

# **Integrated Short Contact Time Hydrogen Generator (SCPO)**

**2006 DOE Project Review Meeting**

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**University of Minnesota**

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imagination at work

**Project ID # PD3**

# Overview

## Timeline

Project start date: 05/30/2005  
Project end date: 05/30/2008  
Percent complete: 38%

## Budget

Total project funding

A DOE share: \$2.6M

A Contractor share: \$1.4M

Funding received in FY05: \$490K

Funding for FY06: \$400K

## Barriers

- Technical Barriers Addressed:
  - A. Cost of Fuel Processor
  - C. Operation and Maintenance (O&M)
  - D. Feedstock Issues
  - E. Catalyst sulfur tolerance & durability
- Technical Targets (2010):
  - Total Energy Efficiency (%LHV) > 75%
  - Total H<sub>2</sub> Cost < \$3.00/gge H<sub>2</sub>

## Partners

- University of Minnesota
- Argonne National Lab



# SCPO Project Objectives & Highlights

## Project Team

### **GE Global Research**

- System & Economic Analysis
- Catalyst Dev. & High P Valid.
- Prototype Reactor Design
- Overall Project Management

### **University of Minnesota**

- CPO Catalyst Discovery
- Parametric Testing & Modeling
- Catalyst Characterization

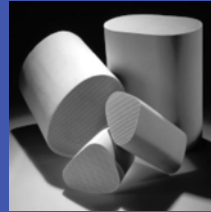
### **Argonne National Laboratory**

- SMR Catalyst Discovery
- Catalyst Durability
- Catalyst Characterization

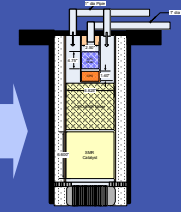
**Project Objective: To Develop a Compact Hydrogen Generator that can Deliver H<sub>2</sub> at a Cost of <\$3.00/kg**



Lab Screen



Prototype Scale



Pilot

## Technical Approach

- Develop Robust Short Contact Time Catalysts
- Develop & Design Comp. CPO, SMR, WGS & HE
- Demonstrate Critical Components

## Anticipated Benefits

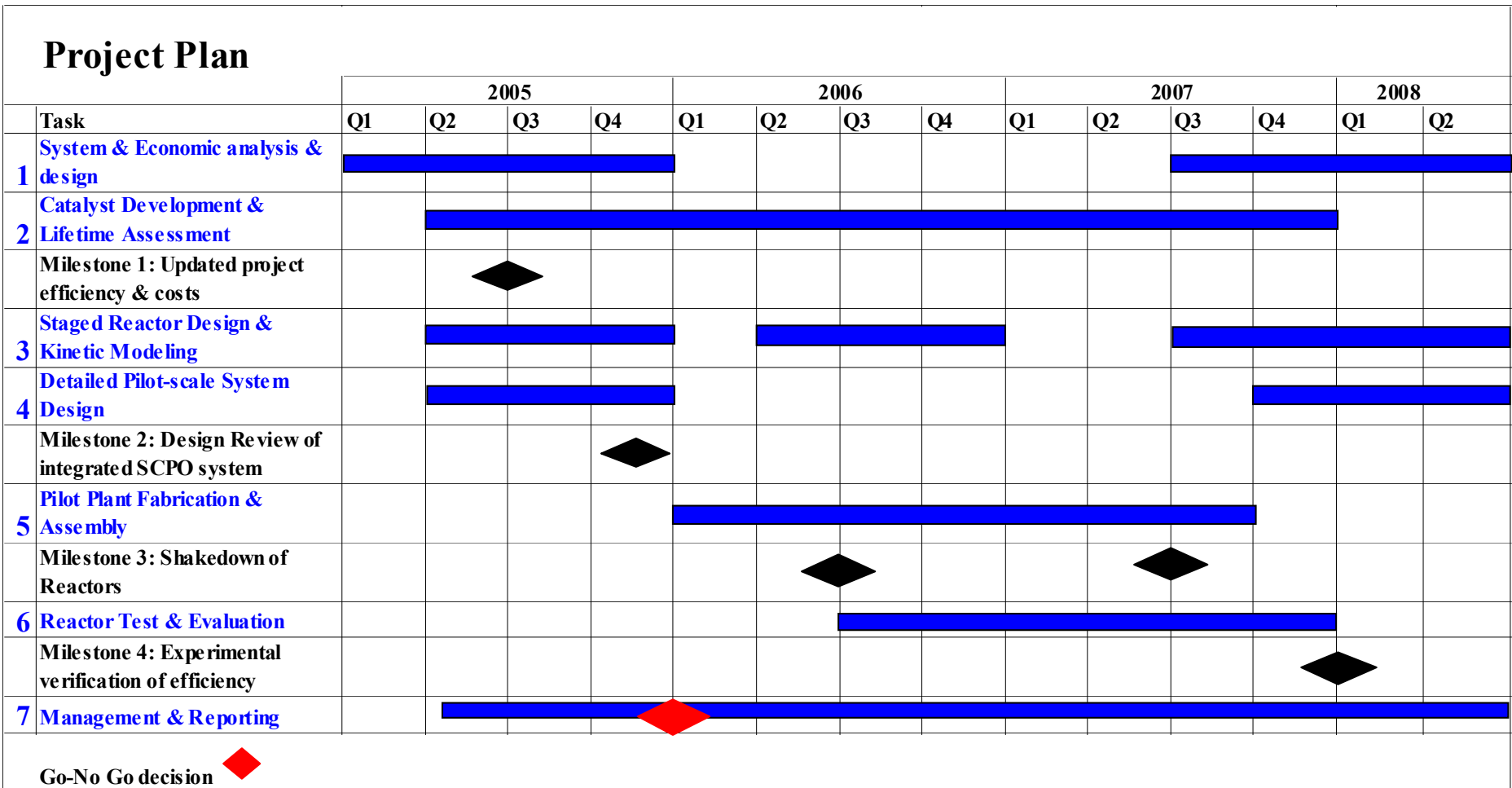
- Compact, Low Cost, H<sub>2</sub> Generation Technology
- Applications in Refueling Stations, NGCC NO<sub>x</sub> Reduction & CO<sub>2</sub> Capture

## Deliverables

- Short Contact Time Catalysts
- Demonstration of Critical Technology & Components
- Reactor & Process Model for Scale-up

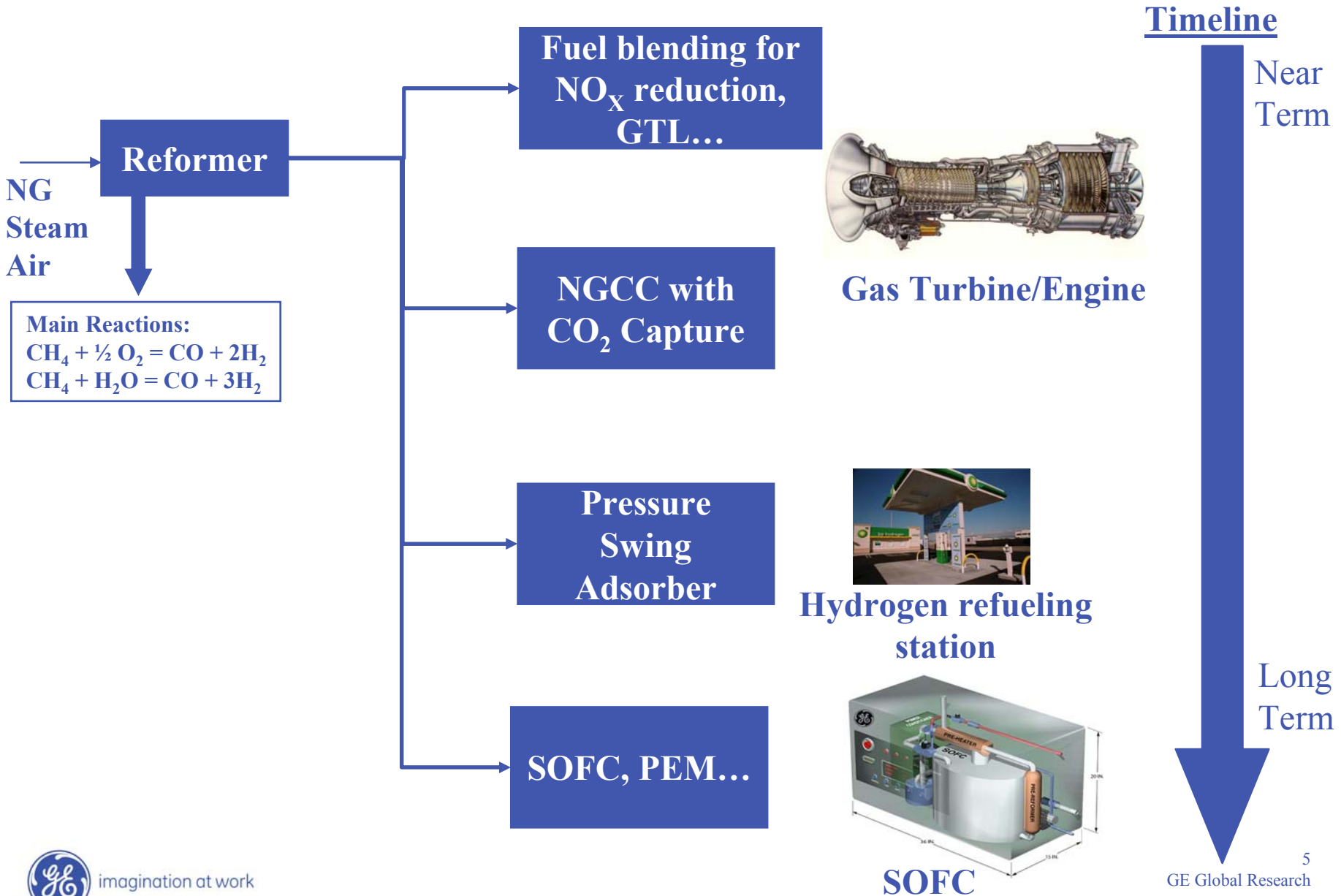
- DOE award announced in November 2004
- Initiated in January 2005

# Overall Project Plan



YE '05 Go/No Go

# Reforming & Potential Applications

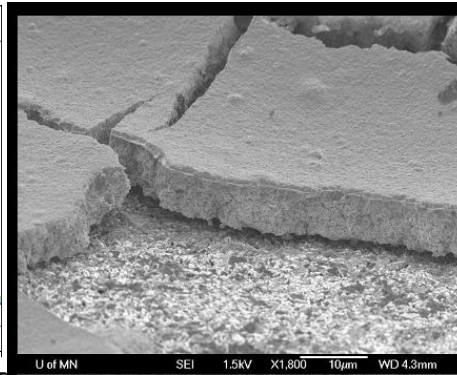
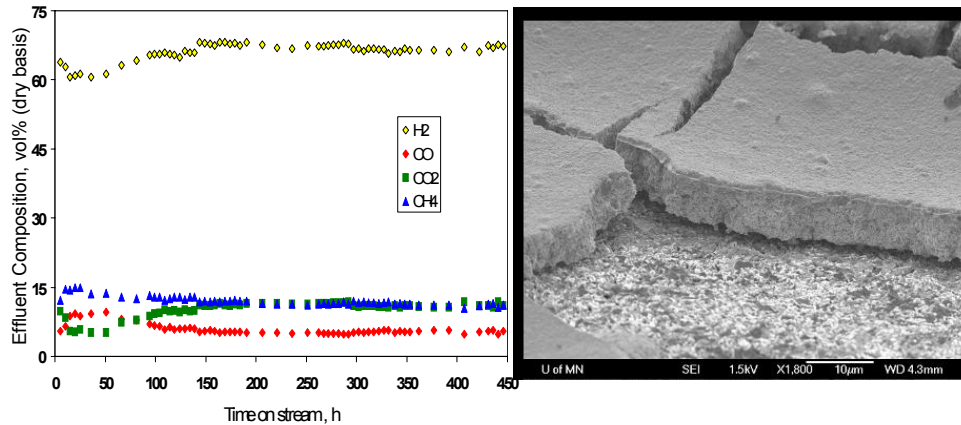


# Approach: Leverage Partners' Facilities & Knowledge Base

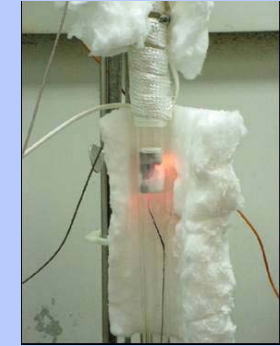
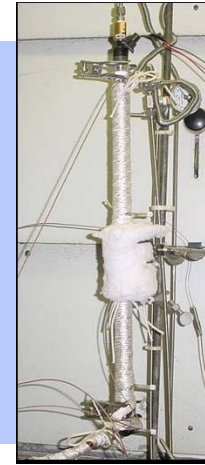
## Integrated Activities

- GE design the overall system & define system conditions
- ANL & U of Mn have created catalysts and tested them at conditions GE identified
- U of Mn: New CPO catalyst & kinetics model
- ANL: New SMR catalyst & long term stability of catalysts
- Goal: Increase GHSV & S tolerance to lower capital cost.

## Example Data



## U of Mn Invented the CPO



## ANL Has the State-of-Art Cat Testing Facilities



# Argonne National Laboratory – Activities and Objectives

Evaluate the performance and durability of the “best available” CPO, SMR, and WGS catalysts from commercial catalyst manufacturers

## A Test matrix

- *CPO ( 2 vendors, 5 different formulations)*
- *SMR ( 2 vendors, 3 different formulations)*
- *WGS ( 1 vendor, formulation selection not finalized)*

## A Objectives

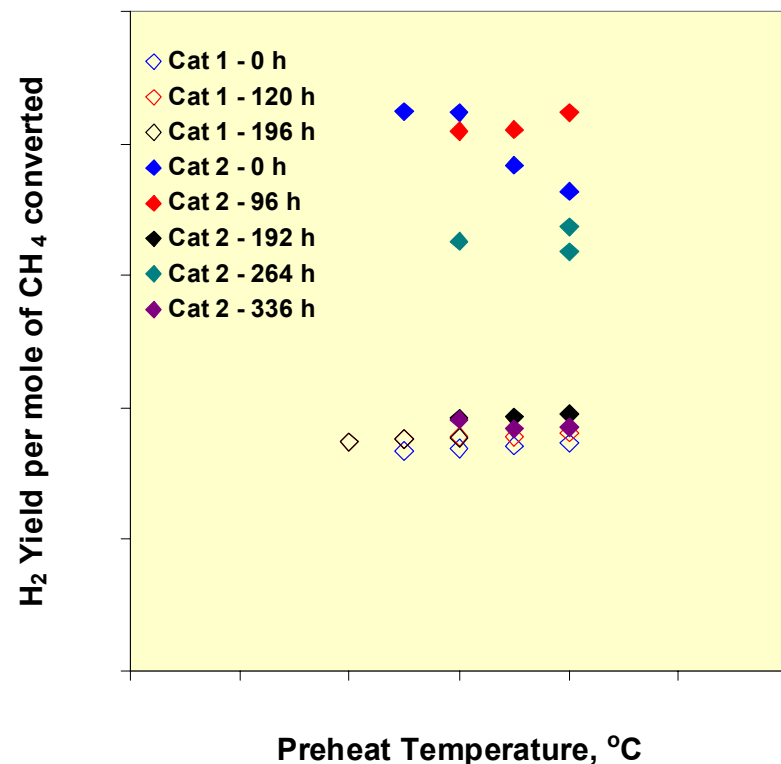
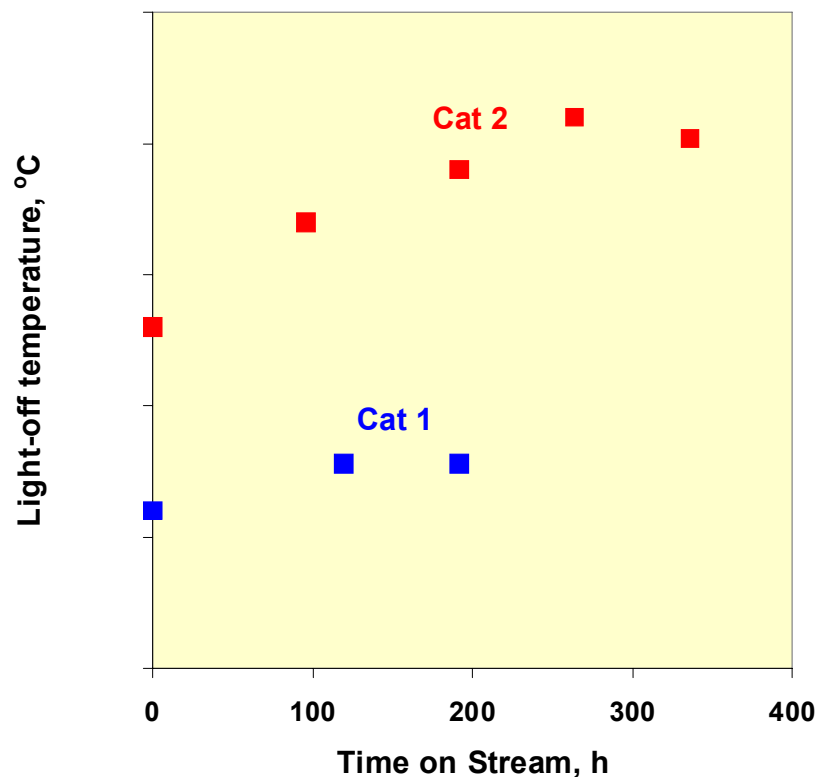
- *Measure conversion and selectivity as a function of operating parameters ( $O_2:C$  and  $H_2O:C$  ratios, temperature, GHSV, sulfur content)*
- *Determine sulfur tolerance and durability*
- *Determine failure modes/deactivation mechanisms (if applicable)*

Argonne steam methane reforming (SMR) catalyst development

## A Improved activity and stability under demanding SMR conditions

- *low  $CH_4$  and high  $H_2$ ,  $CO$ , and  $CO_2$  concentrations*
- *short contact time*

# Results: Evaluating the durability of CPO catalysts



**Cat 2 initially displayed higher activity than Cat 1; however after about 200 h on stream the activities were comparable**



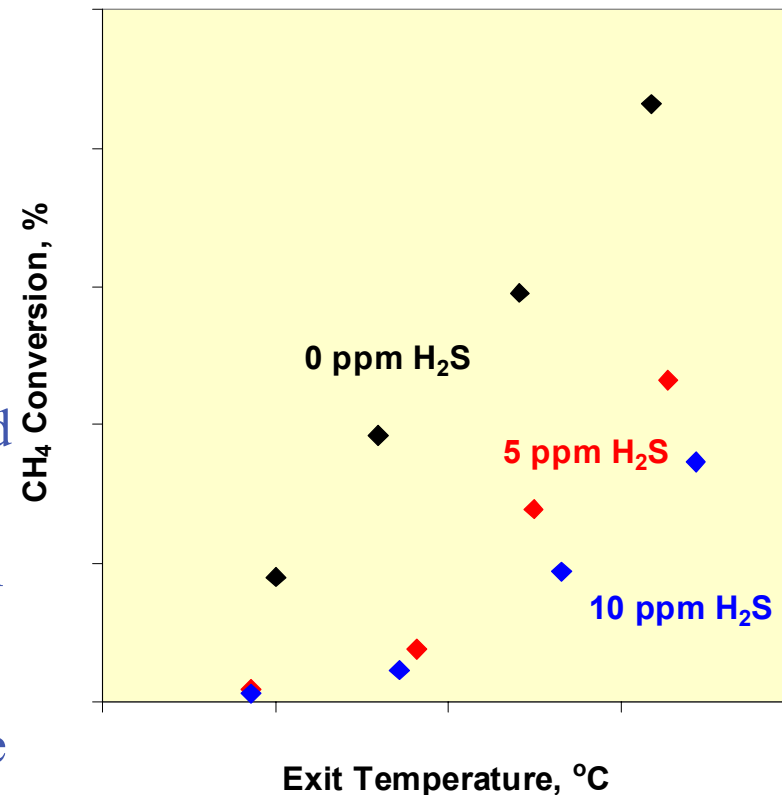
# Results: Evaluating the sulfur-tolerance of commercial SMR catalysts

Sulfur tolerance of SMR catalyst may be more critical than that of CPO catalyst

Sulfur poisoning of SMR catalysts

- A rapid decrease in activity when exposed to a few ppm of H<sub>2</sub>S
- A activity stabilizes after initial decrease with only a very slight decrease in activity observed over next 8-24 h
- A essentially complete recovery of activity when H<sub>2</sub>S is removed

Long-term effect of sulfur on catalyst performance and stability is unknown and being investigated



# Results: Argonne SMR catalysts

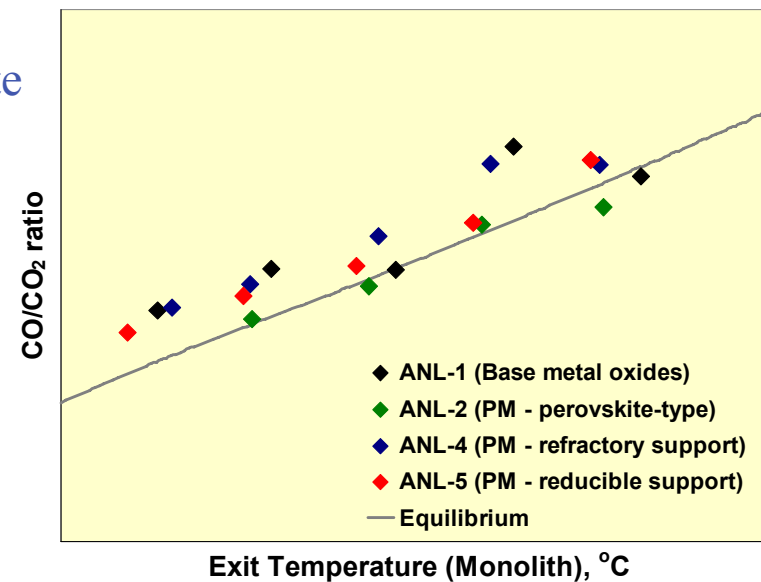
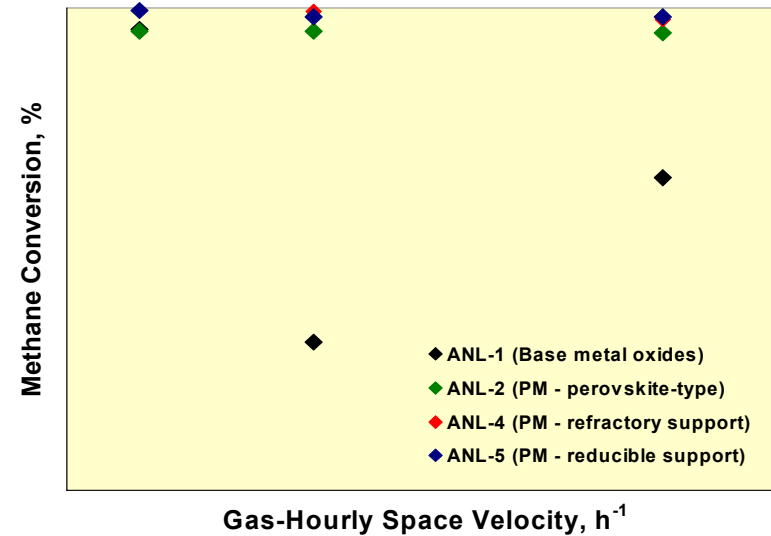
Six different formulations are being evaluated

- A Base metal mixed oxide (ANL-1)
- A Precious metal perovskite-type oxide (ANL-2)
- A Precious metal-modified hexaaluminate (ANL-3)
- A Oxide-supported precious metals (ANL-4, -5, -6)

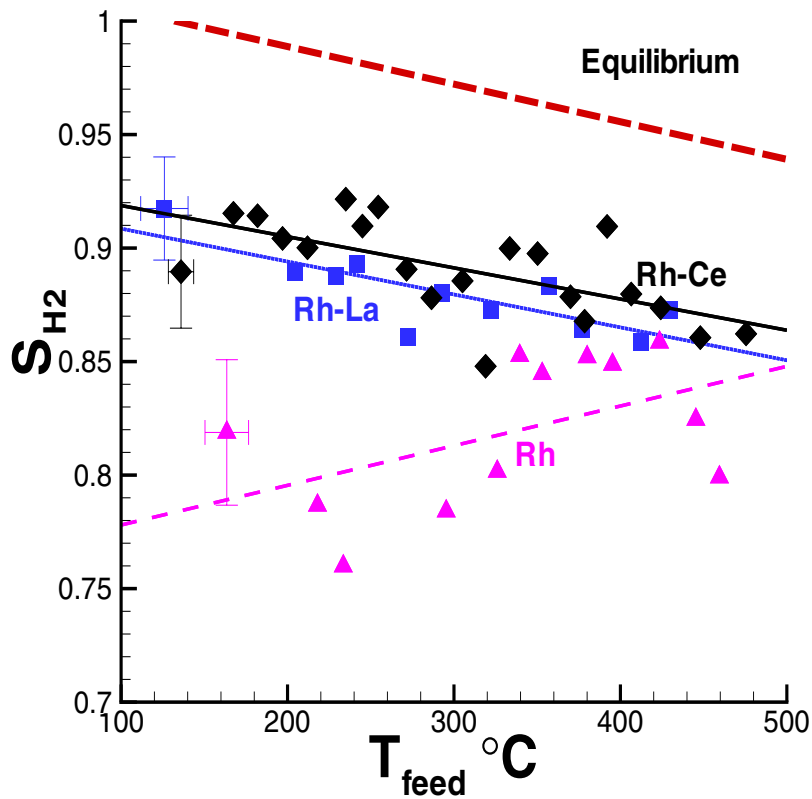
Base metal oxide (ANL-1) - less active and temperature cycling accelerates loss in activity.

PM perovskite-type oxide (ANL-2) and PM hexaaluminate catalysts (ANL-3) - good activity but stability is questionable, especially for the perovskite.

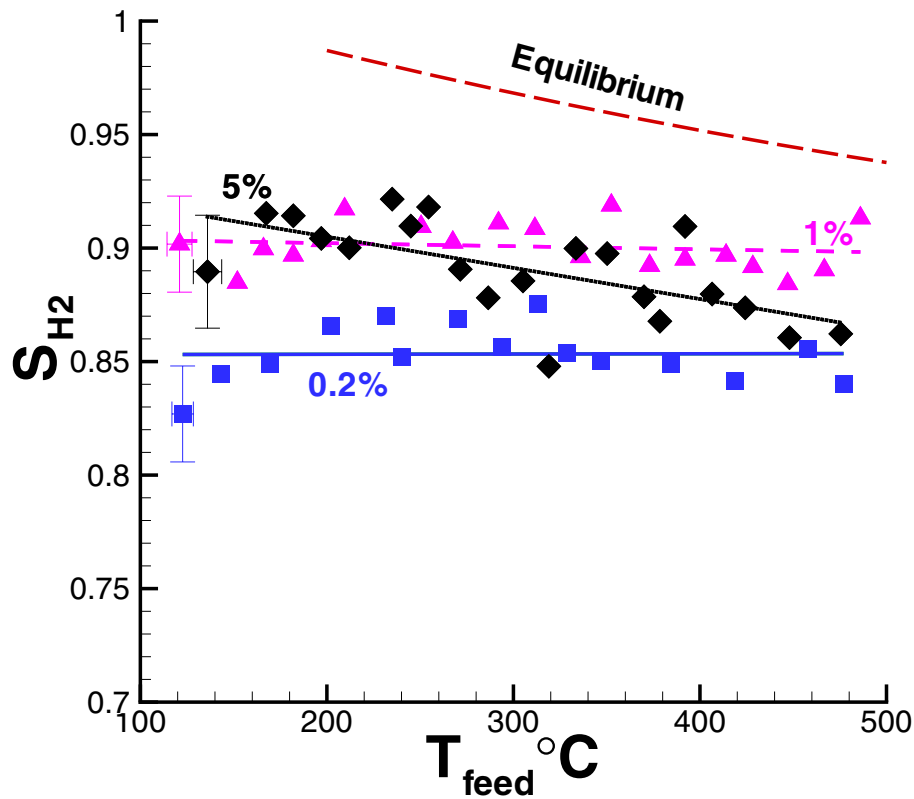
Oxide-supported PM catalysts (ANL-4, -5, -6) – good activity and good temperature cycling stability.



# Results: Investigation of Catalyst system and catalyst loading

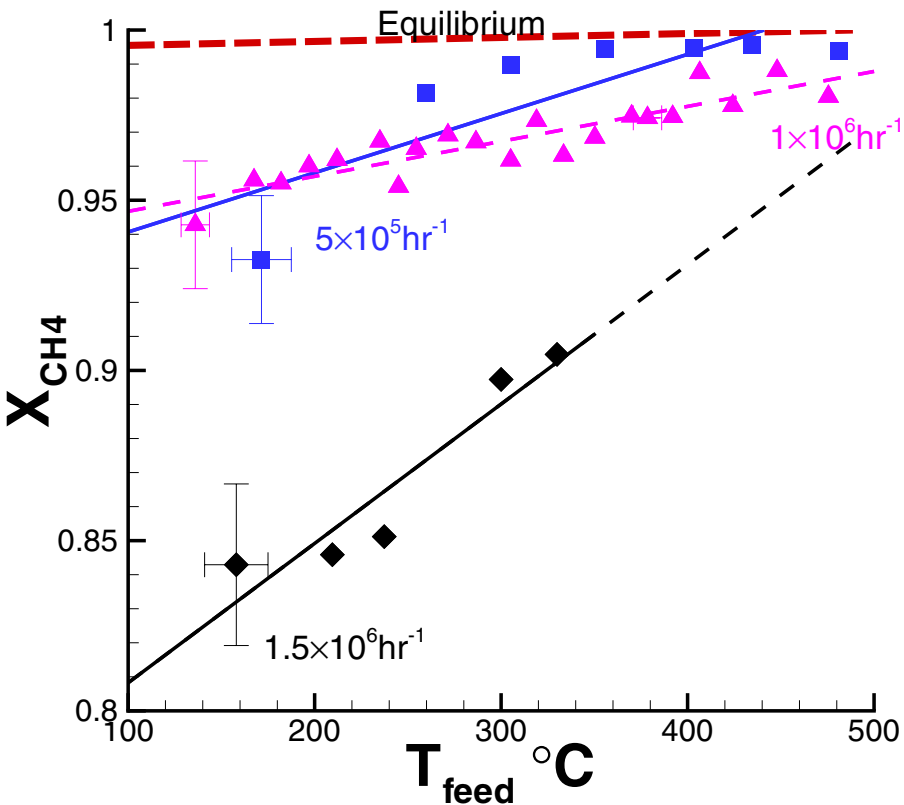


$1 \times 10^6 \text{ hr}^{-1}$ , 5% Rh, 80 ppi, 2% Ce/La



$1 \times 10^6 \text{ hr}^{-1}$ , 80 ppi, 2% Ce/La

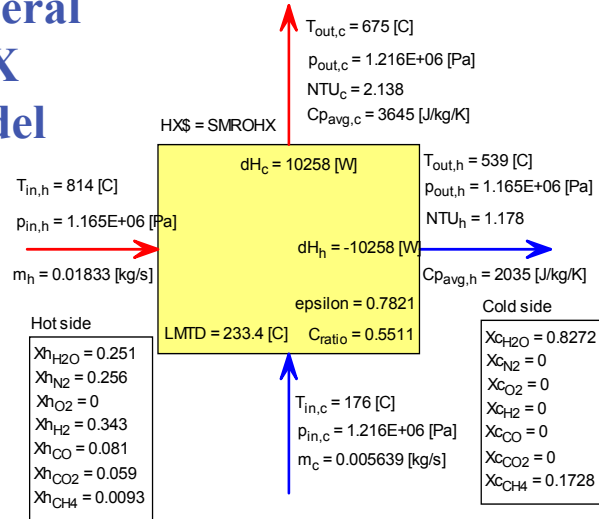
# Results: Effect of Flow rate



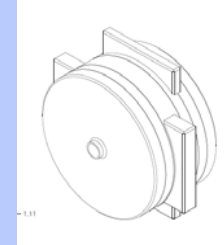
- The reaction zone is pushed to the back with increasing flow
- Experiments with 3mm monoliths show that at  $1 \times 10^6 \text{ hr}^{-1}$  the reaction is not complete
- The support determines the effect of mass & heat transfer which are the limiting factors

# Progress & Results: Heat Exchanger Design Process

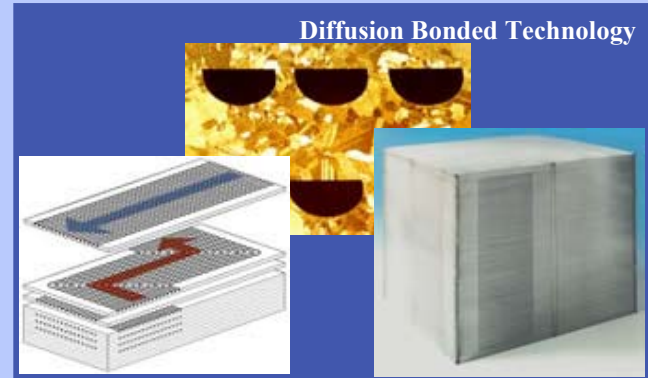
## General HEX Model



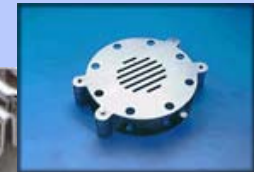
## HEX Technologies Evaluated



Compact shell/tube Technology



Diffusion Bonded Technology



- Vendor database for GRC
- Leverage experience
- Visited vendors
- 6-Sigma tradeoff analysis



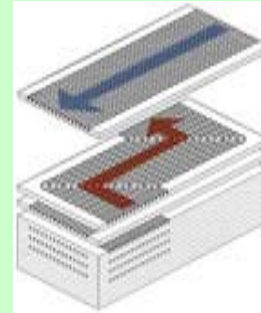
# Results: Identified HEX Technology Among >50 Vendors

- GRC created HEX specifications
- Built Hex vendor database (>100 vendors)
- Vendors dropped off:
  - Missing form factor
  - No high T designs
  - Slow responses
  - Expensive
- ✓ Identified 3 vendors
  - Designs and quotes
  - Visited all of them

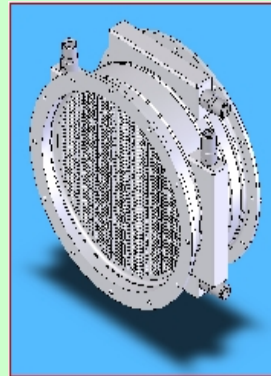
Vendor 1



Vendor 2



Vendor 3



# HEX Technology Trade-Off Matrix

New
Options
About

**Title**

Pass
 Marg
 Fail

1
0.5
0

Concept Sort

Number

Alphabetical

Score

Multi-CTQ

Score

Evaluate  
Score

Automatic

Group Modify

CTQs

System									
	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>			
manufact & cost of scaled unit									
Material selection & handling									
Performance									
ASME stamp, reliability, safety									
Form factor & size									
Cost o pilot unit									
Company confidence & experience									
<b>Importance</b>	2.5	4.5	3	5	3.5	2.5	3		
<b>USL</b>									
<b>LSL</b>	0.6	0.6	0.6	0.6	0.6	0.6	0.6		
<b>Tolerance Units</b>	0.1	0.1	0.1	0.1	0.1	0.1	0.1		
<b>No.</b>									
<b>Concepts</b>									
<b>Score</b>									
3	Vendor 3	3.43	1	1	1	1	1		
1	Vendor 2	3.21	1	1	1	1	0.5		
2	Vendor 1	1.93	0.5	1	1	0	1	0.5	0

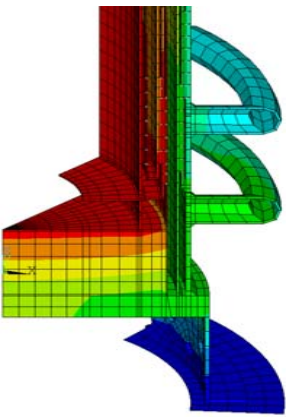
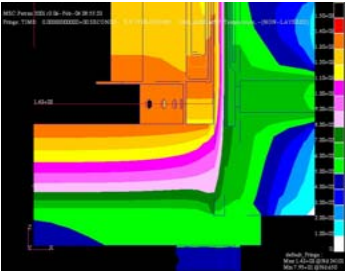
Concepts

- Used DFSS 6-sigma tool to identify HEX vendor & technologies

# Modeling & Analysis Tools will be Used to Ensure Proper Design

Material/Criterias	Importance	SS304	Inconel 600	Inconel 601	Inconel 690	Inconel 693	Inconel 625	Inconel 617	Inconel 800H	Inconel 800HT	RA330	RA333	RA602CA
Maximum Temperature (F)			2000	2100	2000	2100	2000	2000	1900	1900	2200	2200	2200
<b>Material Properties and Resistance</b>													
Thermal Coefficient of Expansion	3		4	4	4	4	5	5	3	3	3	4	4
Oxidation Resistance	4	1	3	4	4	5	5	4	2	2	3	4	5
Carburization Resistance	4	1	4	4	4	5	4	5	3	3	3	4	4
Rupture Life test	4		4	4	2	4	5	5	4	4	3	4	5
Metal Dusting in a Reduced Enviroment	4		3	2	4	5	3	4	1	1	3	3	3
<b>Costs and Availability</b>													
Cost per ft	5		5	5	1	1	4	1	5	5	5	1	1
Lead time	5		5	5	2	1	5	2	4	4	4	2	1
<b>Total</b>			118	118	83	98	128	102	94	94	102	87	90

Material of construction will be selected after careful evaluation



Thermal & stress modeling will be performed to ensure expected vessel lifetime. The design will satisfy ASME codes.

## Leverage prior experience in ACR development



# Progress & Results: PSA System Evaluation



## Separation Summary

- 2 leading PSA technologies evaluated, none currently reach DOE goal of 90 % recovery
- Compressor systems for both storage and feed composition have been found and quotations received
- Alternative technologies for feed compositions (oxygen membranes) were evaluated.
- Pressure of SCPO system becomes important for purification
- Storage systems for hydrogen have been studied

Species	DOE Proposal Specification	CGA Industrial H2, Grade B	Vendor A (120 PSI)	Vendor B (120 PSI )
H2	98%	99.95%	99.996	99.95
CO	<1 ppm	<10ppm	<1.0 ppm	ND
CO2	<100 ppm	<10 ppm	<1.0 ppm	ND
N2	balance	<400 ppm	44.4 ppm	500 ppm
CH4	<100 ppm	<10 ppm	<1.0 ppm	<1 ppm
Recovery			75%	79%

# Assess “Cost of Hydrogen”: DOE H2A

## Model output

Hydrogen cost for 10 year life of refueling station

## Key inputs

- Detailed installed capital costs
- Process operating efficiencies
- Feedstock costs
- O&M

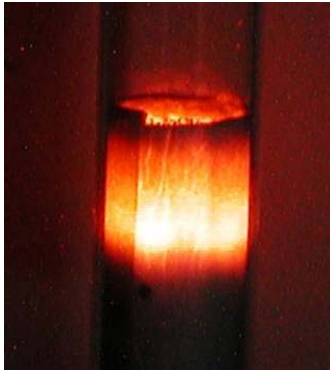
## Enables

Comparison across alternative reforming technologies

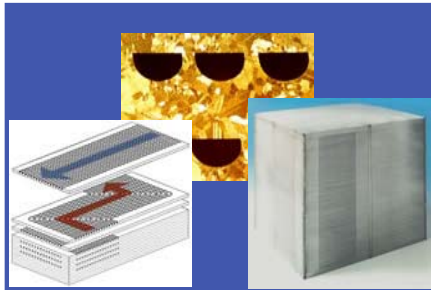
Calculated Base Case Cost of Hydrogen is \$3.05/kg. We believe the SCPO capacity factor >70%, thus we can reach DOE target of <\$3.00/kg

# (SCPO) Staged Catalytic Partial Oxidation Reformer Benefits

## Short Contact Time CPO Catalysts



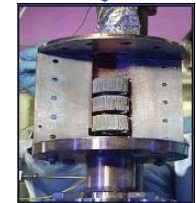
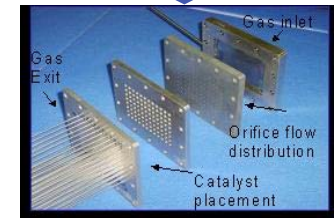
## + Compact HEX



## Cheap Compact Reformer

- ❑ **Most cost effective hydrogen production unit**
  - Compact (5 times smaller than ACR)
  - Modular design for mass production
  - Balance efficiency & cost
- ❑ **Ease of ownership**
  - “Maintenance free” – Reformer life >10 y; Catalyst life >5 y
  - Fuel flexibility
- ❑ **Environmentally sound**
  - Higher efficiency
  - No emissions

## Patented Staging of CPO & SMR Catalysts



# SCPO Accomplishments So far

- ❑ System analysis/design completed.
- ❑ System pressure trade off analysis completed
- ❑ Base case catalysts identified
- ❑ Reactor sizing / design completed
- ❑ HEX technology tradeoff completed
- ❑ HEX technology selected, design completed
- ❑ Control strategy, start-up & shut-down procedure developed
- ❑ Completed cost analysis using GE's process model & DOE's H2A model
- ❑ Prototype & Lab unit design / budgeting completed.
- ❑ ANL & U of Mn worked closely with GE and delivered catalyst test results
- ❑ Conducted preliminary FMEA analysis, major risks identified



# Conclusions & Recommendations

- ❑ SCPO will be the leading technology for H<sub>2</sub> production from NG. It is the most cost-effective H<sub>2</sub> production technology based on the economic analysis of different H<sub>2</sub> production technologies. With minor modification, we can extend the feed to gasoline, diesel, ethanol & methanol.
- ❑ The technologies developed in this program has good synergies with application in fuel blending, NGCC with CO<sub>2</sub> capture, SOFC & syngas production for GTL....

Design and build CPO & SMR reactors in 2006 and conduct testing in 2006 & 2007.

# Supplemental Slides

The following three slides are for the purposes of the reviewers only – they are not to be presented as part of your oral or poster presentation. They will be included in the hardcopies of your presentation that might be made for review purposes.

# Publications and Presentations

- No publications so far, except last year's DOE H2 conference presentation & DOE quarterly reports.
- Two patent applications filed into US patent office.