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50 kW Absorption Enhanced Natural Gas Reformer

Jim Stevens

ChevronTexaco Technology Ventures

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Project ID #: FC44

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Overview

Timeline

- Start: 10/1/03
- End: 9/31/06
- Percent Complete: 33%

Barriers

- **Hydrogen Production**
  - **A. Fuel Processor CAPEX**
  - **B. Operation and Maintenance**
- **Crosscutting Barriers**
  - **Catalysts**
  - **Hydrogen Separation**
- **Fuel Flexible Processors**
  - **J. Durability**
  - **K. Emissions**
  - **L. Hydrogen Purification**
  - **M. Efficiency**
  - **N. Cost**

Budget

- Total Project: $9.0 MM
  - DOE share: $5.6 MM
  - CTTV share: $3.4 MM
- FY04 funding: $1.4 MM
- FY05 funding: $1.9 MM

Partners

CABOT Superior MicroPowders

ZETON INC.

ENGELHARD

Objectives

- Overall Objective
  - Develop materials, process, and 50 kW natural gas absorption enhanced reformer capable of providing near pure H_2 that meet DOE targets for efficiency and H_2 cost
- 2004 Objectives
  - Develop and test high durability CO_2 sorbents
  - Build and operate two 1kW reformers
  - Model process and demonstrate potential for high efficiency and reduced capital costs

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Approach- Absorption Enhanced Reforming

A. Combine reforming, water gas shift, and CO_2 sorbent in one reactor to produce near pure H_2 with low CO_2 and CO content.
B. Use methanation to reduce CO and CO_2 to <1ppm.
C. Develop CO_2 sorbent with 40,000 hour life while maintaining acceptable CO_2 fixing capacity.

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Chemistry of AER

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

$H_2O + CO \rightarrow H_2 + CO_2$ Water-gas Shift

$CO_2 + CaO \rightarrow CaCO_3$ Carbonation

Reforming Step

$$CH_4 + 2H_2O + CaO \xrightarrow{600^0C} 4H_2 + CaCO_3$$

Regeneration Step

$$CaCO_3 \xrightarrow{800^0C} CO_2 + CaO$$

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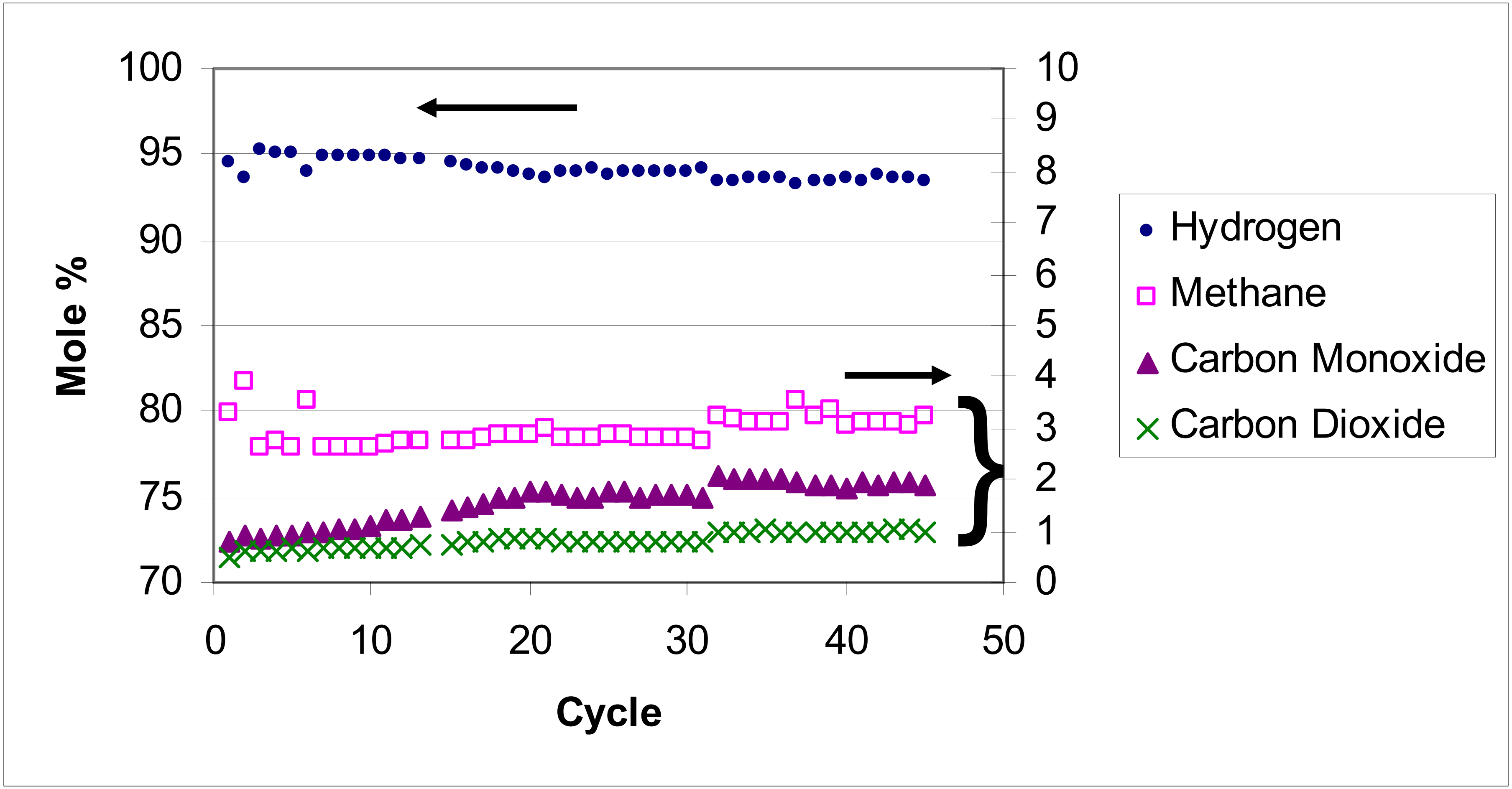
Example Reformate Composition



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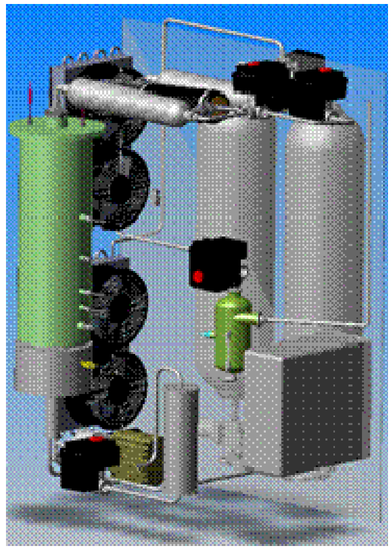
AER Materials Requirements



- Reforming/WGS catalysts active at 600^0C
- Reversible Sorbent
  - High CO_2 sorption capacity (>20 wt%)
  - Fast kinetics
  - Long term stability
  - Crush strength (>2.0 lb/mm)
- Scalable sorbent production

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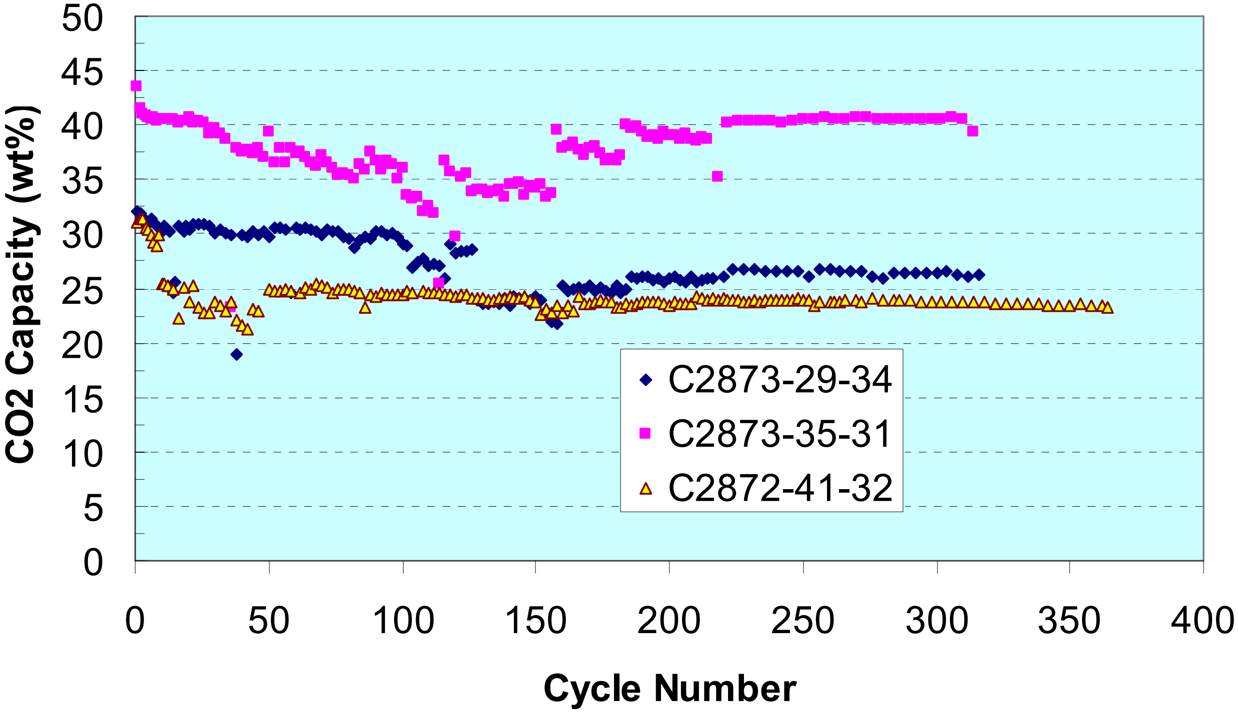
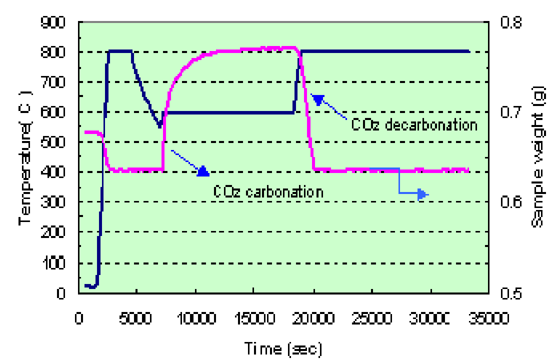
Long Term Stability of CSMP Sorbent Powders CT CO_2-TGA Results from Typical Samples

Carbonation 600C, Decarbonation 800C (for 1~9th cycle of C2872-41-32 decarbonation at 750C



Summary

- C2872-41-32 has been running since 01/27/2003
- >3000 h lifetime



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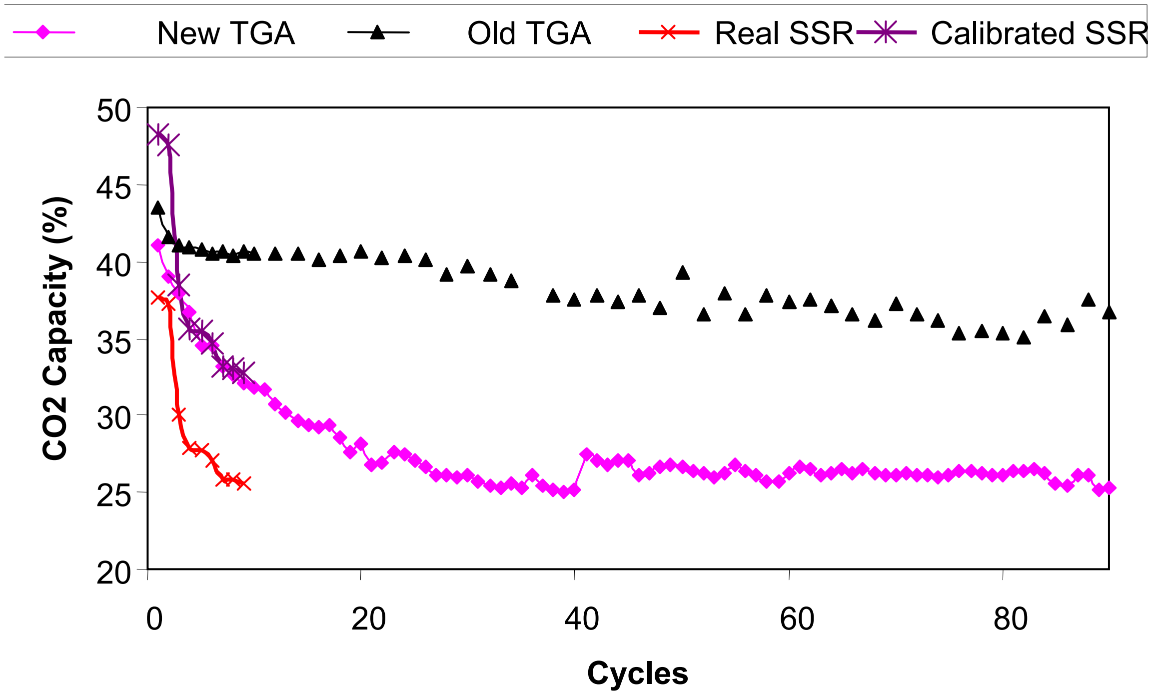
Comparison of CO_2-TGA Testing with Reactor Tests



- More than 225 samples tested since June 2004
  - •111 extrudates
  - •114 powders
  - •30 cycles initial screening
  - •Selected samples – over 500 cycles, 3000 h

– The data from continuous CO_2-TGA cycling test method correlate with the reactor testing results

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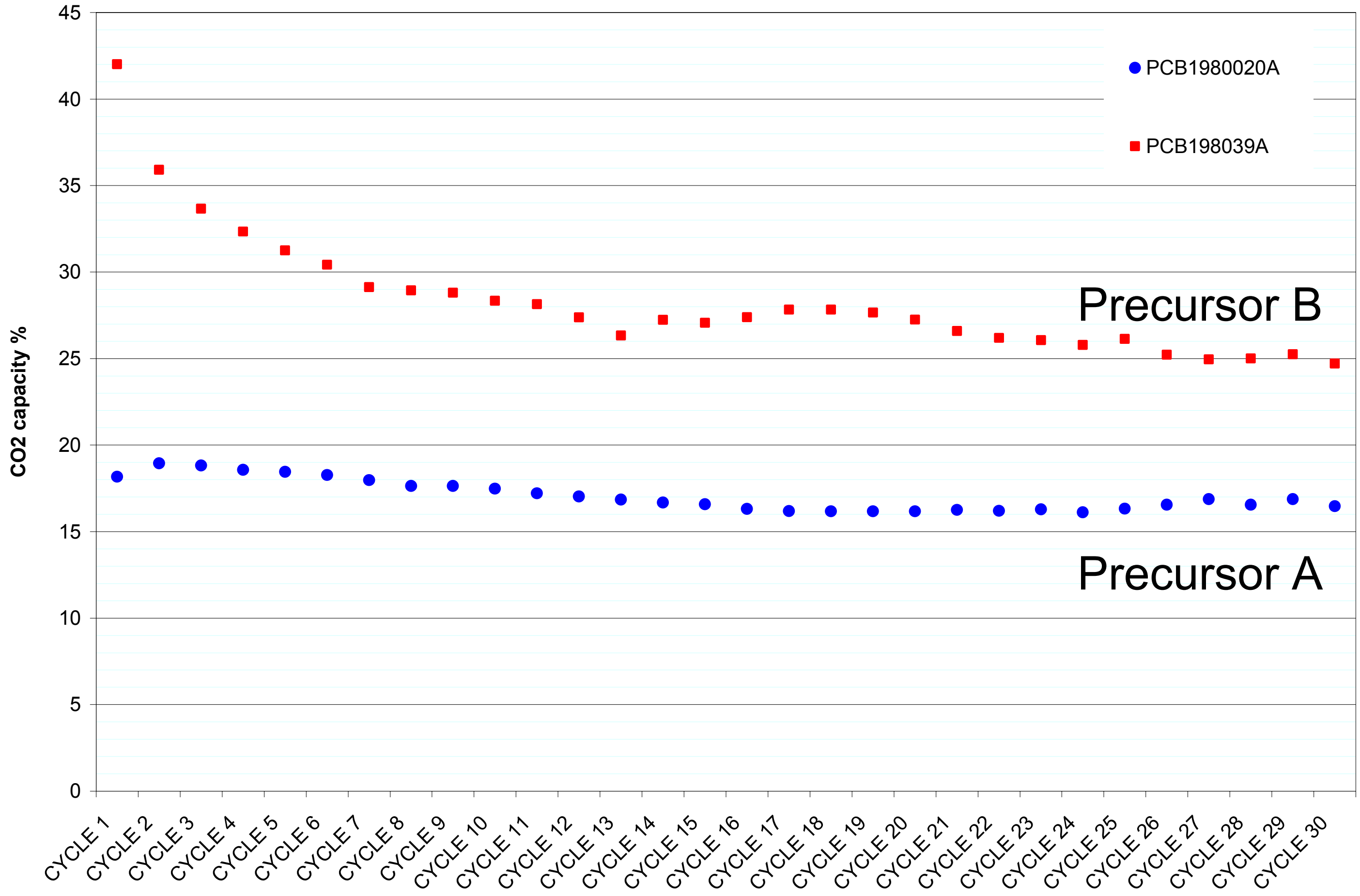
Effect of Precursor Type on CSMP Sorbent

CO_2-TGA performance



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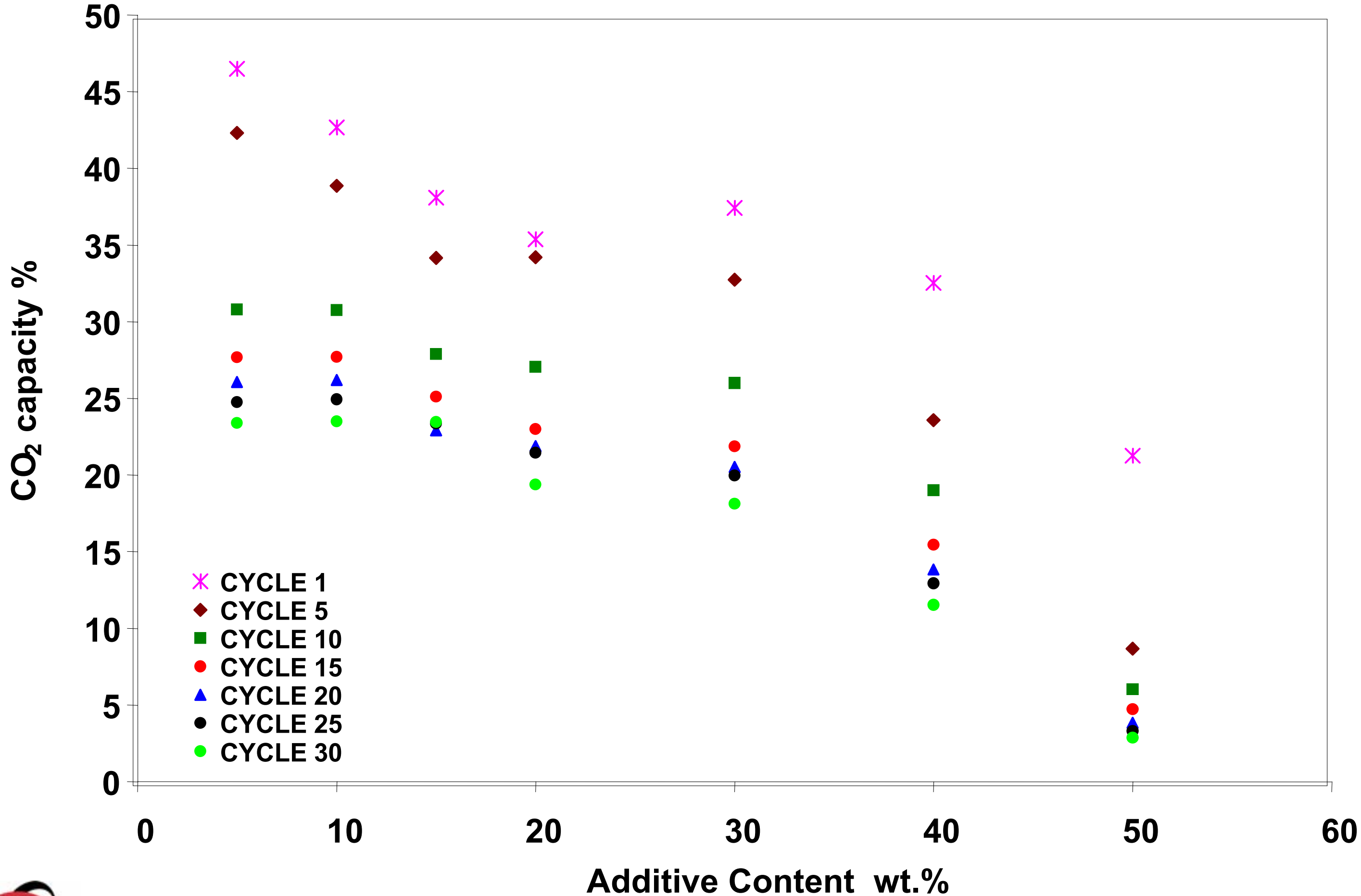
Effect of Inert Additive Content on CSMP Sorbent Performance



- Summary:

  Inert additive loadings of 5-15 % show similar results after 30 cycles

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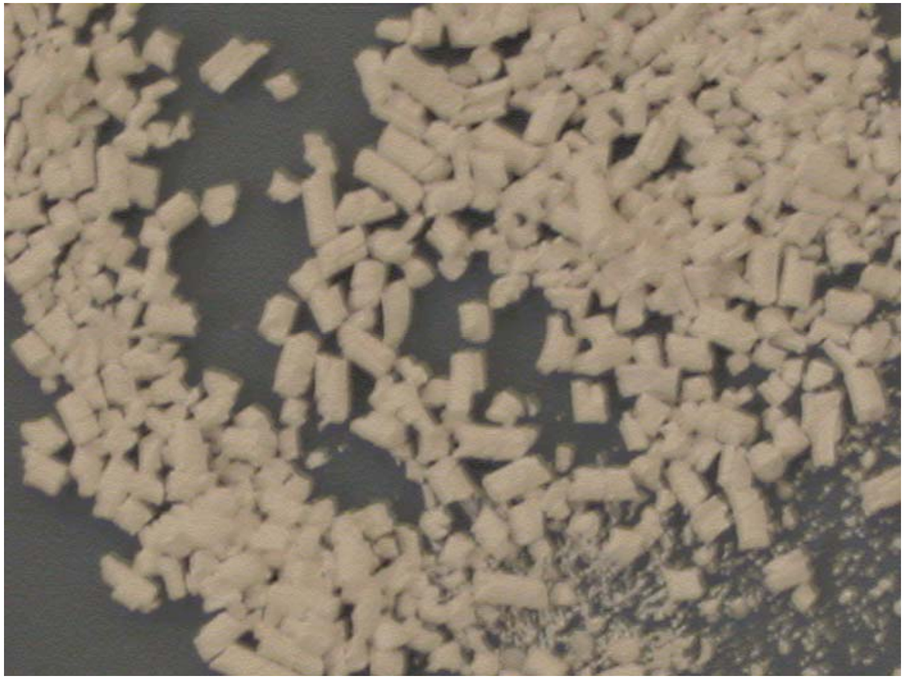
Stability of Extrudates


Extrudate A, after 535 cycles


Extrudate B, after 523 cycles

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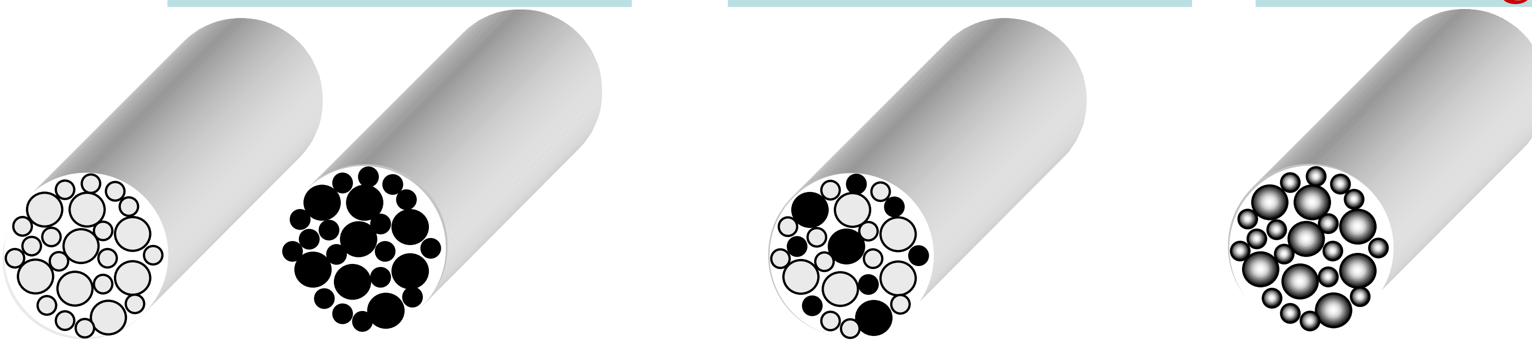
Integrated Materials for AER

Demonstrated | Demonstrated | In Progress



CaO Rh/Al_2O_3 | Mixture | Composite

1. | *2.* | *3.*

1. **Sorbent (S) and reforming catalyst (RC) made in a separate pellets**
2. **Sorbent and reforming catalyst made as separate powders**
3. **Sorbent and reforming catalyst made in one particle**

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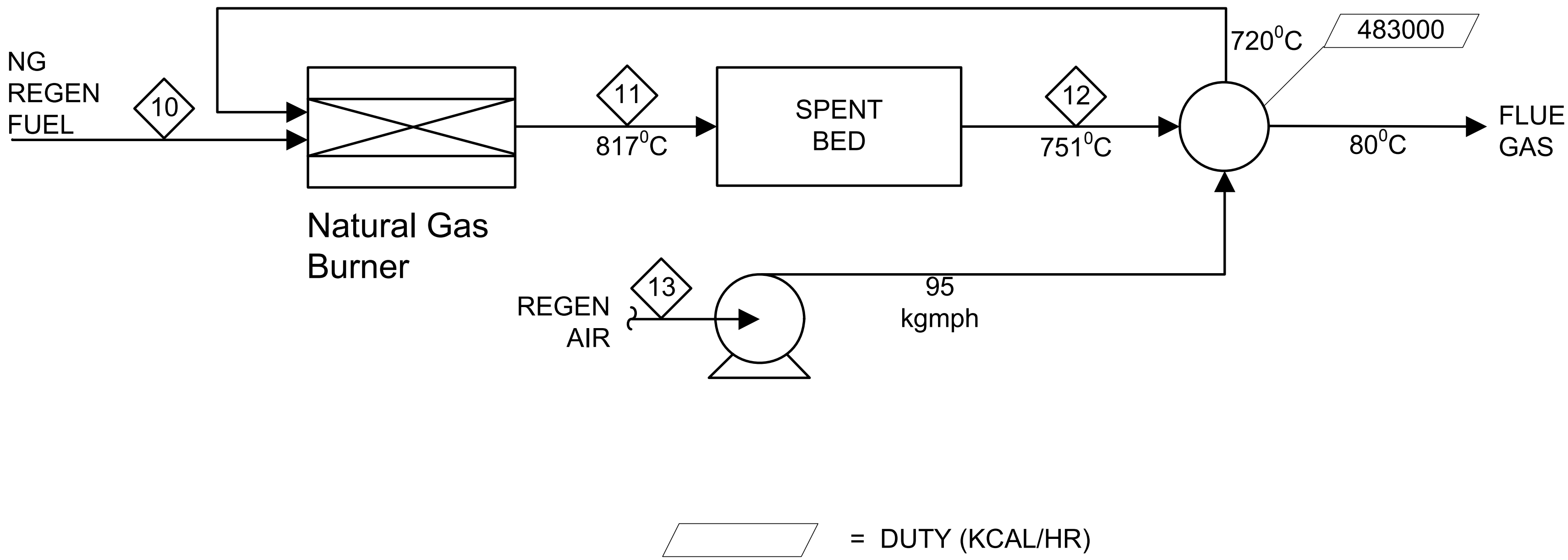
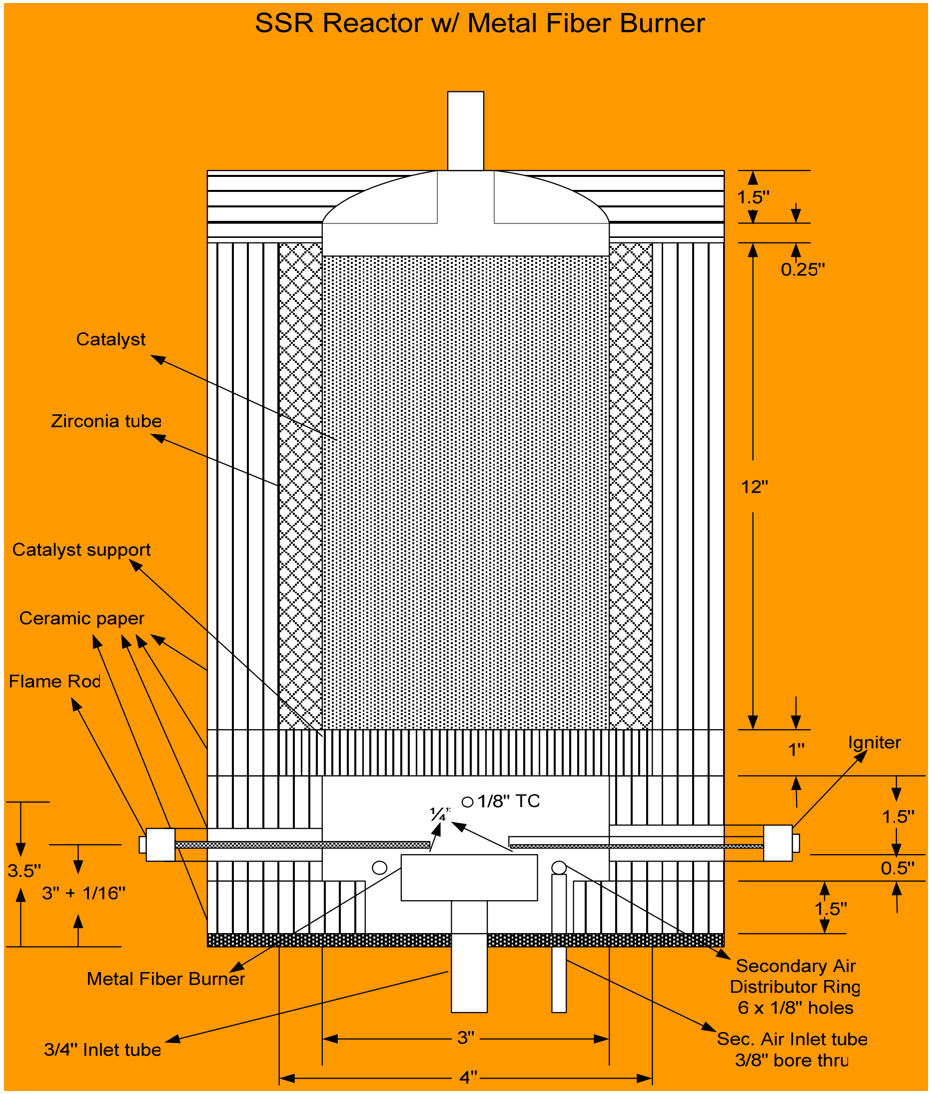
Regeneration Method



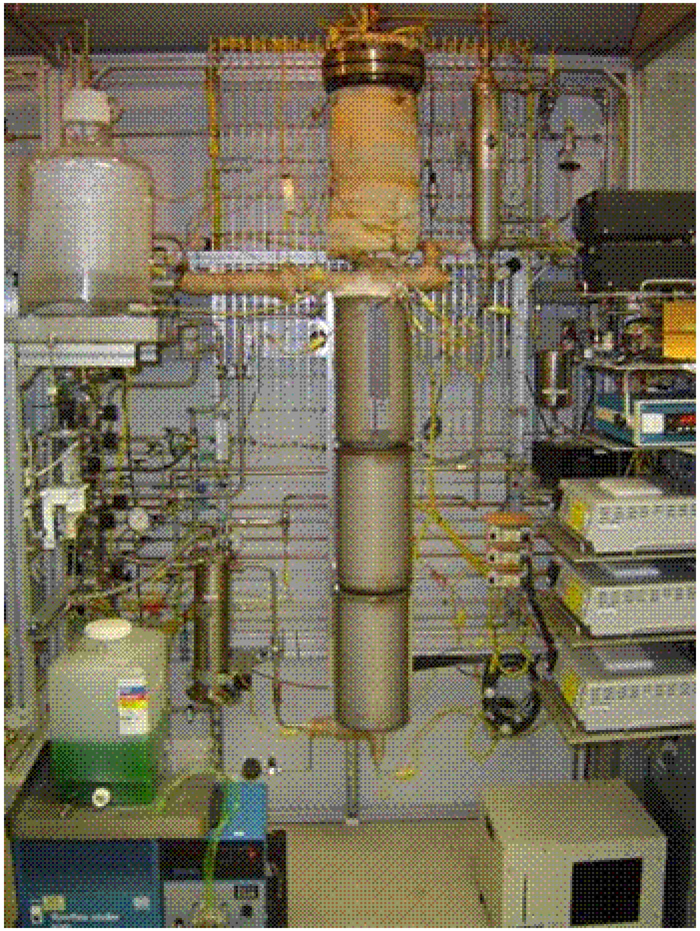
SENSIBLE HEAT REGEN- AIR

1 kW Reactor Design



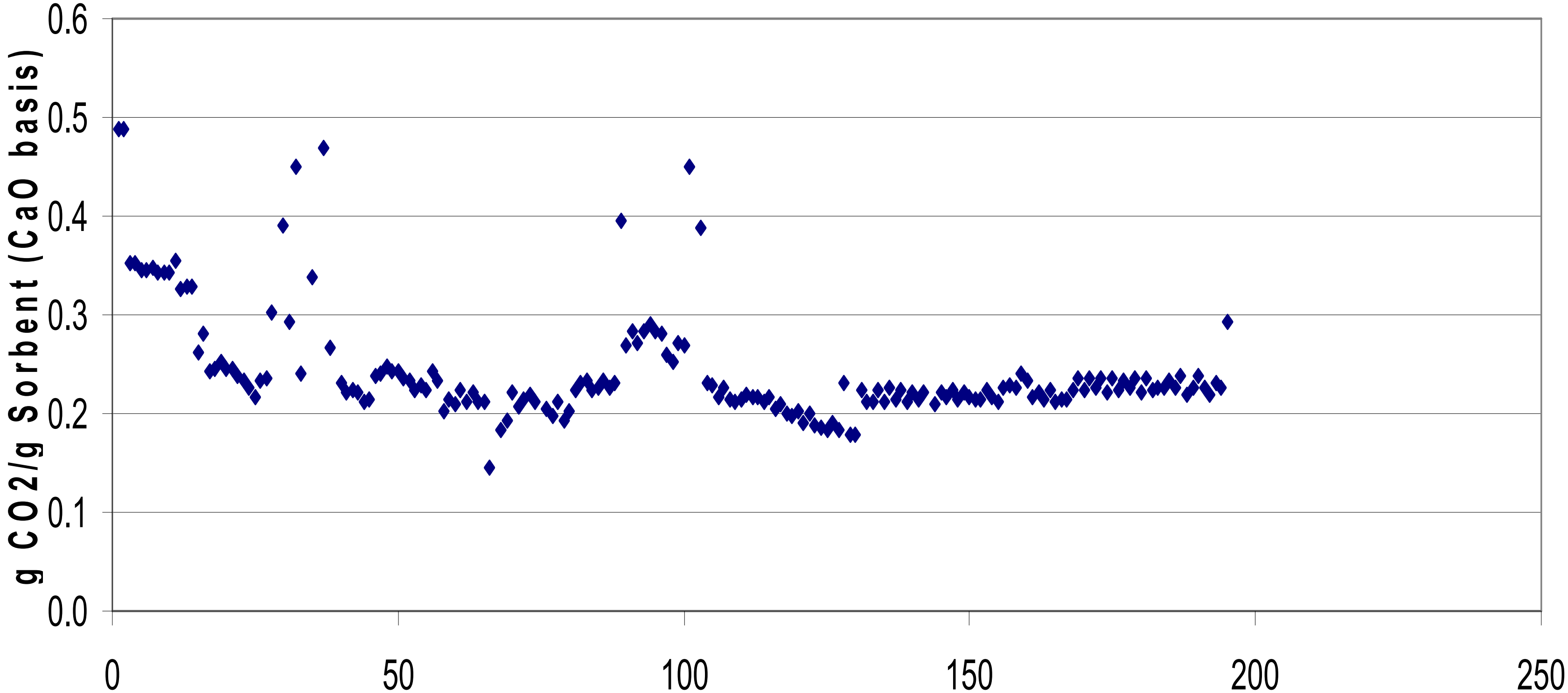
- Simple reactor construction
- Metal fiber burner for combustion during regeneration
- Direct combustion gas/sorbent heat transfer
- Good control of bed temperature.

Constructed and Testing Two 1 kW Reactors



Reviewer Comment: "Durability is a key technical challenge, testing needs to be done under real conditions."

Sorbent Capacity After Multiple Combustion Gas Regenerations



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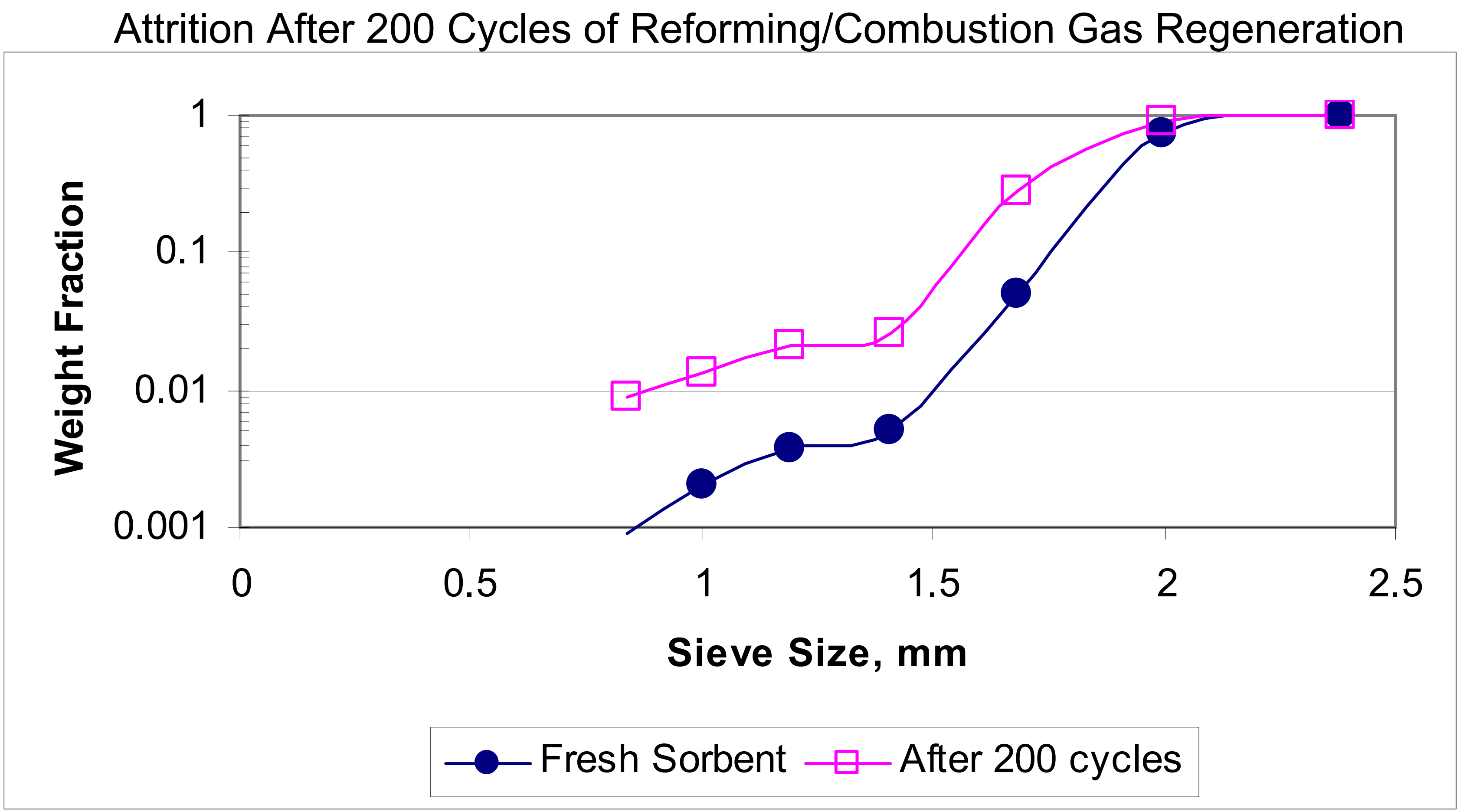

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Reviewer Comment: “No clear plan to expand to large plants or sequestor CO_2.”

- CTTV Working on Large Scale Production for Refineries outside of DOE Grant
  - Completed Rough Cost Study on Large Fixed Bed Process
  - Started Study on Entrained Sorbent Reactor
- Sequestration of CO_2 outside scope of DOE Grant
  - More likely feasible for large scale plants
- **Cabot Actively Marketing Materials**

Reviewer Comment: “No need to develop new reforming catalysts, should use commercial reforming catalysts.”

- **Using Engelhard reforming catalyst. Some development may be required**

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Major Milestones for DOE Project

Task	Milestone/Decision point	Deliverable	Date
Steam Reforming Catalyst	90% of the thermodynamic equilibrium conversion of methane ,Rh content <0.5 %Rh	Test data report	09/30/04
Integrated catalyst /sorbent	>50 % CO_2 fixing capacity after 50 cycles >90 % equilibrium conversion of CO	Test report	09/30/04
Integrated catalyst /sorbent	>98 % H_2, CO/CO_2< 1% on dry after 50 cycles	Pelletized materials	11/15/04
Integrated catalyst/sorbent	>98 % H_2, CO/CO_2< 1% after 500 cycles	Pelletized materials	08/15/05
Reactor concept modeling	Predicted efficiency of system > 78% and capital cost less than currently available systems	Written report	07/06/04
Catalyst production scale up	Deliver enough integrated material for one full scale reactor, estimated 175 kg	Pelletized materials	11/15/04
Integrated Catalyst delivery	Deliver enough integrated material for one full scale fuel processor, estimated 350 kg	Pelletized materials	08/15/05
10 kw Reactor Installation	Reactor ready for testing	Reactor installation	11/12/04
Reactor Testing	Reactor meets design criteria	Test Report	08/03/05
Reformer Installation	Stand alone reformer installed in Houston Test area	Reformer Installed	09/15/05
Reformer Testing	Reformer start-up/shut-down cycle testing, transient testing, durability testing.	Test Report	11/08/06

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Go/No Go Decision Points

Go/No-Go decision points	**Decision review package**	**Criteria**	**Date**
1	Combined reactor concept and materials performance demonstrated	>98 % H_2, CO/CO_2< 1% on dry basis after 50 cycles predicted energy efficiency> 78%	11/15/04
2	1 kw Reactor performance evaluation	>98 % H_2, CO/CO_2< 1% on dry basis after durability testing predicted energy efficiency> 78%	7/30/05
3	Fuel Processor Performance	>98 % H_2, CO/CO_2< 1% on dry basis after 3 months of durability testing measured energy efficiency> 78%	3/30/06

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Future Plans

- 2005
  - Continue testing sorbent formulations
  - Continue operation of 1kW reactors
  - Construct 50kW reformer
- 2006
  - Complete sorbent development
  - Test 50kW reformer

Publications and Presentations

- Development of a Fuel Processor Using Revolutionary Materials for Single Step Absorption Enhanced Natural Gas Reforming, 2004 National Hydrogen Association, Los Angeles California

- Cost Effective Production of Near-Pure Hydrogen, 2004 Fuel Cells and Hydrogen Futures Conference, Perth, Australia

Safety Question #1. What is the most significant hydrogen hazard associated with this project?

- Deflagration in reactor due to mixing of air and hydrogen when switching from reforming cycle to regeneration cycle.
  - During the reforming cycle the CO_2 sorption material is saturated and must be regenerated. After purging the system with steam, flue gas from a natural gas burner passes through the reactor to heat and regenerate the sorbent.

Safety Question #2. What are you doing to deal with this hazard?

- Air to burner is controlled by two sequential valves controlled by two separate control systems/sensors.
- Hydrogen is purged by multiple volumes of steam before regeneration begins.
- System is above ignition temperature so combustion will begin before hydrogen/air mixture can reach explosive range
- Pressure relief valves sized to release pressure
- Reactor vessel designed to withstand pressure wave
- Laboratory access is limited
- System is operated within hazard containment area
- Test area has multiple sensors with automated electrical and natural gas shut-offs