

ENHANCED HYDROGEN PRODUCTION INTEGRATED WITH CO₂ SEPARATION IN A SINGLE-STAGE REACTOR



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PDP1**

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- **Project start date: Oct 2003**
- **Project end date: Sept 2005**
- **Percent complete: 50 %**

Budget

- **Total project funding: \$501,300**
 - DOE share: \$ 399,713
 - Contractor share: \$ 101,587
- **Funding for FY04: \$160,000**
- **Funding for FY05: \$200,000**

Barriers

Technical Target:

- **Cost reduction of H₂ production from fossil fuels. For natural gas sources**
 - \$ 3.00/ggeH₂ (by 2005)
 - \$1.50/ggeH₂ (by 2010)

Technical Barriers:

- **Cost effective CO₂ avoidance**
- **Reduction in impurities (CO, H₂S)**
- **Selectivity towards H₂ capture**
- **Desired Operating Temp range**
- **Cost of H₂ production**

Partners

Ohio State University

Project Objectives

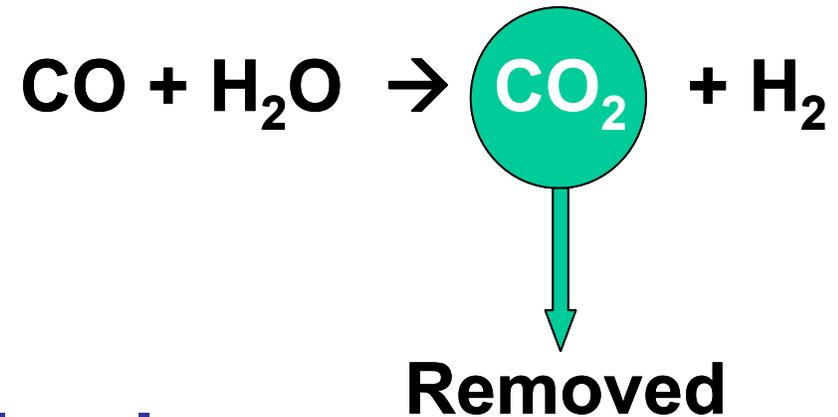
To assist DOE in the development of hydrogen production technologies by maximizing H₂ production from fossil fuels

- **To develop a high temperature reaction based process from syn gas (CO + H₂) which:**
 - **Maximizes H₂ production at high temperature & pressure (current year)**
 - **Maximizes H₂ purity by enhancing water-gas-shift reaction**
 - **Creates a sequestration ready CO₂ stream**
- **To identify process conditions for maximizing CaO reactivity**
 - **Thermodynamic analyses for optimizing carbonation, hydration and sulfidation**
 - **Testing of mesoporous calcium sorbents**
 - **Optimizing carbonation and calcination reactions (current year)**
 - **Multicyclic testing (current year)**

Overall Technical Approach

- ***In-situ* CO₂ removal from the Water gas mixture**
- **Drive the equilibrium limited WGS reaction forward**

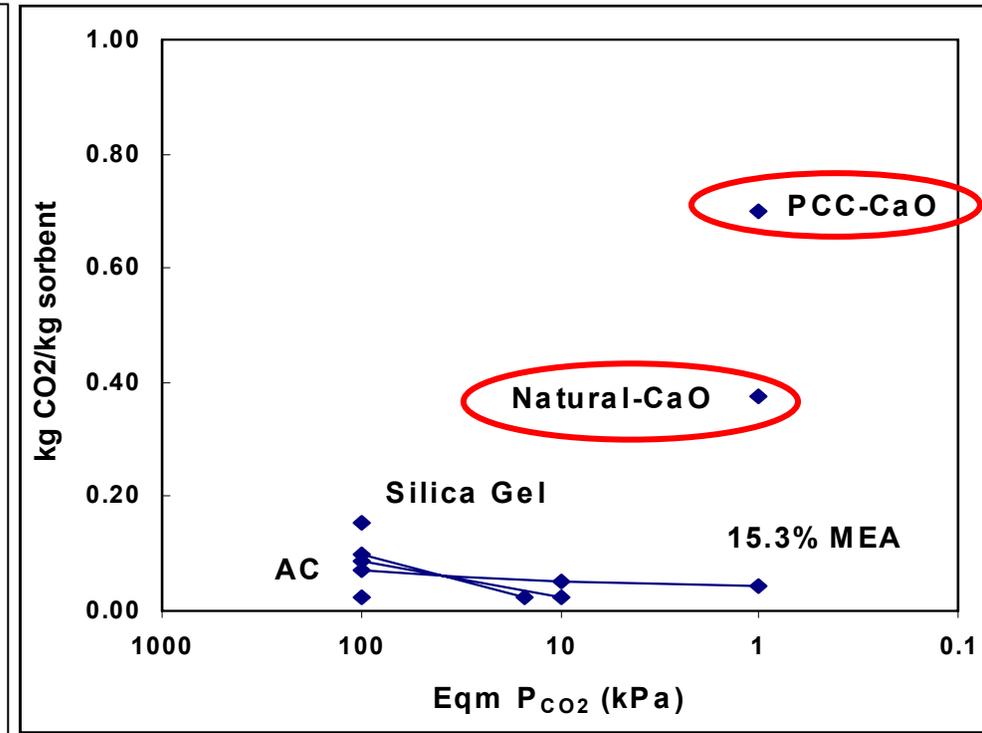
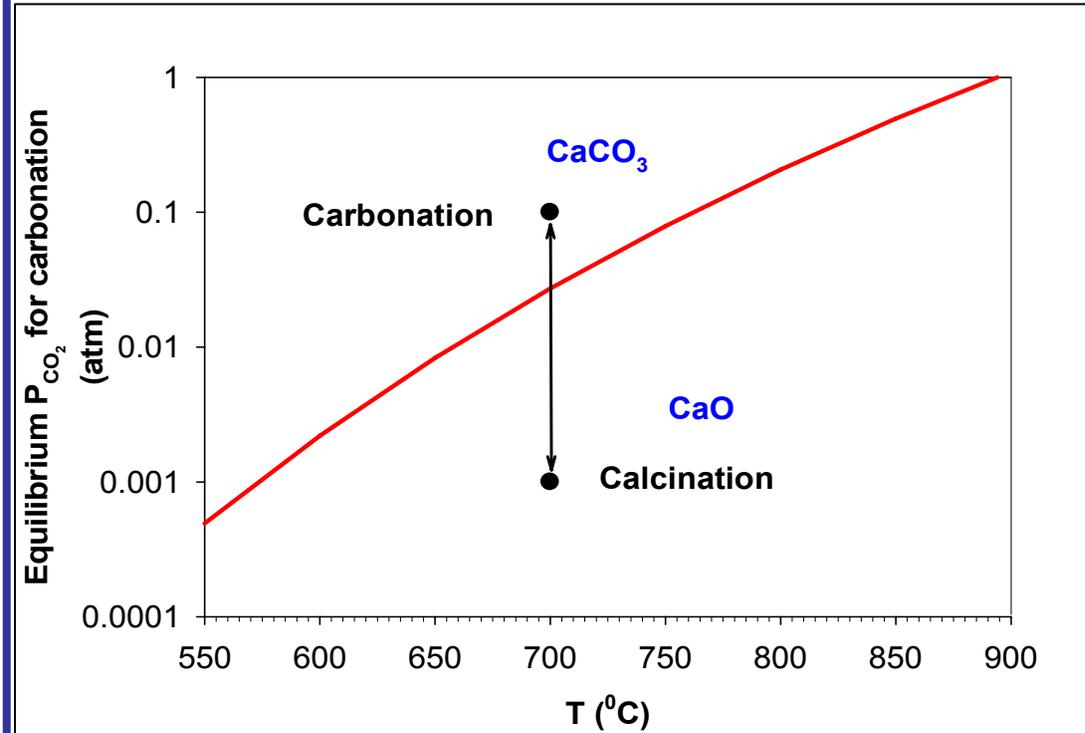
- ✓ Maximize H₂ production
- ✓ High T/P/Purity H₂ possible
- ✓ Reduce Steam consumption
- ✓ Remove CO and CO₂ to ppm levels
- ✓ Integrated **CO₂ separation** making this H₂ Production process **CO₂ sequestration ready** as well
- ✓ **In membrane reactors, H₂ production limited by WGS catalysis and not H₂ diffusion**



Approach: Experimental

- **Integral bed for simultaneous WGS and Carbonation**
 - Breakthrough studies for extent/purity of hydrogen production
 - Sorbent reactivity
 - Catalyst activity (blank testing)
 - Catalyst deactivation avoidance
- **MSB-TGA testing**
 - Extent of carbonation (High pressures)
 - Multicyclic carbonation-calcination reaction testing
 - Competing carbonation/sulfidation reactions
- **Sub-atmospheric calcination**
 - Vacuum calcination
 - Steam calcination

Carbonation Calcination Reaction System (CCR)



➤ **Regenerable metal oxides**

➤ **Carbonation**



➤ **Calcination**



^a15.3% MEA, ^bAC, 1393 m²/g, ^cAC: Norit R1, ^dSilica Gel, ^eAC 1018 m²/g

^aSong et al., 1996; ^bHeuchel et al., 1999; ^cDreisbach et al., 1999; ^dZhang et al., 1998; ^eSarkar and Bose, 1997₆

Computed from HSC Chemistry v 5.0

Reaction Schemes

Reaction phase:



Regeneration phase:

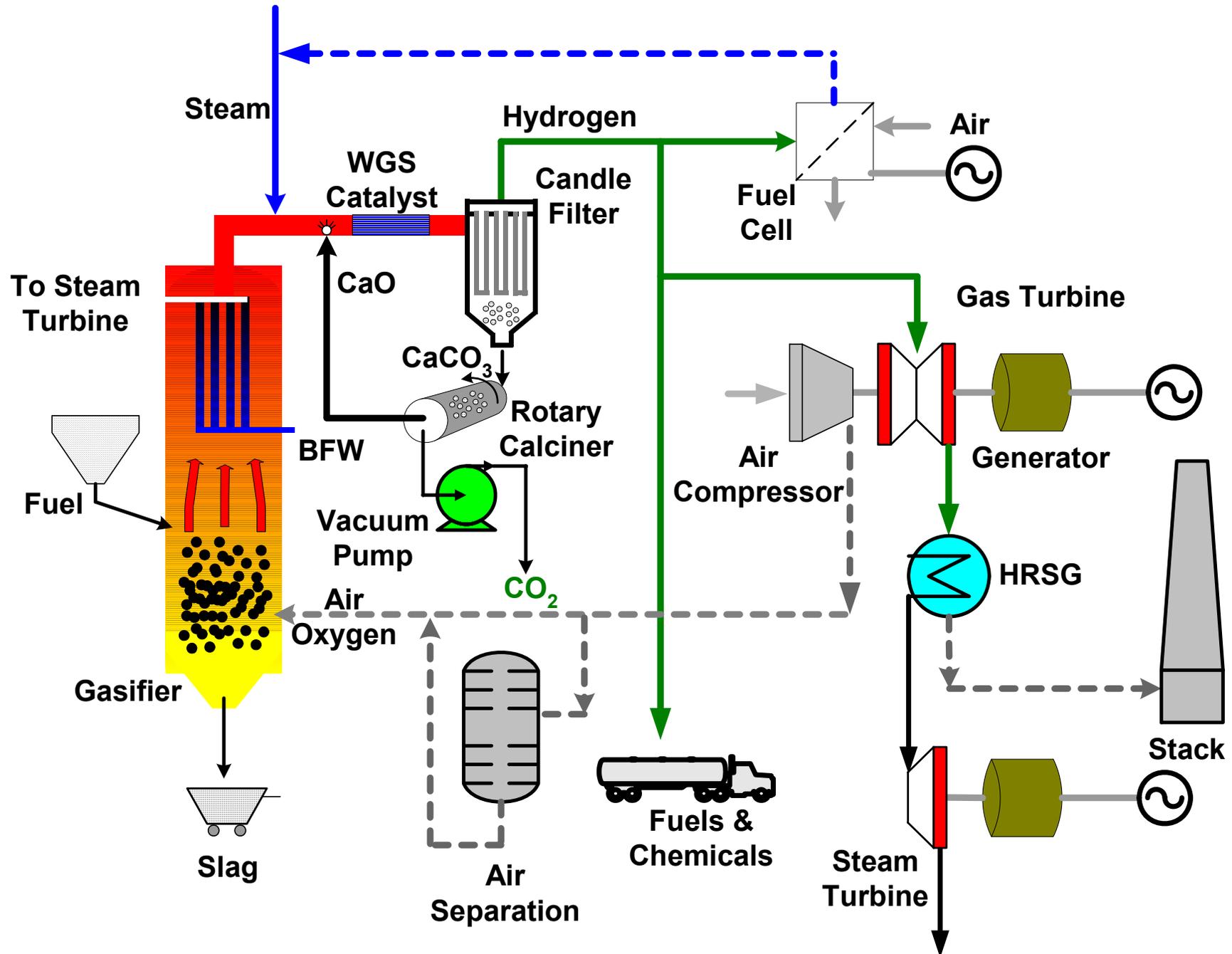


Parasitic Reactions:

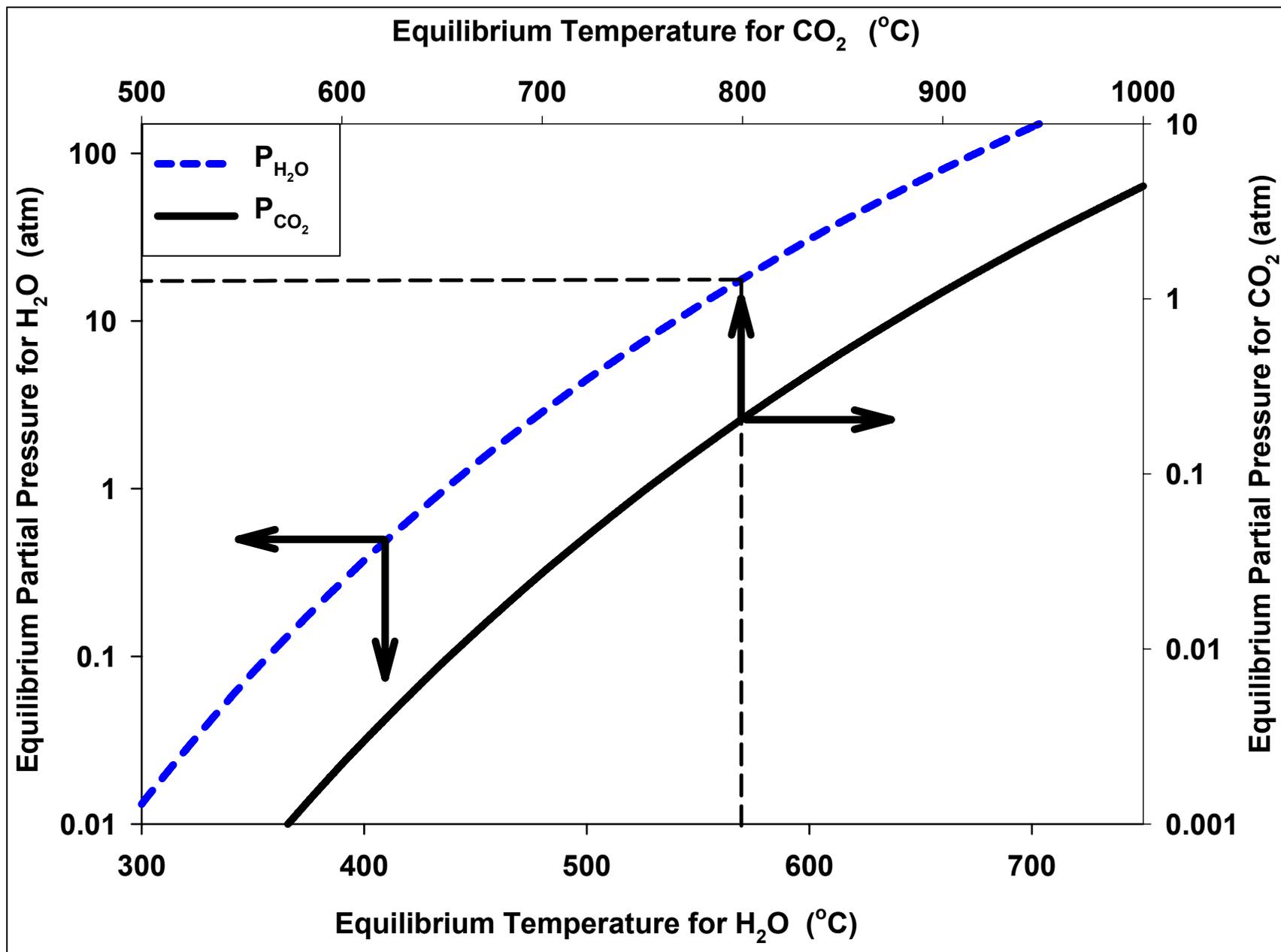
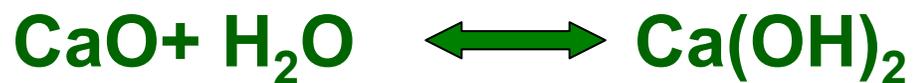


- High Steam/CO
- H₂/CO ratio can be improved
- But can never maximize H₂ production
- Further CO cleanup required for PEM fuel Cells (ppm levels) ⁷

Overall integration scheme



Thermodynamic Analyses

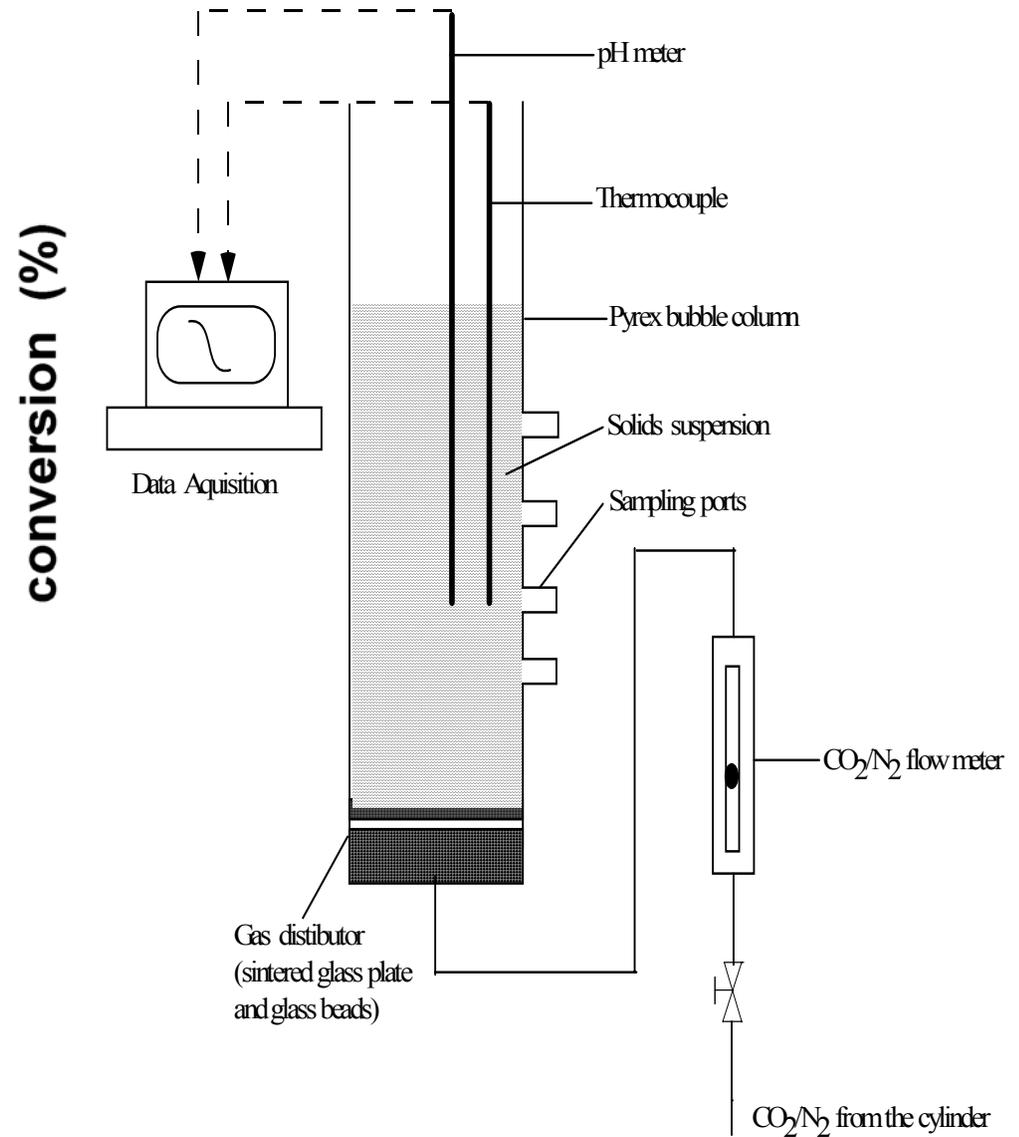
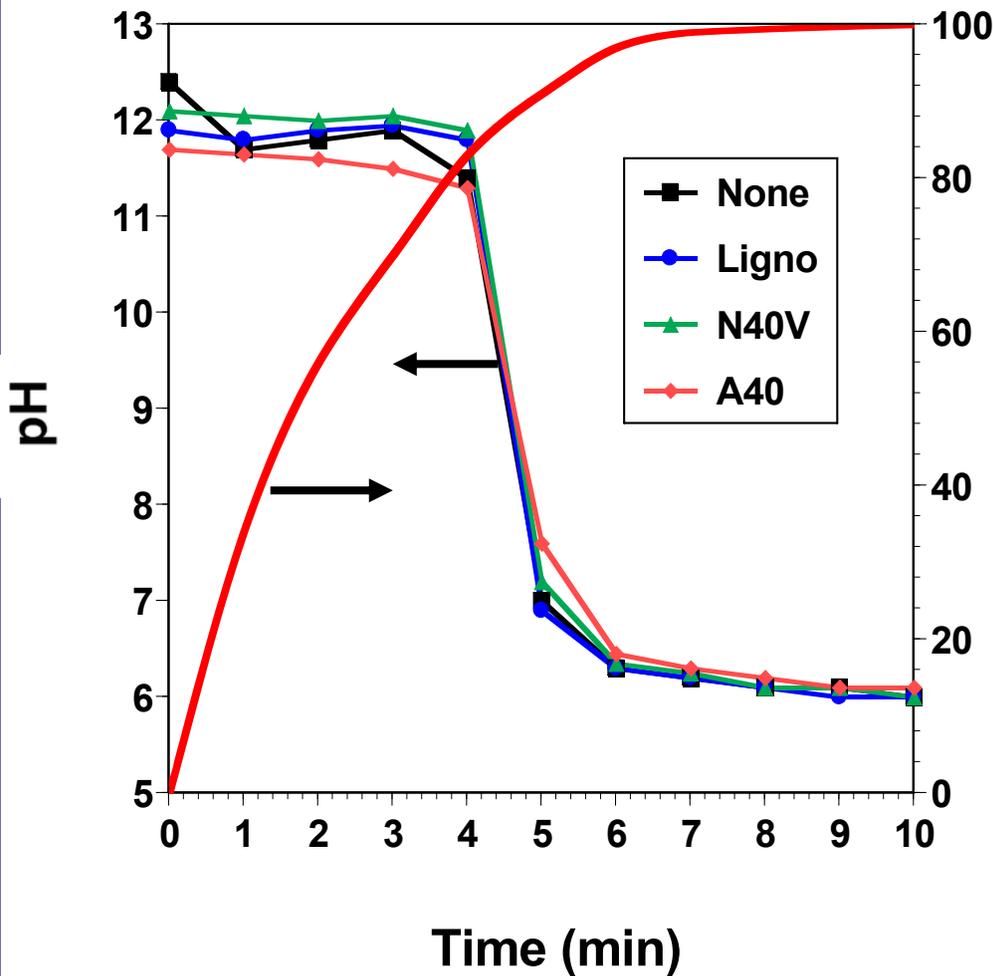


Fuel Gas Compositions

	Moving Bed, dry	Moving Bed slagging	Fluidized Bed	Entrained Flow, slurry	Entrained Flow, dry
Oxidant	air	Oxygen	Oxygen	Oxygen	Oxygen
Fuel	Sub Bituminous	Bituminous	Lignite	Bituminous	Bituminous
Pressure (psi)	295	465	145	615	365
CO	17.4	46	48.2	41	60.3
H₂	23.3	26.4	30.6	29.8	30
CO₂	14.8	2.9	8.2	10.2	1.6
H₂O	...	16.3	9.1	17.1	2
N₂	38.5	2.8	0.7	0.8	4.7
CH₄+ HCs	5.8	4.2	2.8	0.3	...
H₂S + COS	0.2	1.1	0.4	1.1	1.3

- Typical gasifier P_{CO_2} : 0.4 - 4.3 atm
- Equilibrium Temperature: 830 - 1000 °C
- Operate below T_{eq} for carbonation to occur
- Typical gasifier P_{H_2O} : 12 - 20 atm
- Equilibrium Temperatures: 550 - 575°C
- Operate above T_{eq} to prevent hydration of CaO

PCC Synthesis*

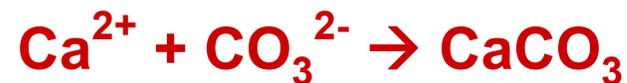


Solids loading: 2.56 wt%

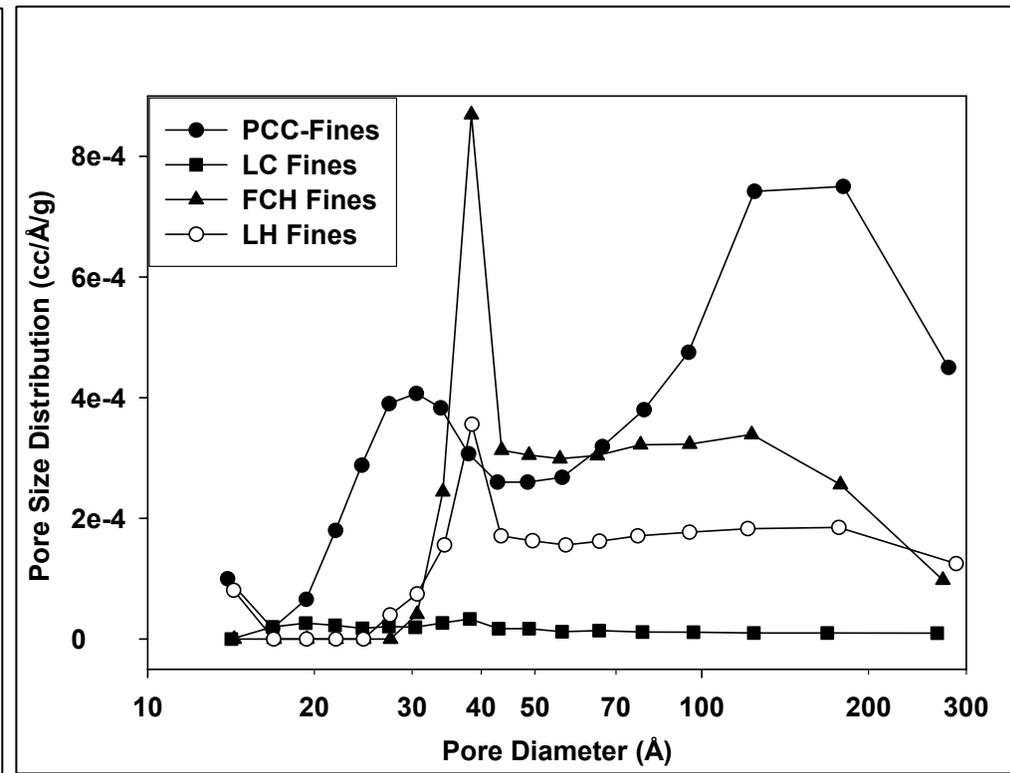
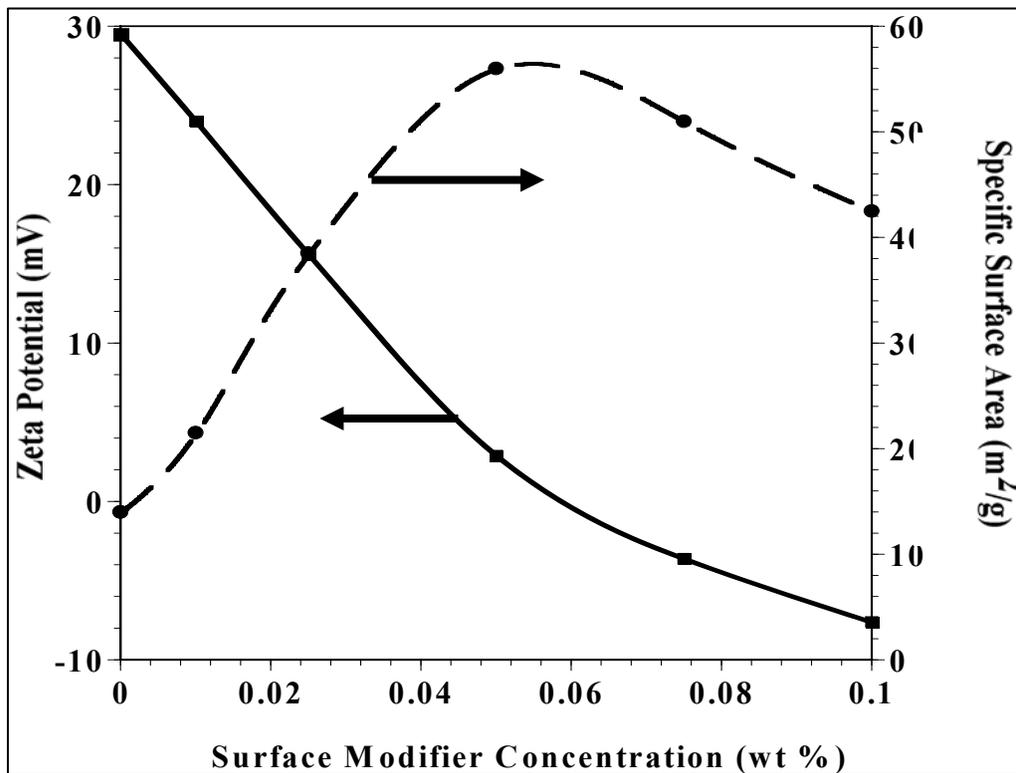
CO₂ flow rate: 5 scfh

*Agnihotri et al., (1999)

CO₃²⁻ and HCO₃⁻ ions



Optimization of Sorbent Morphology



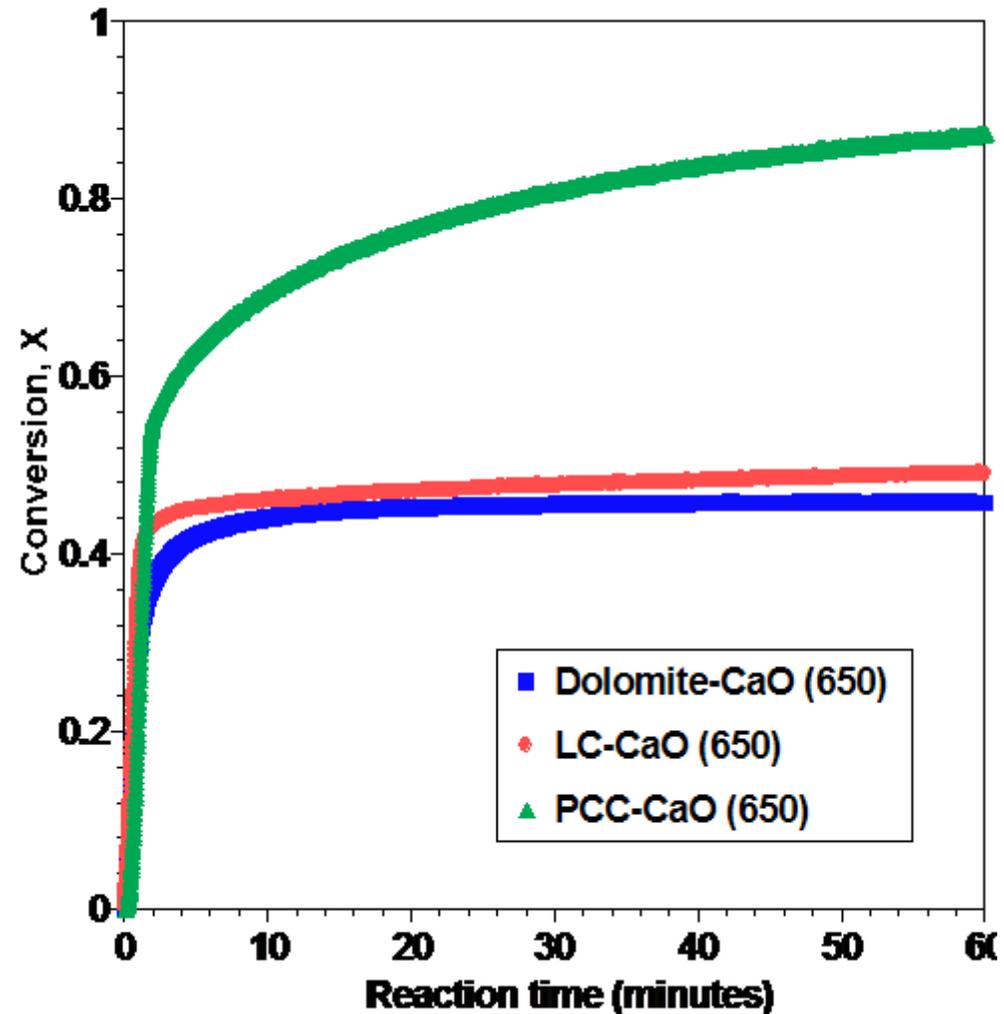
Optimization of Surface area and Zeta potential¹

Comparison of PSD of PCC with other natural lime based sorbents²

¹Gupta and Fan, (2002); ²Gupta et al (2004)

Effect of Initial Sorbent Morphology (carbonation of CaO sorbents)

Name	BET SA (m ² /g)	PV (cc/g)
LC	1.064	0.003
LC-CaO	17.79	0.078
Dolomite	1.822	0.004
FCD-CaO	29.85	0.08
PCC	36.8	0.11
PCC-CaO	12.79	0.027

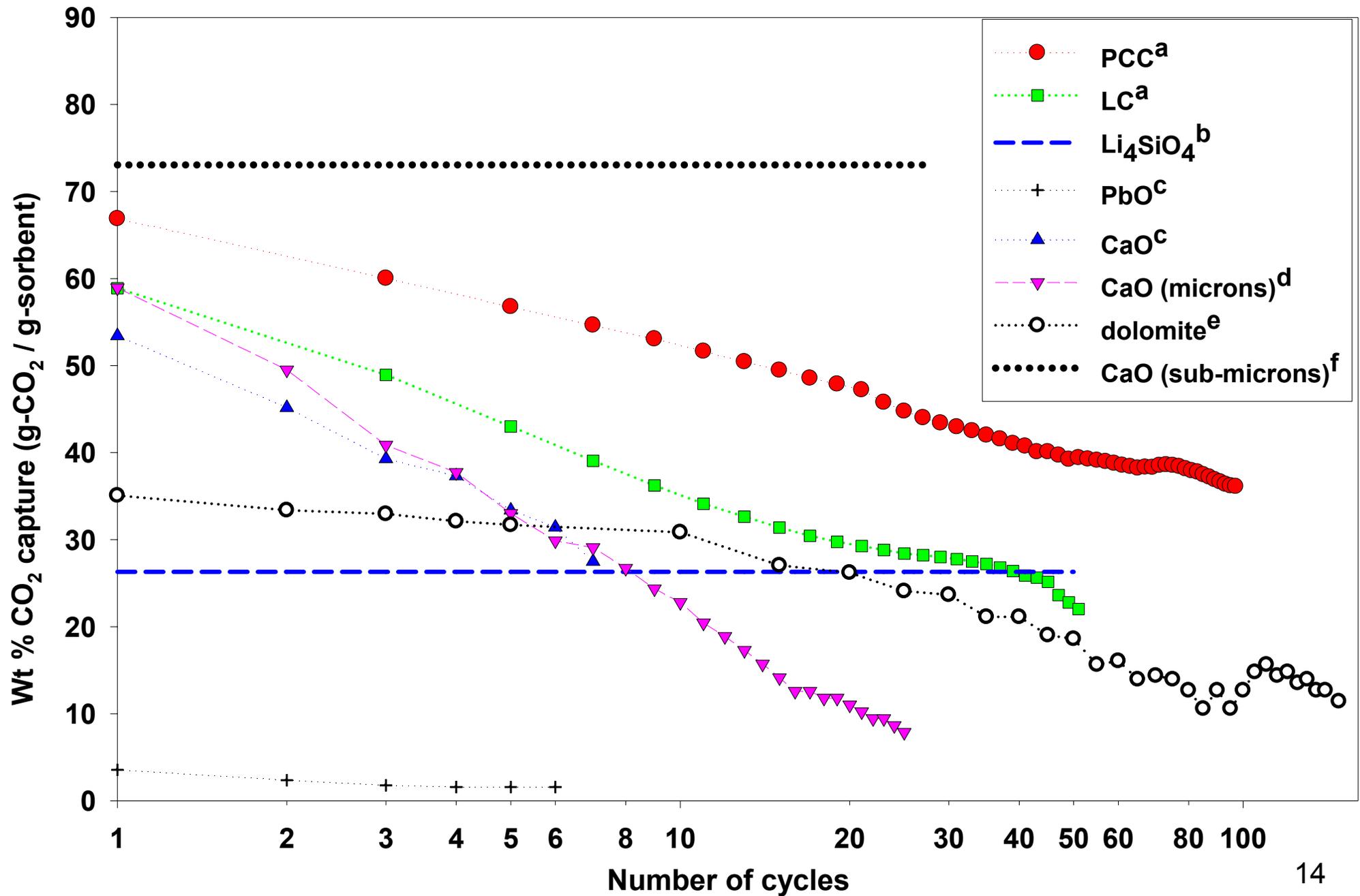


➤ Two-regime heterogeneous Gas-Solid reaction

- ✓ Rapid kinetic regime
- ✓ Slow product layer diffusion regime

Carbonation in TGA at
700 °C under 100 % CO₂

Comparison of High Temperature Sorbents



(^acurrent work; ^bToshiba Corpn., ^cKato et al, 1999; ^dBarker, 1973; ^eHarrison et al, 2001, ^fBarker, 1974)

Experimental Setup

Combined WGSR and Carbonation

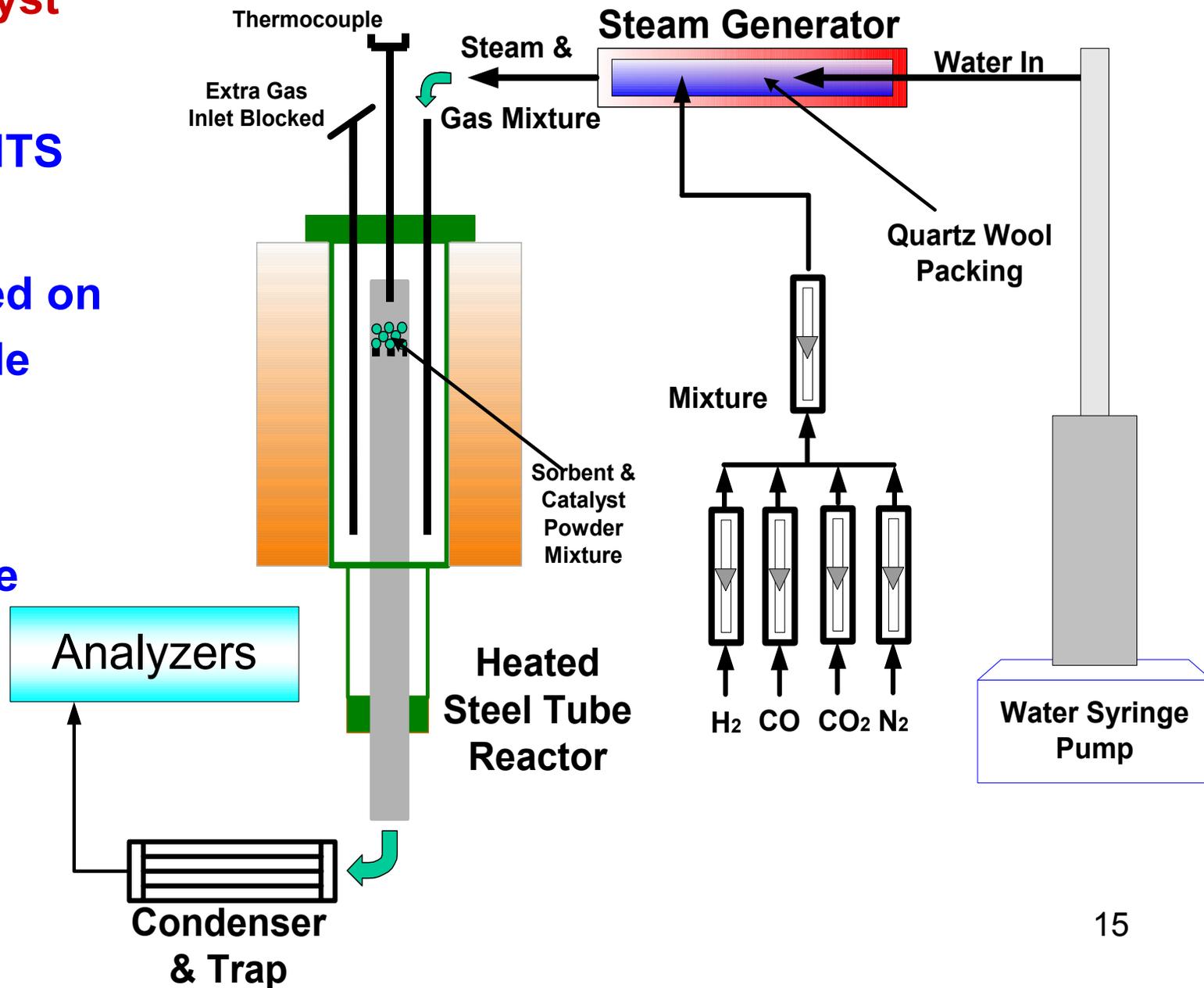
Fixed Bed of catalyst
and CaO mixture

- ✓ Süd-Chemie: HTS catalyst
- ✓ Fe_2O_3 supported on chromium oxide

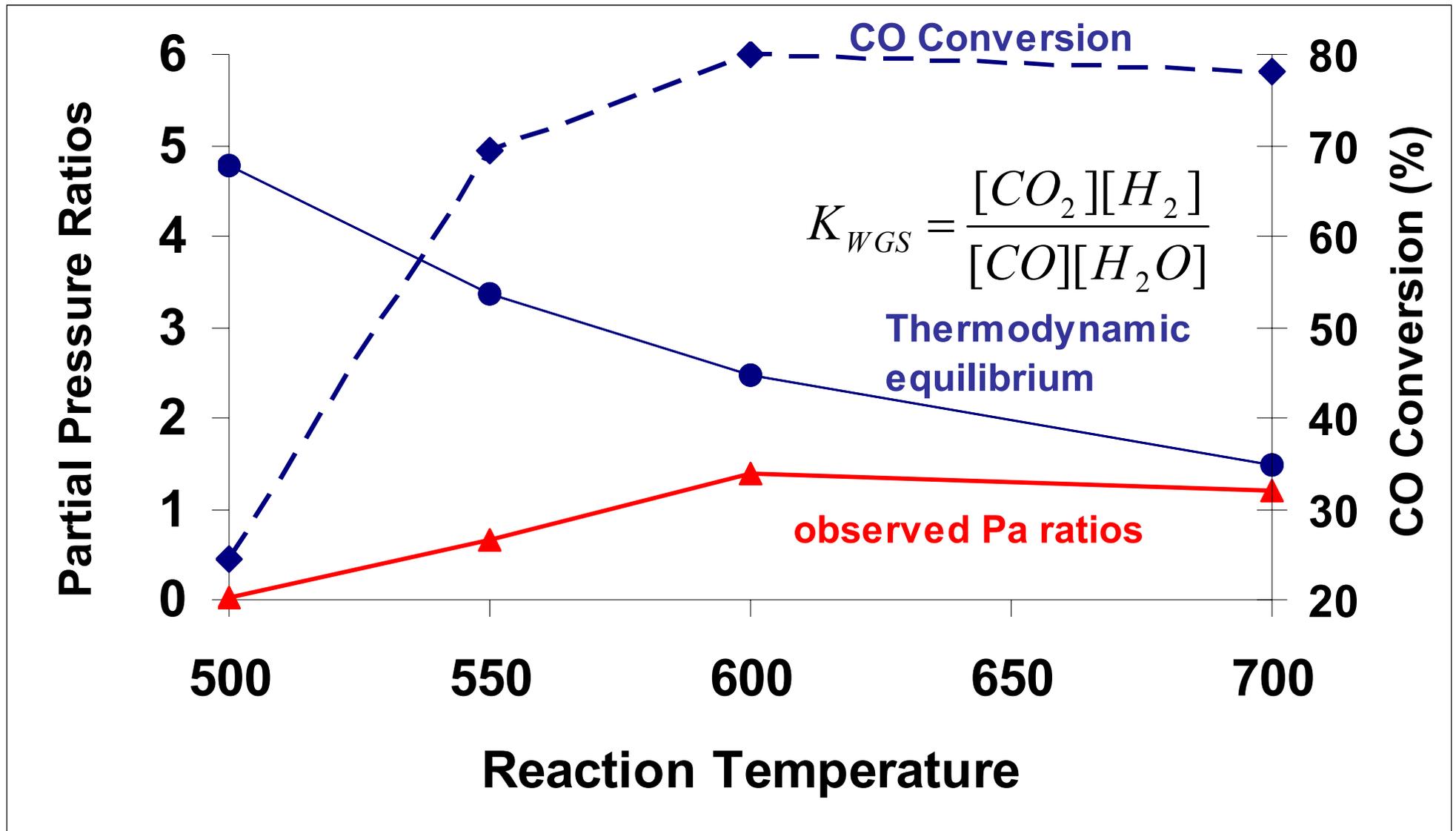
Sorbents

- ✓ PCC (tailored)
- ✓ Linwood hydrate (natural)

- 1500 sccm
- 3 % CO
- Steam/CO = 3
- 600 °C

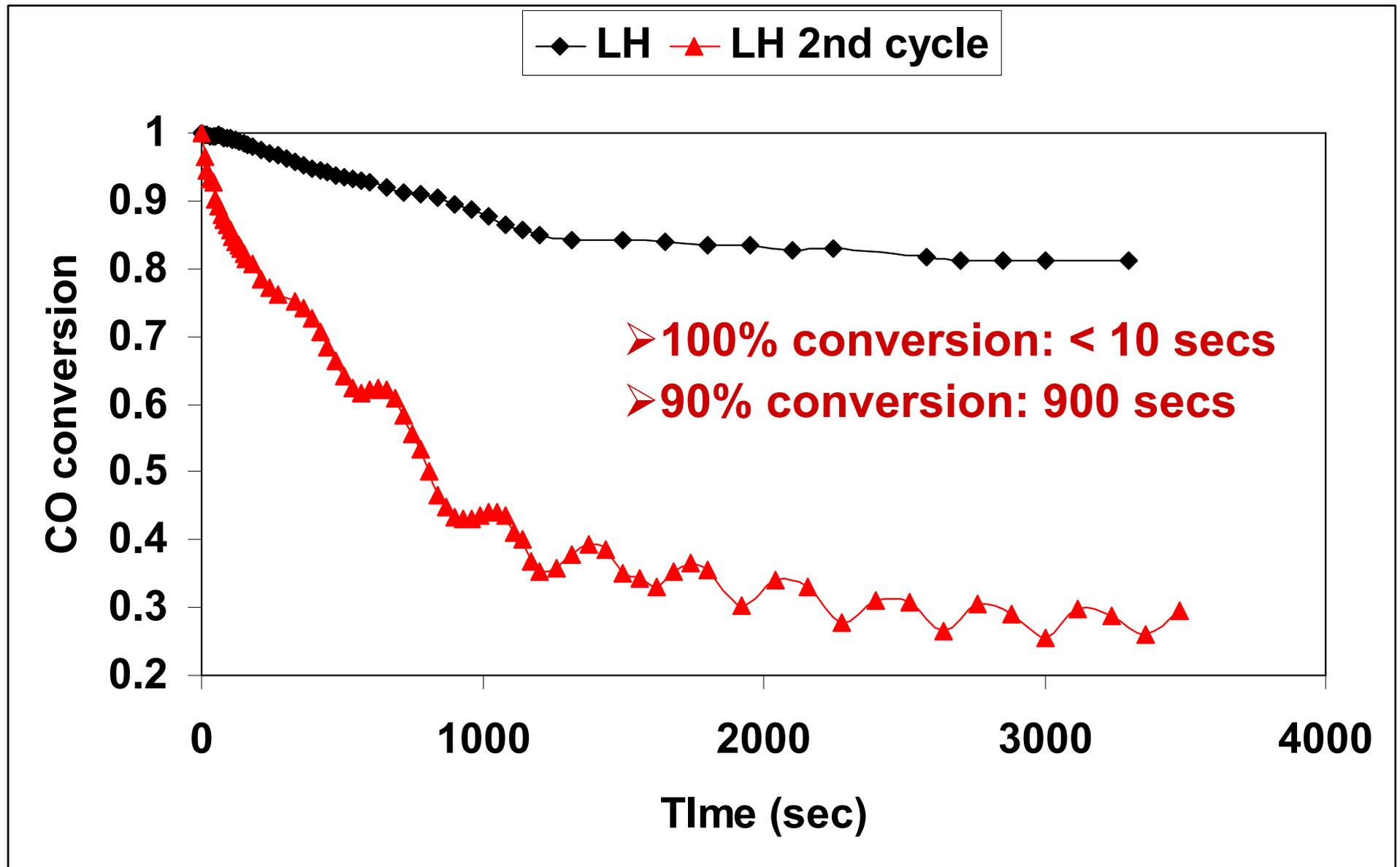


WGS Catalyst Testing w/o Sorbent



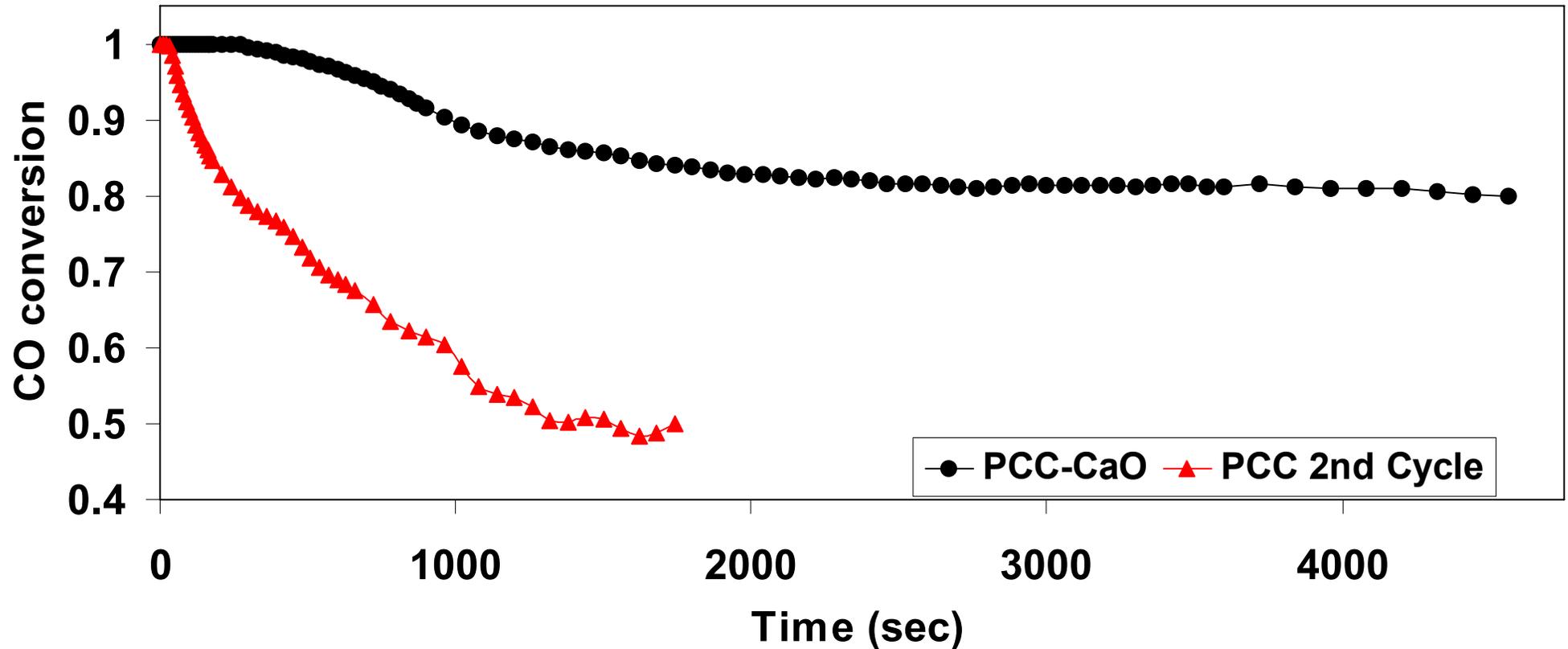
0.5 g HTS catalyst, 3% CO H₂O/CO ratio = 3, Total flow = 1.5 slpm

Performance of Linwood Hydrate



T = 600 °C, 3% CO, 9% H₂O, Total flow = 1.5 slpm

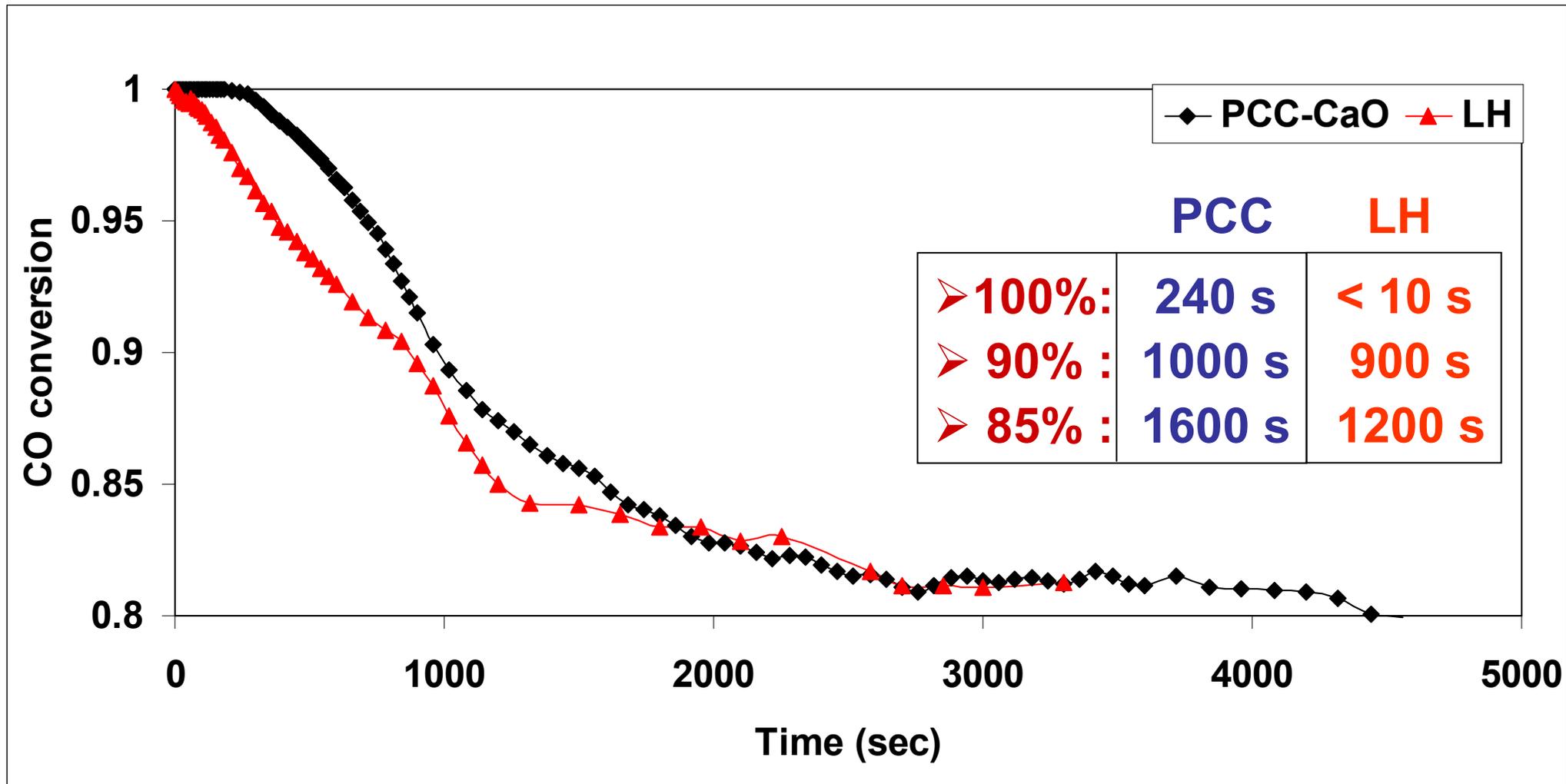
Performance of PCC



- **100% conversion: 240 secs (4 min)**
- **90% conversion: 1000 secs (16.5 min)**
- **Final breakthrough: 2500 secs (42 min)**

T = 600 °C, 3% CO, 9% H₂O, Total flow = 1.5 slpm

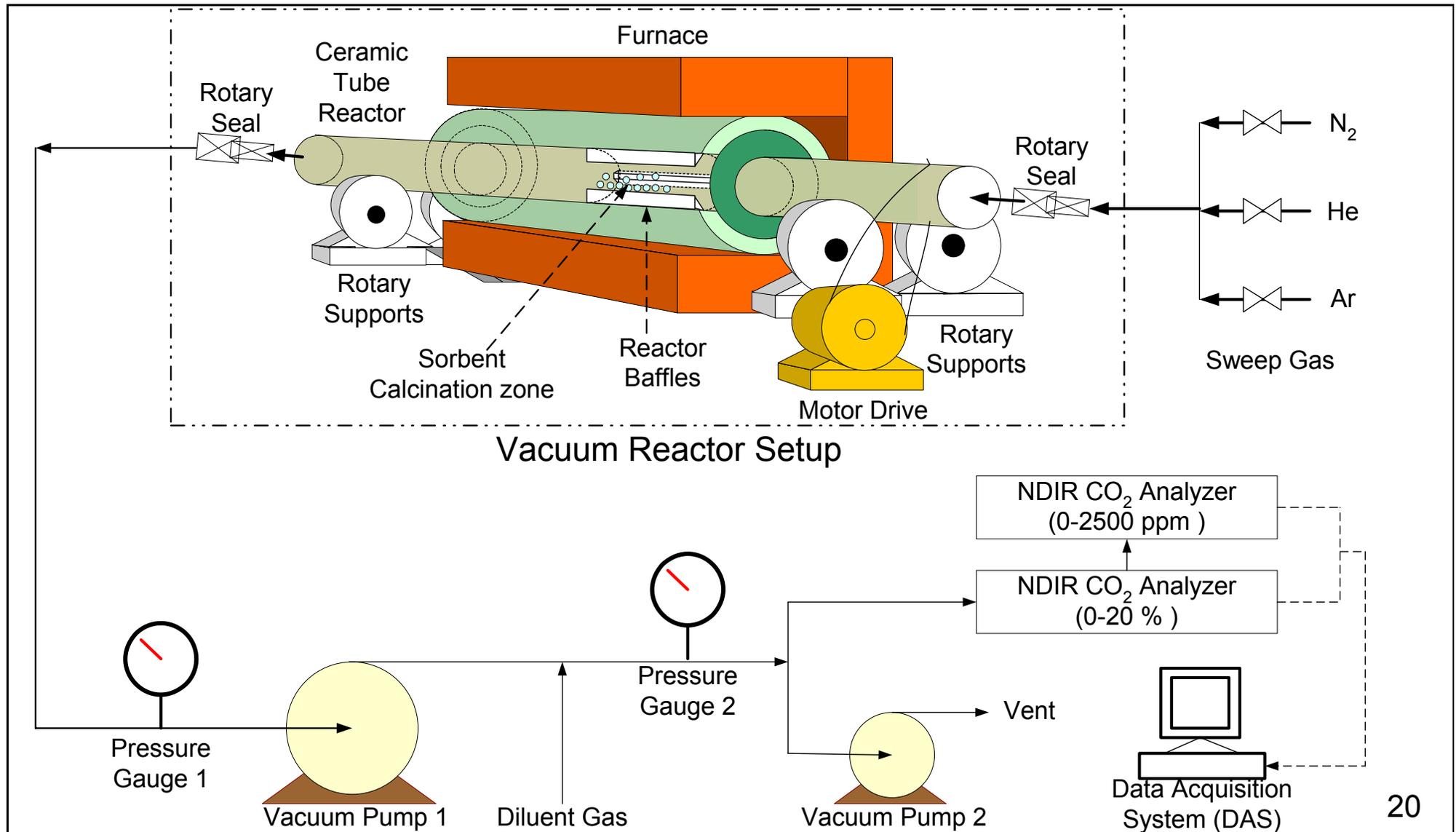
Comparison of PCC and LH



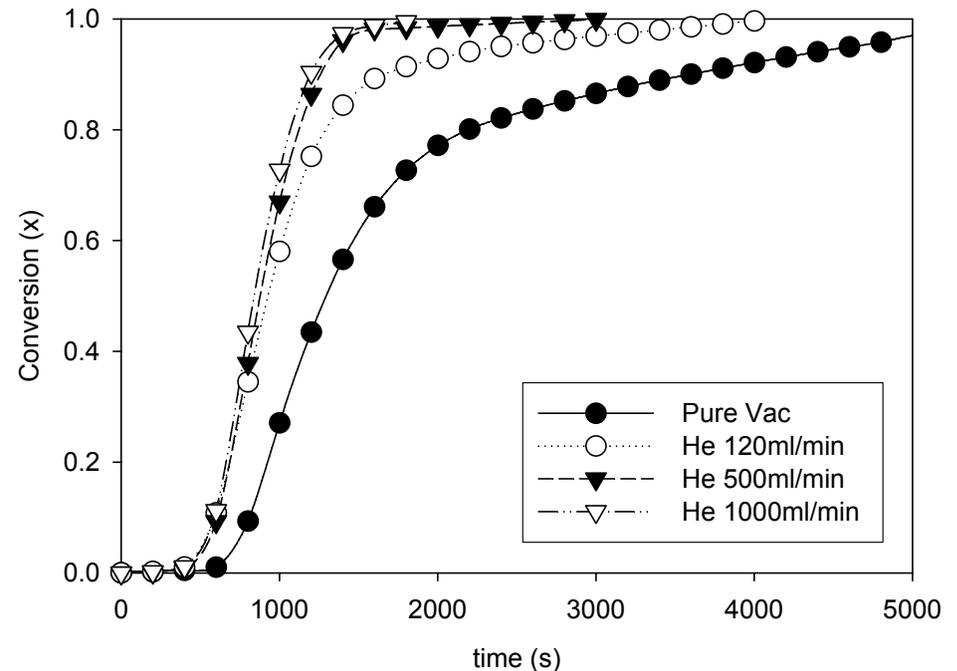
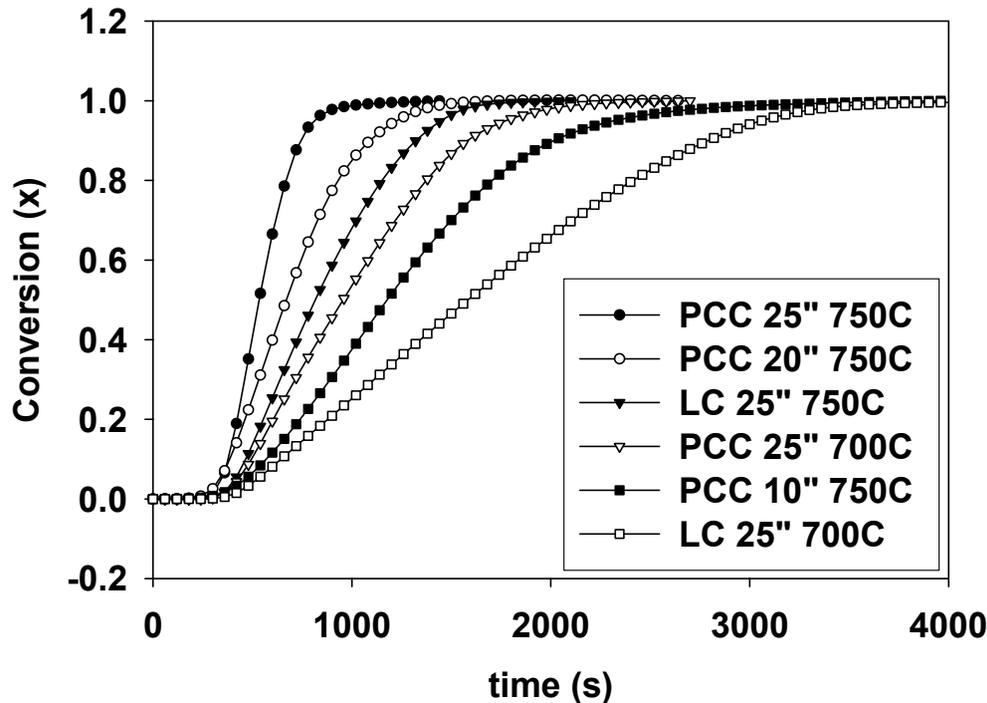
T = 600 °C, 3% CO, 9% H₂O, Total flow = 1.5 slpm

Sub-atmospheric Calcination

Schematic diagram of the calciner reactor setup



Sub-atmospheric Calcination



- Effect of vacuum on calcination rate
- Higher vacuum favors the rate
- PCC calcines faster than LC
- Lower calcination temperature favors sorbent morphology

- Effect of diluent gas flow rate
- 0-1000ml/min of He
- Calcination of 10g LC
- 28" Hg vacuum
- T=880 °C

Future Work (FY 2005)

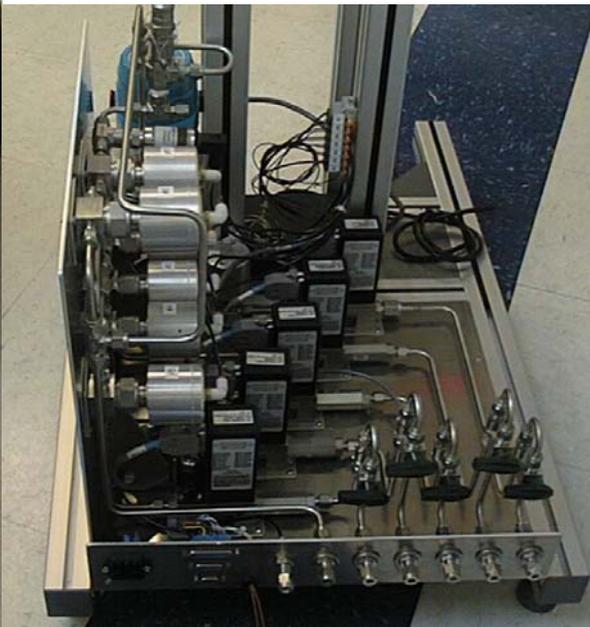
MSB Testing

– Multicyclical Testing that includes:

- Carbonation
 - Simulated WG mixtures
 - Effect of Pressure
- Calcination
 - $N_2/H_2O/CO_2$ /Vacuum combination

– Effect of H_2S :

- Competing sulfidation and carbonation
- Effect of steam to prevent sulfidation
- Optimization of X_{CO_2}/X_{H_2S}



Future Work (FY 2005)

- Breakthrough Testing

- Hydrogen Generation

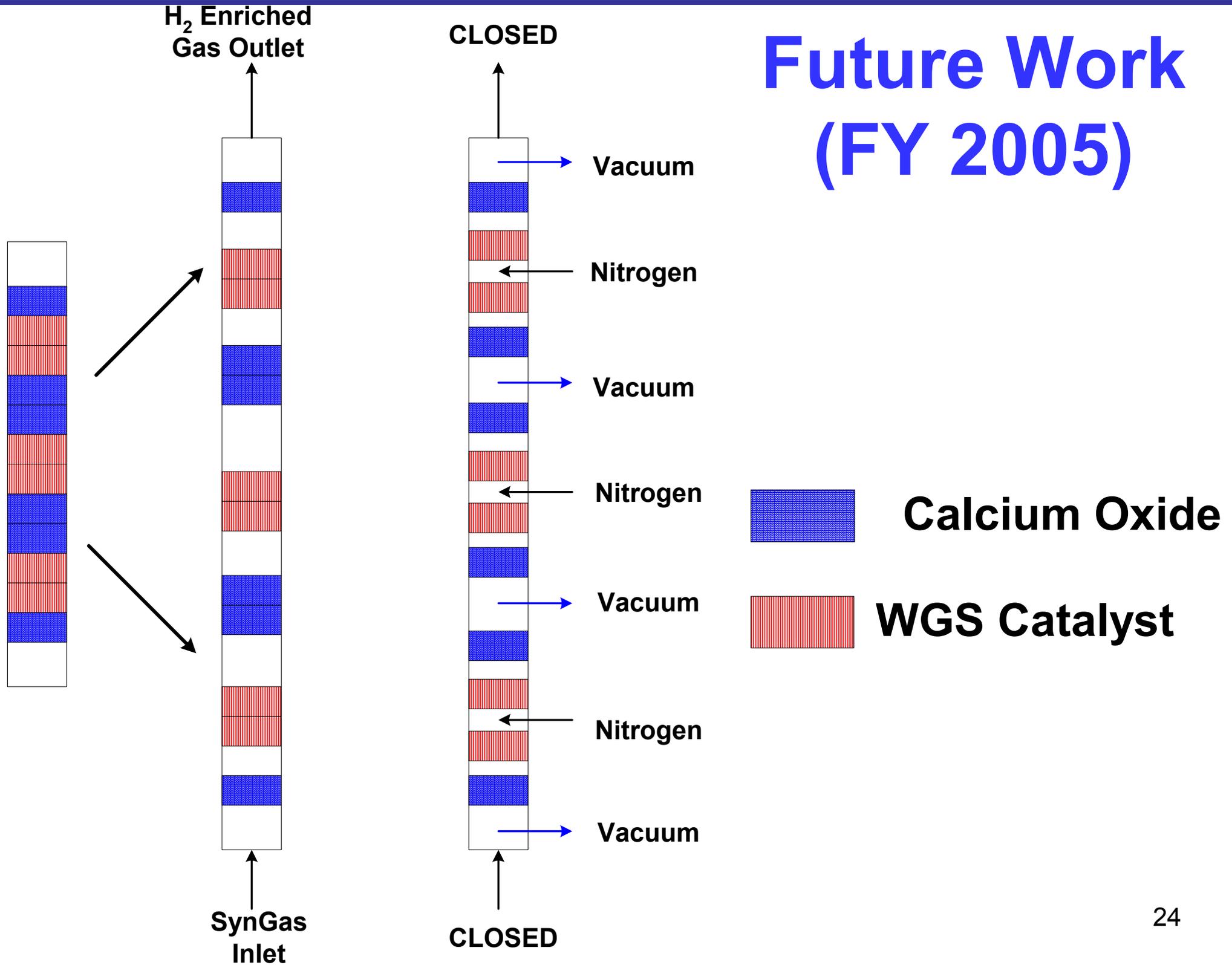
- Purity of hydrogen
 - Thermal Conductivity
 - Density
 - Specific Heat
 - CO exit concentration
 - CO₂ exit concentration

- Multicyclic Catalyst Performance

- Catalyst maintained under inert gas

- No exposure to CO₂, H₂O

Future Work (FY 2005)



Publications and Presentations

Presentations:

“Enhancing Hydrogen Production With In-Situ CO₂ Separation Using CaO/Catalyst Systems” Iyer, M., Gupta, H., Sakadjian, B. and Iyer, M. *AIChE Annual Tech. Meeting*, Austin, TX, 2004.

Gupta, H; Iyer, M.V.; Sakadjian, B.B.; and Fan, L.-S., “The Role of CaO in Maximizing Hydrogen Production from Fossil Fuels” Fuel Cell Seminar, San Antonio, TX, 2004

H. Gupta, M. V. Iyer, B. Sakadjian and L.-S. Fan, “Reaction Enhanced Hydrogen Production from Water Gas Mixtures.” 29th International Technical Conference on Coal Utilization & Fuel Systems, April 17-22, 2004, Clearwater, Florida, USA.

Publications:

Gupta, H; Iyer, M.V.; Sakadjian, B.B.; and Fan, L.-S., “The Role of CaO in Maximizing Hydrogen Production from Fossil Fuels” Proceedings from Fuel Cell Seminar, San Antonio, TX, 2004

Hydrogen Safety

Most significant hydrogen hazard associated with this project is

- The experiments involved in this project use a gas mixture consisting of CO, H₂, H₂O, H₂S, CO₂ and N₂.
- High temperatures (100-700°C) and pressure (1-20 bars)
- The most significant hydrogen hazard associated with this project is the combustion/explosion of hydrogen inside and/or outside the reactor. In addition, carbon monoxide could pose a similar safety hazard.

Hydrogen Safety

Our approach to deal with this hazard is

- Minimize gas flow rates and reactor footprint
- Double sash well-ventilated walk-in hood (81 fpm)
- 13 ppmv Hydrogen in the vicinity of reactor
- Manual controls are outside the hood