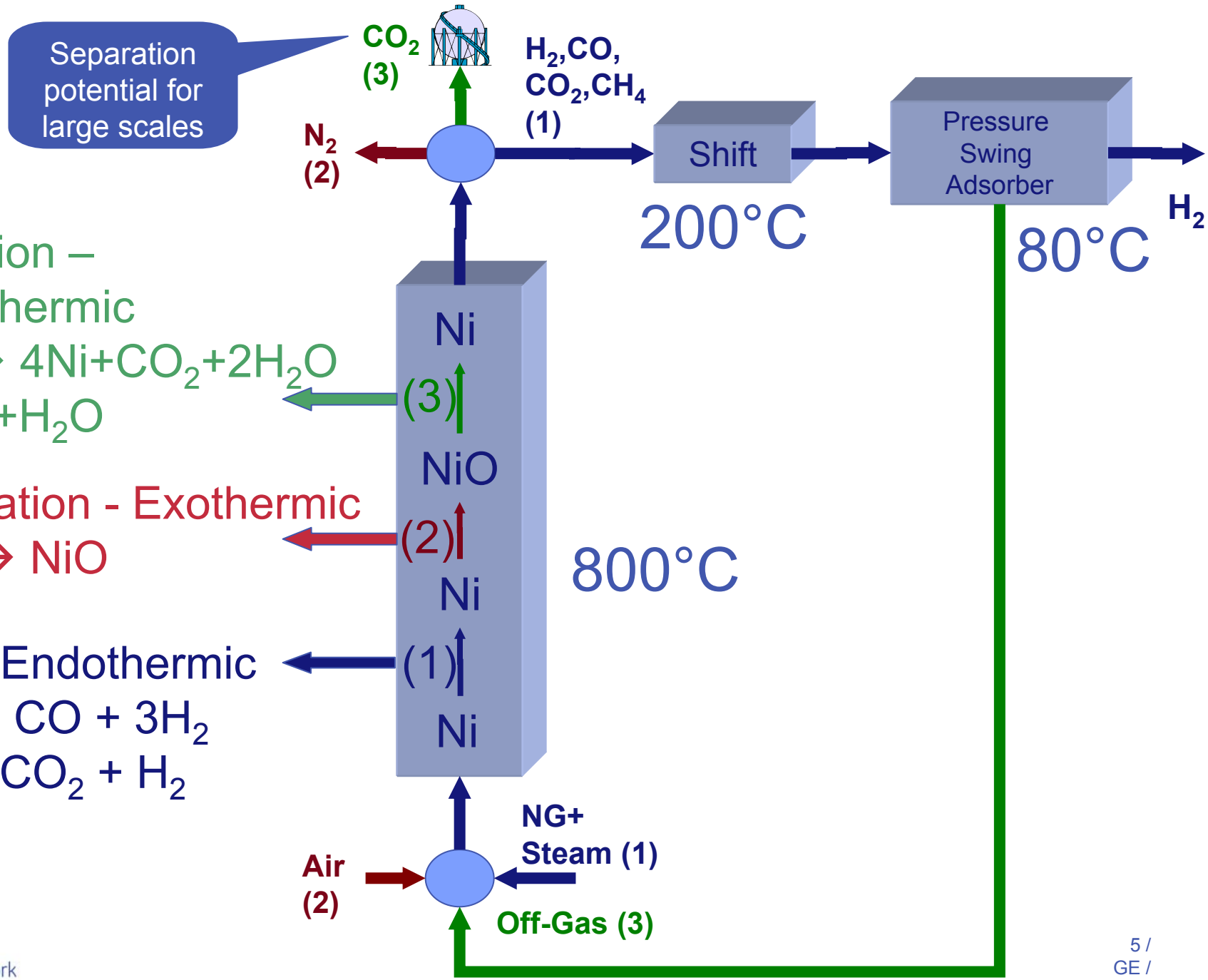
Objectives

Overall	• Design a generating & refueling system that can meet the DOE cost target of <$3.00/gge • Fabricate and operate an integrated 60 kg of H_2/day generating system
2004	• High-pressure reformer & pressure swing adsorber (PSA) – Design – Fabrication & Installation • Compression, storage & dispensing system – Design
2005	• Permitting • High-pressure reformer & PSA – Integration & Operation • Update economic analysis

Technical Approach

Reformer	• Minimize capital cost • Design for 1000s of cold start cycles • Modeling of advanced control systems for stabilizing temperature and flows • Catalyst durability – thermal/RedOx cycles • Increase methane conversion
Shift	• Increase CO conversion
Pressure Swing Adsorber	• Impurities – CO, Sulfur • >75% recovery of Hydrogen
Safety & Permitting	• Gas Sensors – Lower Explosive Limit (LEL) • Seismic zone 4 classifications • Class I Div II explosion proof electrical

Autothermal Cyclic Reforming Process



Fuel Reduction – Mildly Endothermic

$4NiO+CH_4 \rightarrow 4Ni+CO_2+2H_2O$

$NiO+H_2 \rightarrow Ni+H_2O$

Air Regeneration - Exothermic

$Ni + 1/2\ O_2 \rightarrow NiO$

Reforming - Endothermic

$CH_4+H_2O \rightarrow CO + 3H_2$

$CO+H_2O \rightarrow CO_2 + H_2$

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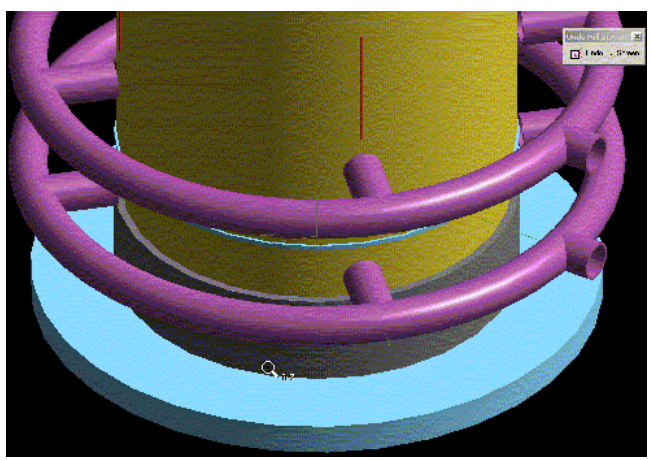
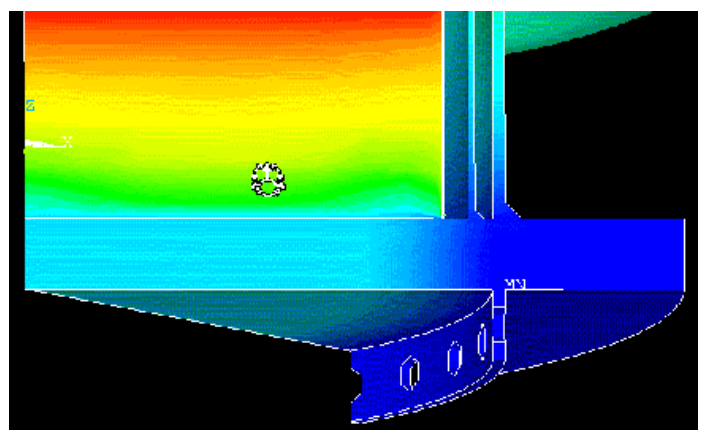
High Pressure ACR Reactor Design Meets the Performance Targets

CTQ	Targets	Current Status (modeling)
ASME: Outer shell temperature	< 400°C	~ 300°C
Cold start cycles to failure	> 1,000	12,984
Reforming cycles	> 2E+6	5.8E+7
CH_4 slip	< 10%	< 5%
Heat loss from the reactor	< 5 kW	3.4 kW

3D Modeling
- Thermal
- Mechanical Stresses
- Reactions

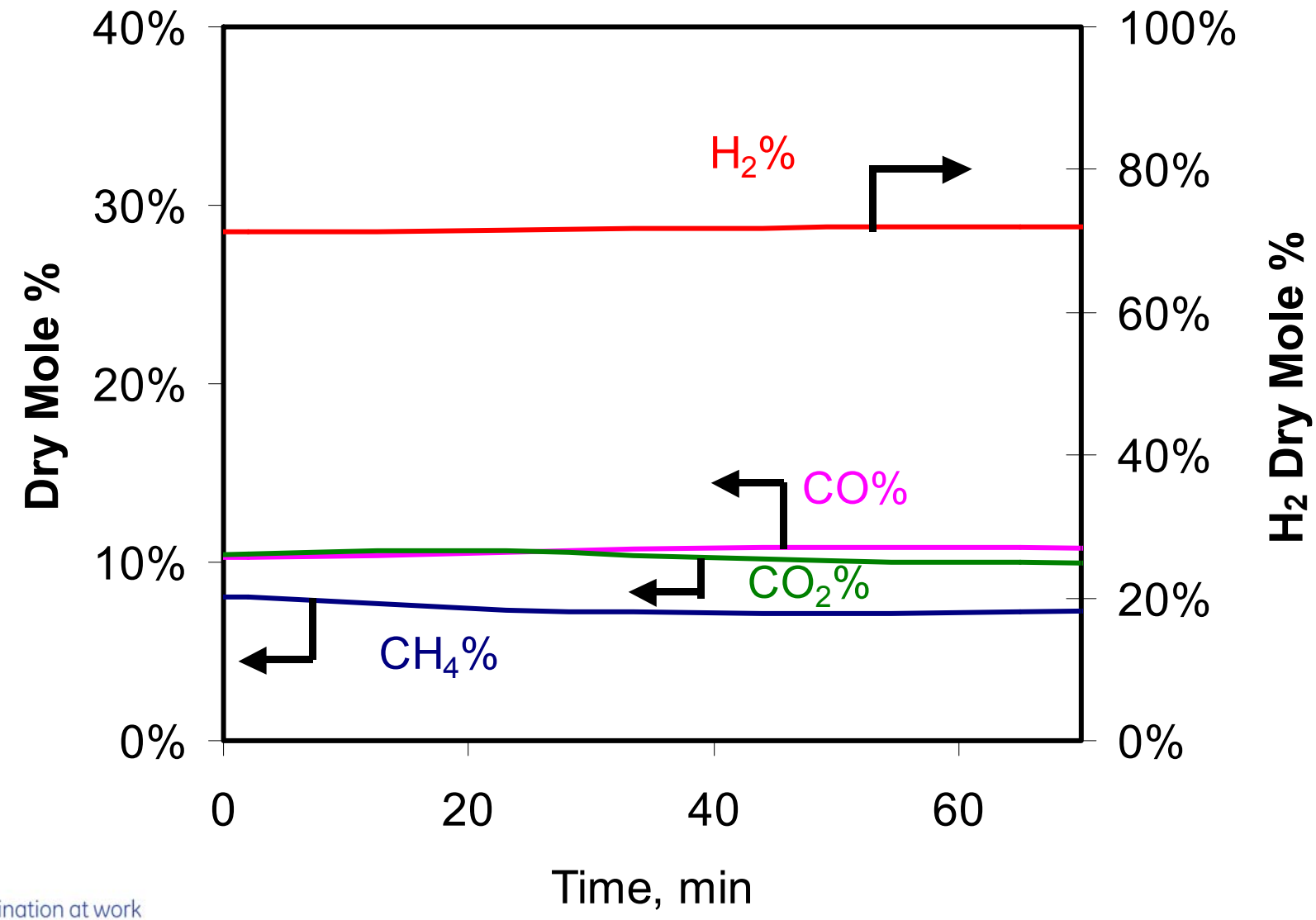




Rigorous QA on welds – Visual, X-Ray, Ultrasonic Inspection

Developed Dynamic Cascade Control Algorithms for Stabilizing the Process

Model Results at High Pressure



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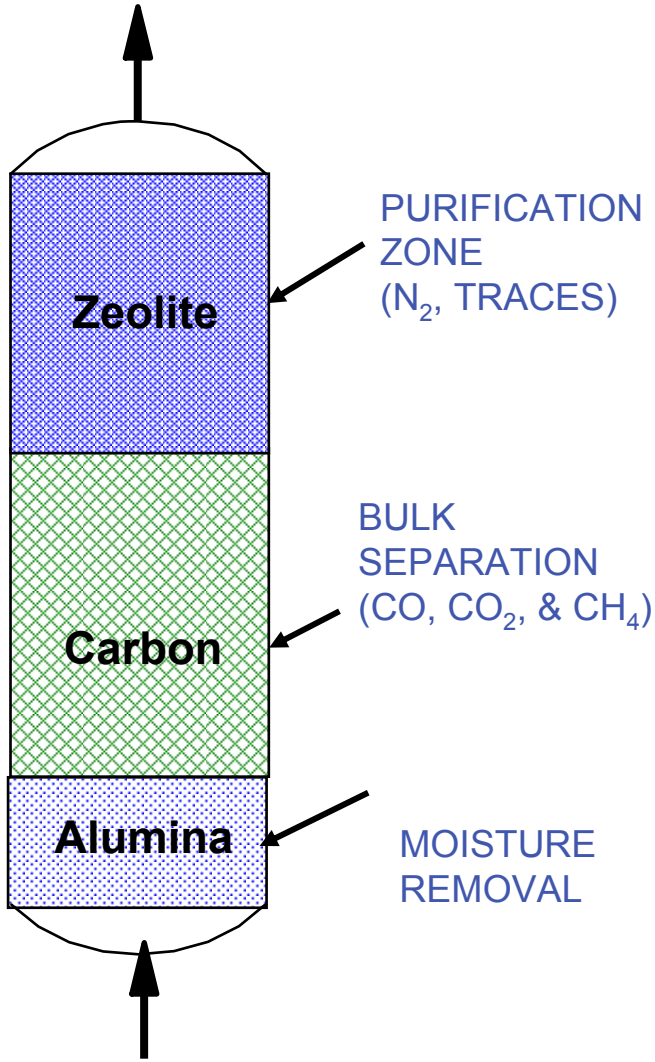
Pressure Swing Adsorber

Product Species	DOE Targets	Current Status	Projected
H_2	> 98%	99.99%	> 99.99%
CO	< 1 ppm	< 5 ppm	< 1 ppm
CO_2	< 100 ppm	< 10 ppm	< 5 ppm
Sulfur	< 10 ppb	< 50 ppb	< 10 ppb
Ammonia	< 1 ppm	< 10 ppm	< 1 ppm
Hydro-carbons	< 100 ppm	< 10 ppm	< 10 ppm
O_2, N_2 & Ar	< 2%	~ 100 ppm	~ 100 ppm



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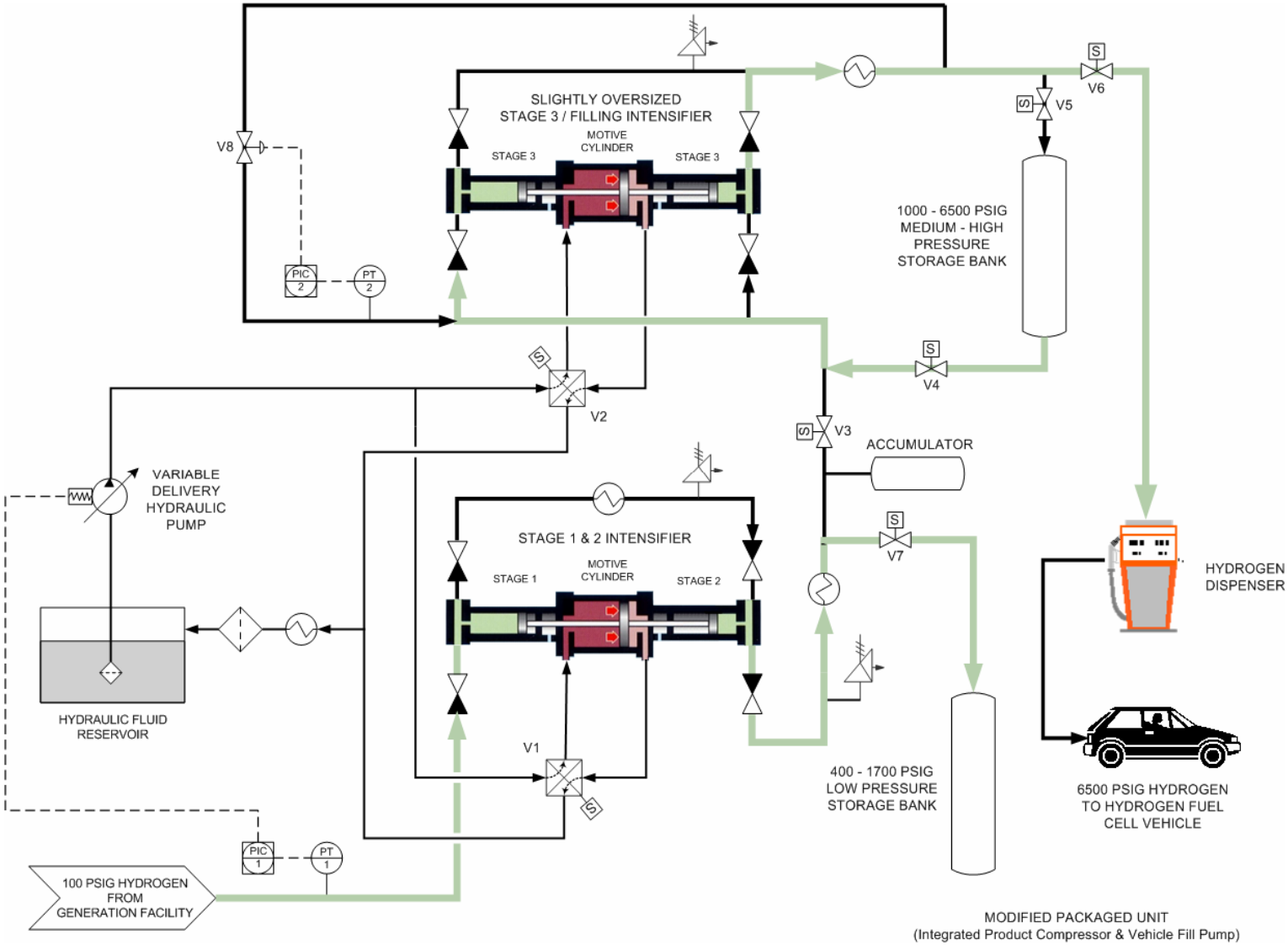
Reformer and PSA - Fabrication Status

- Next generation high pressure reformer and H_2 purifier fabricated and installed at University of California at Irvine
- Upgraded to ASME stamped pressure vessels & class I div II electrical

H_2 Compression & Dispensing System

- Design completed -Praxair



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Hydrogen Compressor Skid Design

Ventilation system prevents the accumulation of H_2

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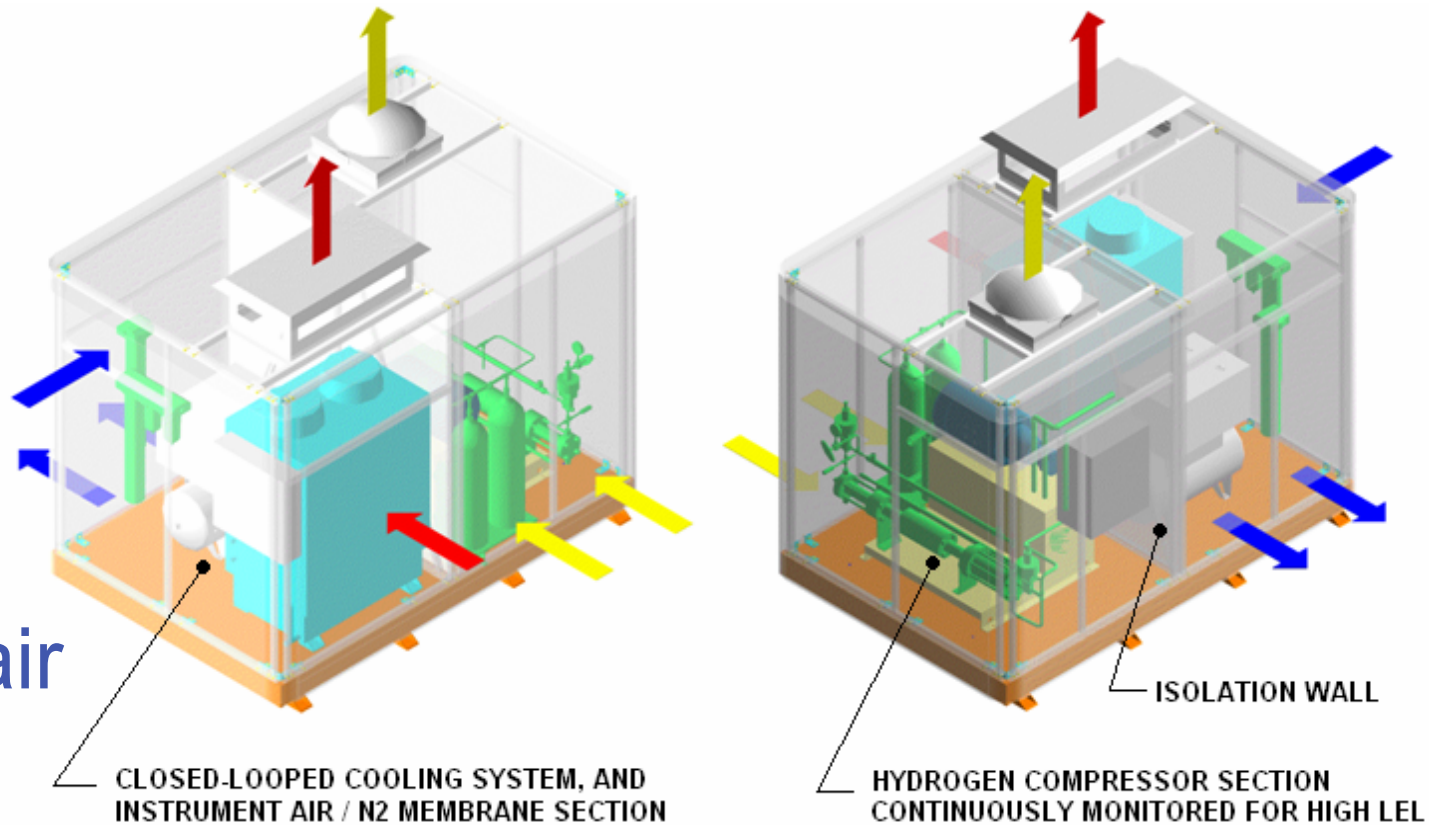


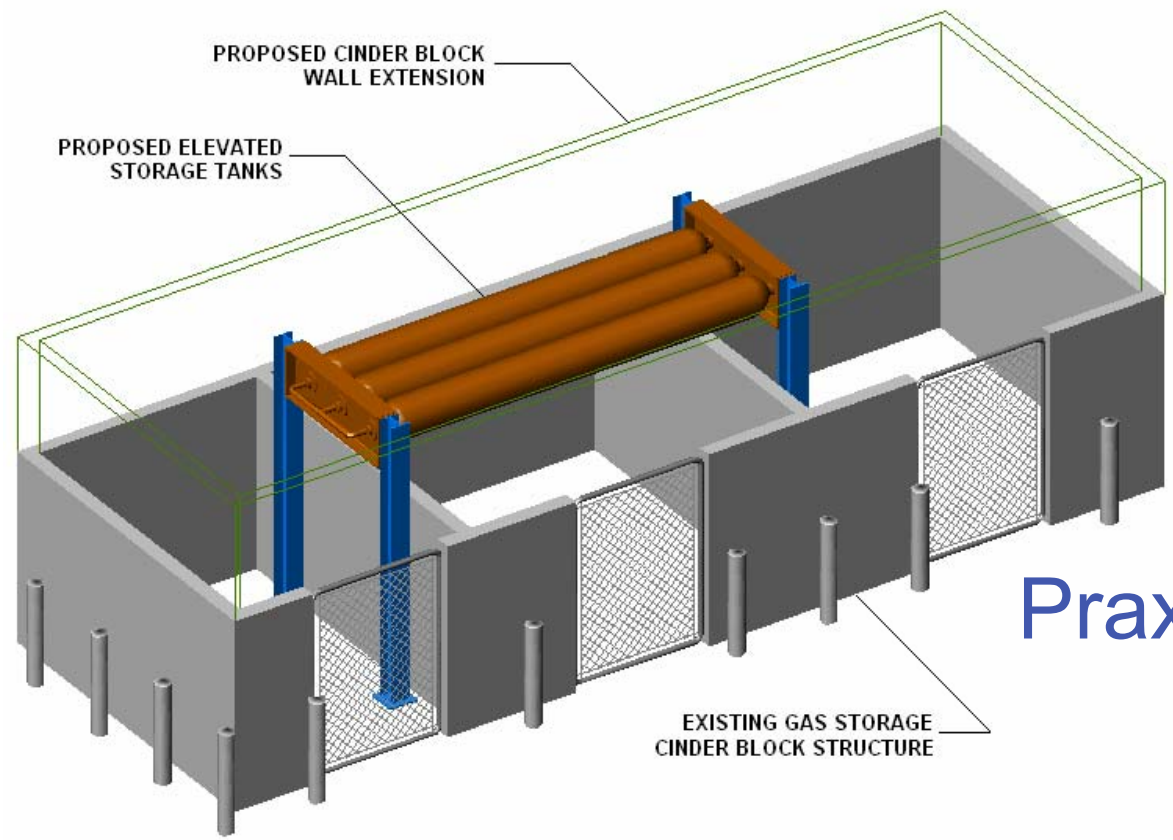
VENTILATION FAN DRAWS AIR OUT OF ENCLOSURE SECTION, RESULTING IN NEGATIVE PRESSURE

VENTILATION FAN DRAWS AIR INTO ENCLOSURE SECTION, RESULTING IN POSITIVE PRESSURE

CLOSED-LOOPED COOLER FANS DRAW AIR INTO UNIT AND OUT OF ENCLOSURE (AIR FLOW DOES NOT CONTRIBUTE TO ENCLOSURE VENTILATION)

Hydrogen Storage – Elevated Design Strategy

- Leaks will quickly rise and dissipate.
- Out of the line of sight
- Design completed



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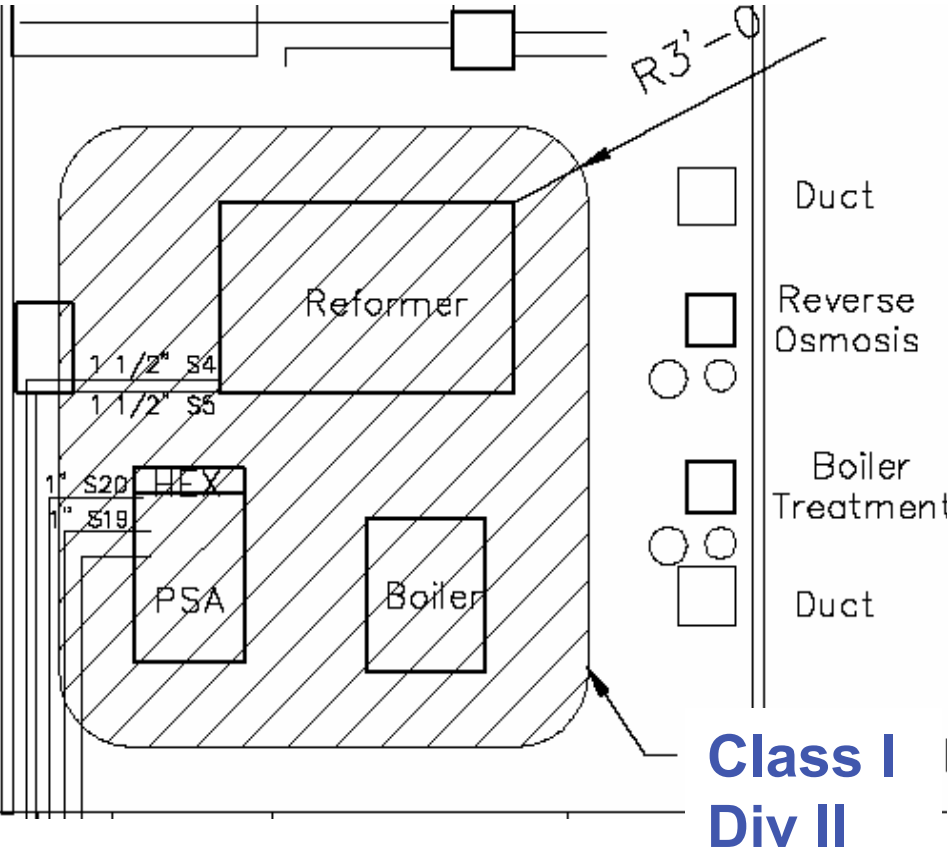
Discussed Area Classification w/ Fire Marshal Only 3' around reformer & PSA is Class I Div II



Safety Case Studies

- Rupture of all vessels and room blower is off
  - > Will reach 10% of Lower Flammability Limit (LFL)
- Sensors shut down system, if
  - > 20% LFL is reached
  - > Room blower is off

Permitting

- Fire Marshal
  - > Hired 4 professional engineers certified by State of California – mechanical, electrical, structural, chemical
  - > Best practices from National Fire Protection Agency (NPFA) 50A, 52 & 497
  - > 99% complete
- Campus Architect (Completed)
- South Coast Air Quality Management District (Completed)

Responses to Previous Year Reviewer's Comments

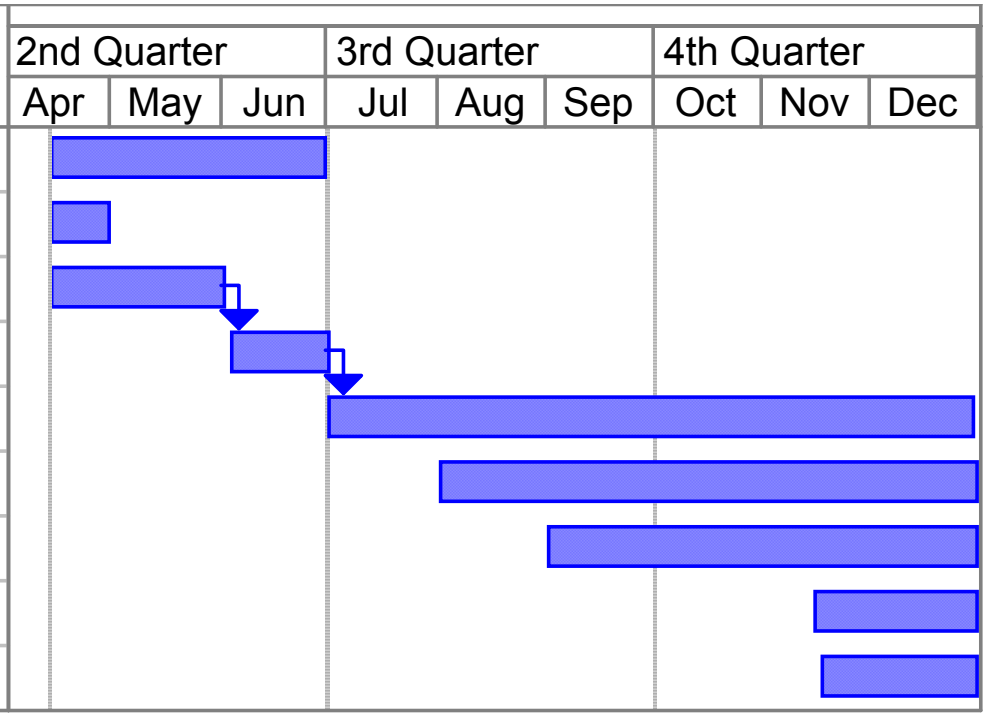
- High pressure reforming vs. low pressure reforming with compression decision
  - Compressing natural gas vs. compressing syngas is more efficient and more cost effective
- Current lifetime of catalyst is 3 months
  - Designed reactor to replace catalyst in a day
- Performance goal and detailed operation plan needs to be worked out
  - Developed advanced controls and tested them in the process model
  - Low pressure reformer was stable for extended periods of time during experimental runs

Technical Approach for 2005

Safety	• HAZOP – UCI, Praxair & GE • Independent peer review
Reformer process control	• Cascade dynamic control algorithm being optimized in a model • Monitor temperature, pressure & flows • Methane conversion
Reformer catalyst durability	• Thermal cycles • Reduction/Oxidation cycles
H_2 impurities	• CO & Sulfur
System Optimization	• Load changes – 20 to 60 kg/day • Optimize efficiency • Optimize startup times

Remaining Project Tasks - Completion by Dec 2005

ID	Task Name
1	Optimize dynamic process control model
2	Fire marshal approval
3	Fabrication - electrical/structural
4	Shakedown
5	Operation of reformer+shift
6	Integration & operation of PSA
7	System optimization
8	Update cost models
9	Final report



Supplemental Slides

Publications and Presentations

- Patent # 6,878,362 - Issued to GE
- Patent # 6,792,981 - Issued to Praxair
- World Hydrogen Energy Conference, Yokohama, Japan - June 27th – July 2nd 2004

Hydrogen Safety

- H_2, CO and natural gas leaks – electrical spark
- Pressure vessel rupture
- Piping rupture
- Earthquakes
- Structural failures
- Over-pressurization or high temperatures

Hydrogen Safety

H_2, CO and natural gas leaks	• Class I Div II electrical • Intrinsically safe electrical barriers • Lower explosive limit (LEL) sensors • CO sensors • Emergency egress lights • Alarm to 24 hr monitoring station • Electrical shunt trips
Pressure vessel rupture	• ASME stamped vessels • Design structural supports to seismic zone 4 specifications
Piping rupture	• ANSI B31.3 codes
Over-pressurization or high temperatures	• Pressure and temperature switches

Ackowledgements

- Department of Energy
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- California Air Resources Board
  - Steve Church